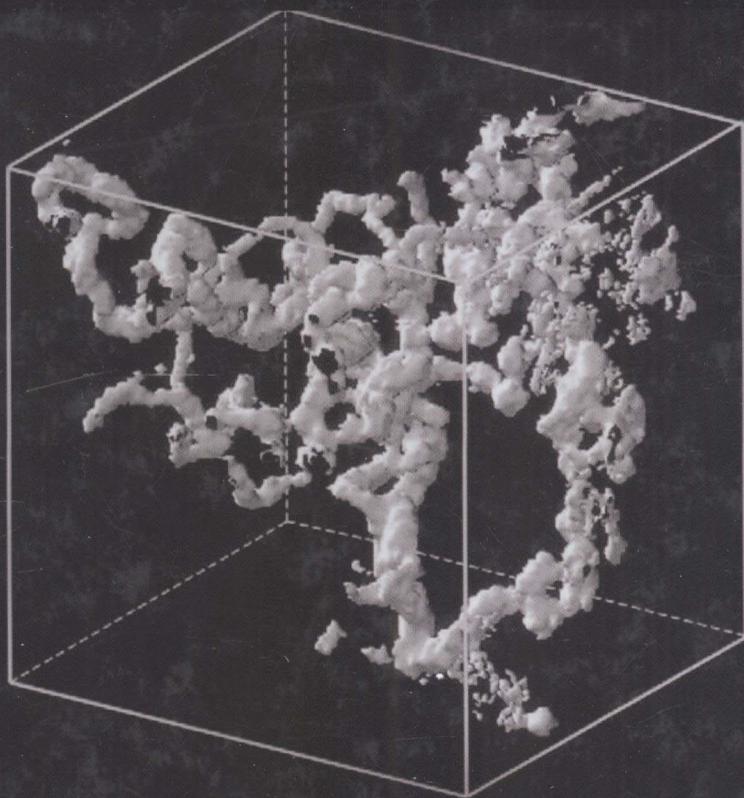


CAMBRIDGE MOLECULAR SCIENCE

# NMR Studies of Translational Motion

**Principles and Applications**

**William S. Price**



CAMBRIDGE

# NMR STUDIES OF TRANSLATIONAL MOTION

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## Preface

Translational motion in solution (e.g., diffusion, flow or advection) plays a central role in science. Self-diffusion can be rightfully considered as being the most fundamental form of transport at the molecular level and, consequently, it lies at the heart of many chemical reactions and can even govern the kinetics. Diffusion, due to its very ubiquity, is encountered in a myriad of scientific studies ranging from diseases to separation science and nanotechnology. Further, the translational motion of a species not only reflects intrinsic properties of the species itself (e.g., hydrodynamics), but can also shed light on the surrounding environment (e.g., intermolecular dynamics or motional restriction). Consequently, being able to study and ultimately understand the translational motion of molecules and molecular systems in their native environment is of inestimable scientific value.

Measuring translational motion at the molecular level presents special difficulties since labelling (e.g., radiotracers) or the introduction of thermodynamic gradients (which leads to mutual diffusion and consequently irreversible thermodynamics) in the measurement process can have deleterious effects on the outcome. Also, in many instances it is of interest to measure the diffusion of species at quite high concentrations. Fortunately, nuclear magnetic resonance (NMR) provides a means of unparalleled utility and convenience for performing non-invasive measurements of translational motion. Of particular significance is that, in general, the species of interest inherently contain NMR-sensitive nuclei and thus sample preparation generally requires nothing more than placing the sample into the NMR spectrometer.

NMR is an inherently quantum mechanical subject, yet translational motion of molecules lies between the microscopic and the macroscopic and is most conveniently described with classical physics. Abiding by Ockham's razor, this is the path that will be taken here. This is not an NMR textbook per se, and for the fundamentals of NMR numerous excellent texts are currently available.<sup>1-6</sup> A tabulation of many of the commonly used NMR acronyms can be found elsewhere.<sup>7</sup>

The last two decades have seen the advent of widespread commercial availability of MRI imagers and magnetic gradient probes and gradient drivers for NMR spectrometers. Magnetic gradients now pervade almost all areas of NMR ranging from coherence selection, gradient shimming, selective excitation and signal suppression<sup>8–21</sup> in high-resolution NMR to inputting spatial dependencies into NMR imaging (also known as MRI, and NMR microscopy) and NMR diffusion measurements. The use of gradient NMR allows diffusion to be added to the list of standard NMR observables.

