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Review article

Neutron scattering, a powerful tool to study clay minerals

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ABSTRACT

Of the techniques used to study clay minerals, neutron scattering has become more familiar to clay scientists over the past decade. A brief account of neutron scattering theory is given in this review, followed by a description of measurements that can be made using neutron diffraction and neutron scattering spectroscopy, and especially quasi-elastic neutron scattering. Then recent examples of the application of neutron scattering methods to the study of clay minerals are presented, and finally the potential advantages of such experimental results when combined to molecular dynamics are discussed. To conclude, the potential perspectives that the European Spallation Source brings to this subject are pointed out.

1. Introduction

The usefulness of smectites in many industries stems from their ability to take up and retain large amounts of water due largely to their high interlayer surface area and presence of hydrated cations (Bérend et al., 1995; Cases et al., 1992, 1997; Ormerod and Newman, 1983). Neutron scattering spectroscopy has been used to probe water mobility dynamics in clay minerals for more than 4 decades (Adams et al., 1979; Cebula et al., 1981; Hunter et al., 1971; Olejnik and White, 1972; Olejnik et al., 1970; Poinsignon et al., 1987; Ross and Hall, 1978; Tuck et al., 1984, 1985), but interest in this methodology has increased markedly since the mid 1990s (Bordallo et al., 2008; Chakrabarty et al., 2006; Gates et al., 2012; Kamitakahara and Wada, 2008; Malikova et al., 2006; Michot et al., 2007; Nair et al., 2005; Powell et al., 1997, 1998; Swenson et al., 2000, 2001a; Williams et al., 1998) in conjunction with developments in molecular dynamic simulations (Skipper et al., 1991, 1994, 1995; de Siqueira et al., 1999; Greathouse et al., 2000; Skipper et al., 2000; de Carvalho and Skipper, 2001; Sutton and Sposito, 2001; Marry et al., 2002; Marry and Turq, 2003; Marry et al., 2008; Wang et al., 2004, 2006; Malikova et al., 2006).

Water mobility in smectites is largely controlled by the type of interlayer cation (Bordallo et al., 2008; Cases et al., 1992; Gates et al. 2012). The interactions of water (solutes) with the different surfaces of smectites often have diffusion or exchange times on the order of 10 ps to 100 ms that correspond in part to the time scale probed by neutron spectroscopy. Other methods, such as nuclear magnetic resonance (e.g., Bowers et al., 2011), are also highly successful at probing these interactions, but will not be discussed here.

Neutron scattering has several features that make it a powerful technique to study the structure and dynamics of heterogeneous systems such as smectite–water dynamics. The wavelength of thermal neutrons is suitable for probing the structure of a clay at the molecular level (neutron powder diffraction, NPD), as well as their long range order in colloidal dispersions and the macroscopic structure of the particles themselves (small-angle neutron scattering, SANS) (Cebula and Thomas, 1978). When compared to X-ray diffraction, neutron diffraction offers the advantage of a smaller attenuation coefficient, thus making surface effects negligible. Moreover in the study of sol or gel states the wavelength of the neutrons can be adjusted, so that Bragg diffraction reflections resulting from the clay mineral structure can be avoided. Additionally, by varying the hydrogen-deuterium ratio of the fluid, or possibly even the clay mineral itself, the contrast between the mineral particles and their surrounding water molecules can be better identified. On the other hand, although water dynamics can be investigated by many experimental techniques, such as infrared and Raman spectroscopies (Brubach et al., 2001) and nuclear magnetic resonance (NMR) (Kyakuno et al., 2011), neutron scattering spectroscopy offers a number of advantages presented in this work (Bordallo et al., 2008; Cebula et al., 1979; Cole et al., 2006; Malikova et al., 2008). Due to the exceptionally large scattering cross-section of the H-atoms, incoherent

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inelastic neutron scattering (IINS) enables probing of diffusive proton motions over a broad time-scale (from few nano to a few hundred ps) as well as the observation of quite high vibrational frequencies (up to 2000 cm^{-1}).

To date, neutron flux has been a key challenge in the study of many interesting problems in clay science, where understanding of kinetic effects is of the foremost importance. The unprecedented neutron flux offered by the European Spallation Source (operational in 2020) will, however, open up new opportunities for enquiry. For example, ESS will enable detailed dynamic analysis of real-time hydration and dehydration processes in clays. In order to better take advantage of this experimental technique, the most important theoretical points that must be known by novices, as well as examples of successful experiments, are described in this review.

2. Neutron scattering: an overview

Neutrons are non-charged subatomic particles, first postulated by Rutherford in 1920 and later observed by J. Chadwick in 1932. They are found in all atomic nuclei with exception of the hydrogen atom (^{1}H) and have a comparable mass to protons, a magnetic moment of $-1.913\ \mu_b$ and a nuclear spin of 1/2.

Neutron scattering techniques are based on the analysis of momentum and energy transfer, which may occur following interactions between neutrons and matter. Note that during such interaction the wave–particle duality must be considered for neutrons, so they can be described either as a classical particle with momentum $\overrightarrow{p} = m\overrightarrow{v}$, where m is the neutron mass ($1.675.10^{-27}$ kg) and $\overrightarrow{v}$ is its velocity, or as a wave with momentum $\overrightarrow{p} = \hbar\overrightarrow{k}$, where $|k| = (2\pi)/\lambda$ is the wave vector of the neutron and λ is the associated wavelength. Therefore, the corresponding neutron energy E can be described as:

$$E = \frac{p^2}{2m} = \frac{1}{2}mv^2 = \frac{h^2}{2m\lambda^2} = \frac{\hbar^2 k^2}{2m} \tag{1}$$

where $h = 2\pi\hbar = 6.626.10^{-34}$ J·s is the Planck's constant.

