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Neutron Diffraction Cryoporometry—A measurement technique for studying mesoporous materials and the phases of contained liquids and their crystalline forms

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Abstract

Neutron diffraction is a standard method for determining the structure of matter on an atomic scale; NMR cryoporometry is a recent widely applicable technique for characterising structure on a 2 nm to 2 μm scale. An extension of these techniques is described, Neutron Diffraction Cryoporometry (NDC). The information from a set of neutron diffraction measurements of liquids and their crystalline forms in meso-pores, as a function of temperature, is displayed as a cryoporometry graph. The data may then be conveniently interpreted using the Gibbs–Thomson relationship by analogy with the existing technique, NMR cryoporometry. Clear information is thus obtained on the relationship between phase and nano-structure, in a form well suited to further analysis. This method is applied to an equilibrium study of water/ice in SBA-15 templated silicas, as model nano- to meso-structured systems. The method described here uses global pattern matching (a one-dimensional morphing algorithm inside a linear least-squares fitting algorithm) applied to the full range of the diffraction data. This is a rapid method by comparison with the conventional method of fitting individual (overlapping) peaks, and has already led to NMR observations indicating plastic (rotator phase) ice in the same system.

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1. Introduction

There are a number of techniques for characterising structured matter at small length scales that employ thermodynamic protocols based on the Kelvin equation or the Gibbs–Thomson equation.

A formalism is applied that was first used with differential scanning calorimetry (DSC) thermoporosimetry [1,2], and more recently with NMR cryoporometry (NMRC) [3,4], whereby the melting behaviour of a liquid in nano- through meso- to micro-scale ores (2 nm to 2 μm) is interpreted using the Gibbs–Thomson relationship [5–7]: this relationship states that the melting point depression of a small crystal of the liquid is inversely proportional to the size of the crystal.

This paper presents an extension of this formalism to neutron diffraction data, ''Neutron Diffraction Cryoporometry'' (NDC), and discusses its application to a study of water/ice in a mesoporous silica. For all these techniques, a signal proportional to the quantity of each observed phase of the liquid/crystalline systems is plotted as a function of temperature, for cooling and/or warming temperature ramps. This information is then interpreted using the Gibbs–Thomson relationship, to give information on the

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structural features of the phases within the sample, as well as information on the confinement dimensions.

2. DSC thermoporosimetry, NMR and NDC

2.1. The Gibbs–Thomson equation

The Gibbs–Thomson equation is the constant-pressure variant of a set of thermodynamic equations [5,8], whereas the Kelvin equation [6, Eq. (2), p. 450; 7, Eq. (171), p. 163] is the constant temperature variant.

This behaviour is closely related to the capillary effect and both reflect the change in free energy caused by the curvature of an interfacial surface under tension [9,10]. Consequently, the Gibbs–Thomson equation for the melting point depression, ΔT_m, for a small isolated spherical crystal of diameter x may be written [2] as

$$\Delta T_m = T_m^\infty - T_m(x) = \frac{4\sigma_{cl} T_m^\infty}{x \Delta H_f \rho_s} \quad (1)$$

where T_m^∞ is the normal melting point (i.e. of a crystal of infinite size), $T_m(x)$ the melting point of crystals of diameter x, σ_{cl} the surface energy at the crystalline–liquid interface, ΔH_f the bulk enthalpy of fusion (per gram of material), and ρ_s the density of the solid.

ΔT_m depends only on the properties of the liquid, its solid, and the interfacial interaction between these two states.

The presence of a confining geometry requires additional terms to be incorporated into the Kelvin and Gibbs–Thomson equations to accommodate the interaction between the adsorbate and the pore walls. For a crystal melting in a pore of arbitrary geometry, with a characteristic dimension x, the Gibbs–Thomson equation (1) may be written as

$$\Delta T_m = \frac{k_{GT}}{x} = \frac{k_g \cdot k_s \cdot k_i}{x} \quad (2)$$

where k_g is a geometric constant dependent on the interfacial shape [11], k_s is a constant specific to the solid crystal thermodynamic parameters, and k_i is a constant specific to the two inter-surface interaction terms of the crystal. There is further discussion of these terms elsewhere [12].