This book grew out of two widely cited pedagogical papers that I wrote sometime ago on measuring diffusion with NMR<sup>22,23</sup> using magnetic field (i.e.,  $B_0$ ) gradient methods. The overall aim of the book is rather modest: to present a clear overview of this field with particular emphasis on trying to impart a clear physical picture – ideally such that the literature may become more accessible to readers interested in expanding their research into this field. Specifically, this book endeavours first to explain the physical basis of magnetic gradient-based NMR measurements of translational motion – especially diffusion measurements involving pulsed magnetic field gradients. Flow- and imaging-based measurements are closely related technically and theoretically and so some coverage of these kindred fields is presented. Secondly, to provide a clear correlation between experimental methodology and theoretical data analysis and the sorts of applications that are feasible. I have cited rather more references than is typical in a monograph to give the reader more chance of understanding the present text and also the opportunity to read further. I also liberally cite some textbooks that I found particularly lucid – especially in mathematical areas since many of the readers of this book may not come from a strong mathematics/physics background and to this end I also include the derivations of some of the more important equations. Although in general I have tried to maintain historical lineage, in some cases I have cited a more accessible reference for a concept than the original reference. As is so often the case, what started as my attempt to clearly explain an area of science became an exercise in trying to make myself really understand the area. This area of NMR application, theory and methodology has grown exponentially in the past three decades. Thus, it is neither possible nor reasonable to attempt anything approaching a comprehensive coverage; further the ordering of the material was made particularly difficult by many of the studies being justifiably included under more than one of the subheadings.

The outline of this book is as follows: Chapter 1 serves as an introduction to translational motion with special attention to diffusion and begins with some introductory remarks on the relationship between diffusion and chemical and biological phenomena, followed by a detailed exposition on its physical basis and how it can be mathematically modelled – these concepts will be heavily drawn upon in later chapters. This basis also allows the final section, where some of the more

common techniques for measuring diffusion are briefly reviewed, to be placed in perspective as it allows the strengths and limitations of the different methods of diffusion measurements to be more clearly understood. Chapter 1 is rather solid and parts can be skipped on a first read or by those only interested in the NMR techniques and not the fundamental aspects of diffusion and its modelling.

Chapter 2 introduces the basic concepts behind magnetic gradient-based NMR diffusion measurements in freely diffusing systems and in particular the workings of basic pulsed gradient spin-echoes (PGSE), the most common (analytical and approximate) mathematical procedures for correlating the experimental variables, diffusion (and flow) with the observed NMR signal. Measurements of samples containing mixtures of species and aggregating species, but where the exchange is slow on the measurement timescale, are also considered.

Chapter 3 builds upon Chapter 2 and extends the coverage to the cases of simple porous systems, that is where a species is confined to a single highly symmetrical pore of some description. Whereas analytical relations could be given for the relationship between experimental variables and observed signal in the case of free diffusion, such analysis even for simple highly symmetrical pores rapidly becomes mathematically intractable and thus some consideration is given to the validity of the commonly used mathematical approximations and the various numerical approaches that are sometimes used.

Chapter 4 continues on from Chapter 3 and considers phenomena such as exchange, anisotropic and flowing systems and diffusion in polymers. Diffusion measurements in internal magnetic fields are also given brief mention.

Chapter 5 provides an overview of the additional instrumentation for an NMR spectrometer needed to conduct diffusion, flow and, by extension to a system capable of generating magnetic field gradients in three orthogonal directions, imaging-based measurements.

Chapter 6 details fundamental experimental considerations such as the selection of delays, gradient parameters and solvent suppression technique in diffusion measurements and how the applied gradient strength might be calibrated. This chapter ends with a section on how to transform and analyse the PGSE data resulting from simple freely diffusing samples, complex mixtures and samples involving restricted diffusion.

Chapter 7 concerns most of the issues that thwart attempts to get high-quality data such as background gradients, eddy currents induced by the rapidly pulsed magnetic field gradients and imperfectly generated gradient pulses. The symptoms and suggestions for obviating or at least meliorating their effects are considered.

Chapter 8 provides an overview of some of the more sophisticated sequences for measuring diffusion, flow and related phenomena.

