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NMR cryoporometry: Principles, applications and potential

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1. Introduction

1.1. History and landscape

The method that is today typically called “NMR cryoporometry” was developed roughly simultaneously and in an apparently independent way by four different research groups [1–4]. By that we are not saying that NMR was not used for studying freezing–melting affected by geometric confinement in various earlier [5–7] and contemporary [8] publications. Rather, [1–4] represent a consistent and direct attempt to obtain information, via Gibbs–Thomson-like equations, about the size of pores in porous materials by NMR observation of the phase transition behaviour. In the years that followed 1993–1994, Strange et al. [9–28] and, additionally, Hansen et al. [29–38] spearheaded the development of the methodology and have demonstrated and extended its potential in a number of applications. The name itself seems to have been coined in 1996 [11] and is slowly gaining a more general acceptance. Even though the NMR cryoporometric methodology is dominantly applied for revealing information about the pores, there are individual studies and, indeed, entire research groups, most notably that of Charnaya [39–49], where the same method (though, not called there cryoporometry) is exploited by a different emphasis on freezing–melting processes under confinement.

Indeed, phase transitions under confinement, which frequently means phase transitions in pores, is an enormous research field on its own right [50–53]. One interesting sub-field is the behaviour of polymer systems under those conditions [54–56]. NMR cryoporometry may lead to a better understanding of phase transitions under confinement, probably because this method can sometimes reveal finer features of the phenomenon than, say, its calorimetric counterparts; indeed, much of what we know is due to NMR. In addition, NMR cryoporometry also intersects with the massive research effort that concerns the characterization of porous materials [57–60]. Since NMR cryoporometry is often performed with water as the pore-filling liquid, it also interfaces with other significant topics such as ice science [61] and, in particular, the physics of pre-melting of ice [62–65]. On the NMR side, there exist a multitude of NMR tools by which one may access information about porous structures [66–72]. These methods exploiting, for example, the pore-modified diffusion and/or spin relaxation and/or chemical shift properties of pore-filling liquids are often complementary to NMR cryoporometry with regard to the information provided and can sometimes be combined with NMR cryoporometry to provide a more detailed description of the porous structure [12,73,15,74,37,75–79].

NMR cryoporometry, even if in its most strictly defined form is limited to ca 100 publications, is so intimately connected to other, much larger scientific areas that its development inevitably involved repeated discoveries of the same phenomenon. Hence, we do not attempt to present a comprehensive chronology but try instead to offer a pedagogical account with the main issues being illustrated and enlightened by referring to selected publications.

1.2. Basics of NMR cryoporometry

The basic idea of NMR cryoporometry is to detect the shift of phase transition temperatures for a material that is confined in pores. Those shifts can be interpreted in terms of pore geometry and can, therefore, provide information about pore sizes and their distribution and, in favourable cases, about pore shape. Typically, the investigated phase transition is solid-to-liquid, depending on the direction of the temperature change either melting or freezing. Solid–solid [80,81] or liquid–vapour [82] transitions in pores, though also subject of temperature shift, are seldom used for pore characterization studies. The underlying reason for a shift in the melting and freezing points is the cost of creating a new interface with a non-zero surface tension. In bulk materials with very low surface-to-volume ratios this cost is irrelevant, except for the actual nucleation of the growth of a phase [83]. Practitioners of NMR cryoporometry often rely on one particular [84] recapitulation of the Gibbs–Thomson equation developed for the case of cylindrical pores with radius r . Jackson and McKenna [84] expressed the shift of the pore melting point T_m as

$$\Delta T_m \equiv T_m - T^0 = -\frac{k}{r}, \quad (1)$$

where k is a material constant that depends in a simple fashion on the molar volume v , on the solid–liquid surface energy γ_{sl} , on the latent heat of melting (fusion) ΔH and on the bulk melting point T^0 . (Analogously, $\Delta T_f \equiv T_f - T^0$ denotes below the shift of the freezing point.)

The primary role of NMR is to detect the solid–liquid transition. This is made possible by the tremendous sensitivity of certain NMR parameters to molecular motion. As is well known to NMR practitioners, there is a large difference between the broad signal of a solid and the motionally narrowed signal of a liquid. Indeed, all implementations of NMR cryoporometry depend on that difference between solid and liquid line widths or, conversely, transverse relaxation rates: typically, they detect the emergence/disappearance of the liquid signal upon increasing/decreasing temperature by applying a spin-echo-type detection. In the case of a distribution of pore sizes, and hence a related distribution of melting points according to Eq. (1), the resulting NMR signal $I(T)$ varies smoothly with temperature T , its shape reflecting the pore size distribution. By assuming that $I(T) \propto V(T)$ where $V(T)$ is the pore volume that contains molten liquid at a given temperature T , one can simply obtain a pore-size distribution $p(r)$ as [2]

$$p(r) = \frac{k}{r^2} \frac{dI(T)}{dT}. \quad (2)$$

Note that this pore-size distribution is, in the absence of absolute scaling between $I(T)$ and $V(T)$, a relative one. It is, though, simple to obtain an absolute pore-size distribution and total porosity (or, specific pore volume) by proper procedures of scaling [85,79].

NMR is but only one means used to detect the shift of phase transition points in porous materials. Other methods can also perform the same task, leading to other cryoporometric techniques of

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