Thus, the energy and momentum transfer, $\overrightarrow{Q}$, measured in a neutron scattering experiment, are given by:

$$\Delta E = E_i - E_f = \frac{\hbar^2}{2m}\left(k_i^2 - k_f^2\right) \tag{2}$$

for energy, and

$$\overrightarrow{Q} = \overrightarrow{k}_i - \overrightarrow{k}_f \tag{3}$$

for momentum transfer. Eqs. (2) and (3) can be then graphically described as in Fig. 1.

Since their first observation, neutrons have been used as a powerful probe to study a wide range of materials due to their very unique properties on interaction with matter. First, as will be seen in more detail in the following sections, the scattering cross section, which describes the probability of interactions between neutrons and atoms, follows a complex relation with the atomic number of elements, whereas for X-rays, for example, the relation is generally predictable. Therefore, neutrons turn out to be a perfect probe for studies involving hydrogen, specially considering their isotope sensitivity. For example, while hydrogen presents the highest cross section for interactions with neutrons among all atoms, the probability of such interactions with deuterium is considerably lower. Therefore, one can use this feature in order to generate contrast in a given molecule or a specific portion or region of a material. Additionally, neutrons penetrate deeply into matter, which allows for the study of structure and dynamics of materials under very precise environmental conditions such as pH, pressure, temperature, hydration and others, providing information not easily accessed by NMR, optical microscopy, light scattering, X-ray diffraction or X-ray absorption spectroscopy.

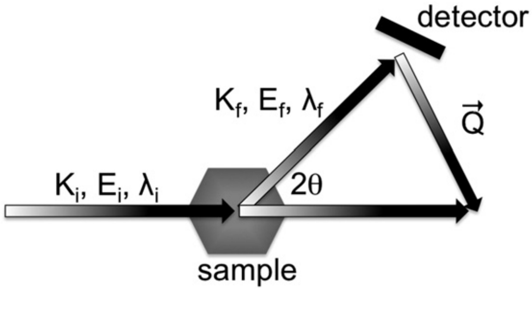

Fig. 1. In a scattering experiment, incoming neutrons with incident wavelength λ_i, energy E_i and wave vector k_i interact with the sample and are detected at an angle 2θ with final λ_f, E_f and k_f. The scattering vector $\overrightarrow{Q}$ is defined as the change in wave vector $\overrightarrow{Q} = k_i - k_f$.

2.1. Production of neutrons

The half-life of a free neutron is about 900 s. Such a short lifetime makes necessary the production of neutrons concurrent with the experiment. Free neutrons for scientific purposes can be obtained by means of nuclear reactions in fission reactors or from spallation sources. In both cases large scale facilities are required in order to operate the sources and provide adequate instrumentation for the users.

In the case of nuclear fission reactors, free neutrons are obtained after a slow neutron is captured by an ^{235}U nucleus, which splits and liberates 2 or 3 additional neutrons with an energy of 1.29 MeV together with fission fragments. Each of these neutrons can hit other ^{235}U nuclei giving rise to 2 or 3 additional neutrons. From those, 1 neutron is used to continue the chain reactions, which can be either accelerated if the fissile materials mass is above the so-called critical mass M_c leading to an uncontrollable reaction or it can stop if the fissile material mass remains below M_c. Research reactors operate below M_c to control the nuclear reaction, but delayed neutrons together with secondary neutrons originating from the highly excited fission fragments allow the reaction to continue practically indefinitely.

The wavelength of neutrons being in thermal equilibrium with the moderator has a Maxwellian distribution (Fig. 2), and one can further describe the neutrons based on their energy as

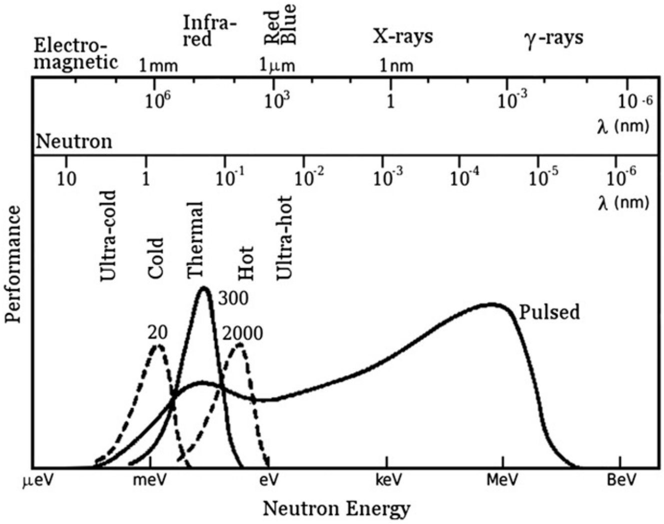

Fig. 2. A reactor's performance depends on the neutron flux at each energy. The solid curve labeled thermal shows the Maxwellian distribution of neutrons from an ambient moderator, which can be shifted by using a cold ≈ 20 K or a hot moderator ≈ 200 K. A pulsed spallation source performance depends on the flux and pulse width. The curve shows the flux per unit fractional energy.