Chapter 9 gives an overview of the inclusion of conventional nuclear magnetic resonance imaging (aka MRI) methodology with diffusion and flow measurements.



Whereas in the previous chapters the systems being studied might be microscopically heterogeneous, there was an implicit assumption that they were macroscopically homogeneous. However, in many cases (biological tissues such as brain being a prominent example) the sample is also heterogeneous on a length scale that can be accessed by MRI methodology. The combination of MRI techniques with gradient-based diffusion and flow-measuring techniques provides powerful tools for characterising natural and synthetic materials.

Chapter 10 gives a brief overview of the use of radio frequency (i.e.,  $B_1$ ) field gradients to measure translational motion.

Chapter 11 surveys some of the applications to which gradient-based measurements of translational motion have been put.

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## Abbreviations and Symbols

|                         |   |
|-------------------------|---|
| $A$                     | cross-sectional area of a sample tube   |
| $a$                     | characteristic distance (e.g., radius of a pore or half the inter-planar separation)      |
| ADC                     | apparent diffusion coefficient ( <i>see also</i> $D^{\text{app}}$ )                       |
| $a_M$                   | relaxation length   |
| $a_{\text{min}}$        | uncertainty in initial and final position during a gradient pulse                         |
| $b$                     | gradient or diffusion weighting factor  |
| $\mathbf{b}$            | gradient or diffusion weighting vector  |
| $\mathbf{B}_0$          | static magnetic field   |
| $\mathbf{B}_1$          | radio frequency (rf) field  |
| BPP                     | bipolar gradient pulses   |
| BSA                     | bovine serum albumin  |
| $C(Z, \Delta)$          | diffusion envelope  |
| CORE                    | component resolved spectroscopy   |
| COSY                    | correlation spectroscopy  |
| CPMG                    | Carr–Purcell–Meiboom–Gill sequence  |
| CTPG                    | constant time, pulse, and gradient and amplitude diffusion experiment                     |
| $D$                     | self-diffusion coefficient  |
| $d$                     | embedding dimension   |
| $D_i$                   | individual self-diffusion coefficient   |
| $D_i^0$                 | self-diffusion coefficient of the $i^{\text{th}}$ oligomeric species at infinite dilution |
| $\langle D \rangle_P$   | population-weighted averaged diffusion coefficient  |
| $\langle D \rangle_W$   | mass averaged diffusion coefficient   |
| $\langle D \rangle_W^C$ | mass averaged diffusion coefficient including obstruction effects                         |

|   |   |
|---|---|
| <b>D</b>  | self-diffusion tensor   |
| <b>D</b> <sup>lab</sup>   | diffusion tensor in the laboratory axes frame ( $x', y', z'$ )  |
| <b>D</b> <sub><math>\omega</math></sub>                         | diffusion coefficient spectrum or tensor  |
| $D_\kappa$  | fractional diffusion coefficient  |
| $D_\omega$  | frequency-dependent diffusion coefficient   |
| $D^\infty$  | effective or long-time self-diffusion coefficient   |
| $D^*$   | asymptotic dispersion coefficient   |
| $D(t)$  | (measuring time-dependent) diffusion coefficient obtained in the SGP limit  |
| <b>D</b> ( $t$ )  | time-dependent diffusion tensor   |
| $D^0$   | infinite dilution (or short time) self-diffusion coefficient  |
| $D_{\text{anion}}$  | anion diffusion coefficient   |
| $D_{\text{cation}}$   | cation diffusion coefficient  |
| $d_f$   | dimension of the fractal space  |
| $d_w$   | random walk dimension   |
| $D^{\text{app}}, D^{\text{app}}(t)$ or $D^{\text{app}}(\Delta)$ | 'apparent diffusion coefficient' obtained by simplistically applying the free diffusion solution to the analysis of a more complicated system |
| $D^{\text{eff}}$  | synonymous with $D^\infty$  |
| $D_{\text{eff}}^*$  | effective time-dependent dispersion coefficient   |
| $D_b$   | bound ligand diffusion coefficient  |
| $D_f$   | free ligand diffusion coefficient   |
| $D_i$   | 'distinct' diffusion coefficient  |
| $D/D^0$   | relative diffusion coefficient  |
| <b>D</b> <sub>M</sub>   | mutual diffusion tensor   |
| $D_M$   | mutual diffusion coefficient  |
| DOSY  | diffusion ordered spectroscopy  |
| <b>D</b> <sup>pr</sup>  | self-diffusion tensor in the principal axes frame ( $x, y, z$ )   |
| DQ  | double quantum  |
| $d_s$   | spectral dimension  |
| DCNMR   | <i>see</i> electrophoretic NMR  |
| DDCOSY  | diffusion–diffusion correlation spectroscopy  |
| DRCOSY  | diffusion–relaxation correlation spectroscopy   |
| DDIF  | diffusion decay in the internal field   |
| DTI   | diffusion tensor imaging  |
| DWI   | diffusion-weighted imaging  |
| $\Delta\bar{P}(\mathbf{R}, \Delta)_{\frac{1}{2}}$               | average propagator width at half-height   |
| $E$   | elliptic integral of the second kind  |
| $E, E(\mathbf{q}, \Delta)$                                      | spin-echo attenuation (normally synonymous with $E_{\text{Diff}}$ )   |