Prior theoretical analysis [11,13] suggests that for the melting event the theoretical ratio for $k_g^{sphere}/k_g^{cylinder}$ may be either $\frac{3}{2}$ or 2, depending on the models used. In this paper what are believed to be the first measured values for this ratio are obtained. The experimental sections on calibration (Section 3), combined with both the NMR cryoporometry results (Section 5) and the ND cryoporometry results (Section 6), show that, for agreement with gas adsorption results, the measured ratio is close to 2.

2.2. DSC thermoporosimetry

Thermoporosimetry [1,2,14–17] is an established technique, whereby thermal fluxes to or from a nanostructured liquid and its crystalline forms are monitored, while raising or lowering the temperature, so as to locate phase transitions as a function of temperature. These measurements may then be interpreted by the Gibbs–Thomson relationship to determine if the liquid is confined, and if so, to determine crystal/pore size distributions. Resolution of mono-modal distributions and precision of measured pore size are limited with this technique by the need to ramp the temperature at a sufficiently high rate so as to maintain measurable temperature fluxes.

2.3. NMR cryoporometry

NMR cryoporometry [3,4] is a recent technique we have been developing [11,18–29], that makes use of the Gibbs–Thomson relationship to deduce information regarding the pore size distributions in nano- to micro-structured materials—i.e. 2 nm to 2 μm.

A quantity of a liquid, such as water, is added to the mesoporous sample (more is added than is needed to fill the pores). On equilibration, the pores are filled leaving excess liquid on the external surfaces of the particulate grains. The sample is placed inside an NMR probe and is cooled until all the liquid is frozen. The sample is warmed gradually, at a controlled rate, while monitoring the amplitude of the NMR signal from the liquid (Fig. 1). Due to the reorientational averaging from motion, the T_2 transverse relaxation time is much longer in liquids than in solids, providing a method of measuring the liquid quantity separately from that of the solid.

Thus the signal from brittle ice decays with a Gaussian free induction decay (FID) in about 10 μs, while the exponential transverse relaxation time T_2 for water in mesopores is typically of the order of 10 ms. The application of

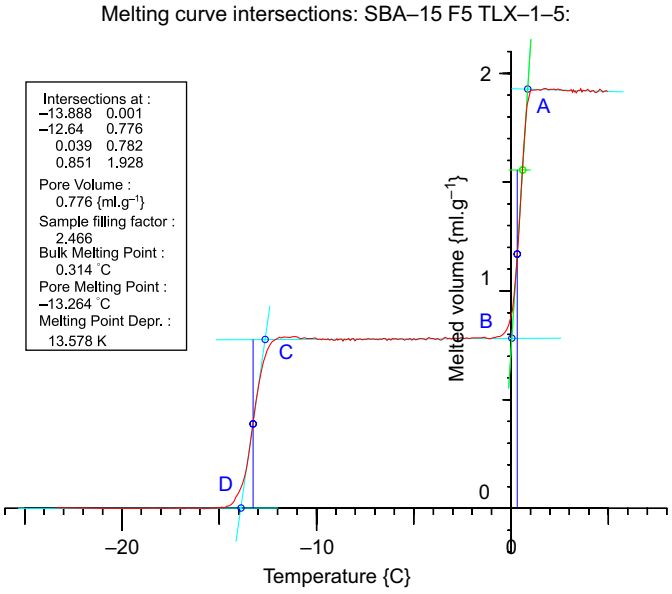

Fig. 1. NMR cryoporometric melting curve for H_2O in SBA-15 TLX-1-5 (F5) templated silica, at a warming rate of 0.05 °C min^{-1}.