|                                      |  |
|--------------------------------------|--|
| $E_{\text{dc}}$                      | pulsed electric field  |
| $E_{\text{Diff}}$                    | spin-echo attenuation due to diffusion   |
| $E(g_1)$                             | spin-echo attenuation due to $B_1$ gradients (normally synonymous with $E_{\text{Diff}}$ )                             |
| $E(\mathbf{q}, \infty)$              | long-time diffusive attenuation  |
| $E_{\text{phase}}$                   | signal attenuation due to the phase-twist or residual phase-twist  |
| $E_{\text{poly}}$                    | spin-echo attenuation in a polydisperse system   |
| $E_{\text{Relax}}$                   | spin-echo attenuation due to relaxation  |
| ENMR                                 | electrophoretic NMR  |
| $F$                                  | Perrin factor  |
| $\text{FT}\{L(Z)\}$                  | reciprocal lattice   |
| $f$                                  | friction coefficient   |
| $F_1$                                | indirectly detected dimension in a 2D NMR experiment   |
| $F_2$                                | directly detected dimension in a 2D NMR experiment   |
| $f_s$                                | free volume contributed by the solvent   |
| FID                                  | free induction decay   |
| FT                                   | Fourier transform  |
| $\mathbf{g}$                         | magnetic field gradient (applied) – normally spatially homogeneous (i.e., constant)                                    |
| $\mathbf{g}_0$                       | background or constant magnetic gradient   |
| $g^{\text{app}}$                     | initial guess of gradient strength   |
| $g_e$                                | encoding gradient  |
| $g_{\text{eff}}$                     | effective gradient   |
| $\mathbf{g}_{\text{int}}$            | magnetic gradient arising from internal susceptibility differences ( <i>see</i> background (magnetic field) gradients) |
| $g_r$                                | read gradient  |
| $G_{x,y,z}$                          | gradient used for spatial localisation in MRI  |
| GPD                                  | Gaussian phase distribution  |
| $\mathbf{H}$                         | mean square displacement tensor  |
| $H$                                  | Hurst exponent   |
| $h$                                  | reduced permeability ( $= Ma/D$ )  |
| HMQC                                 | heteronuclear multiple-quantum coherence   |
| HRMAS                                | high-resolution magic angle spinning   |
| HSA                                  | human serum albumin  |
| $\zeta$                              | tortuosity   |
| $\mathbf{i}, \mathbf{j}, \mathbf{k}$ | unit coordinate vectors  |
| IMFG                                 | internal magnetic field gradient ( <i>see</i> background (magnetic field) gradients)                                   |
| $\mathbf{J}_A(t)$                    | flux associated with species $A$ at time $t$   |

|                            |  |
|----------------------------|--|
| $J_n(x)$                   | Bessel function of the first kind of order $n$   |
| $j_n(x)$                   | spherical Bessel function of order $n$   |
| $K$                        | modified Bessel function of the third kind   |
| $K$                        | elliptic integral of the first kind  |
| $K$                        | mobility factor  |
| $\mathbf{k}$ (or $k$ )     | dephasing strength of gradients when used in imaging ( <i>see</i> $\mathbf{k}$ , $k$ -space) |
| $k$                        | gradient or diffusion weighting factor, more commonly written as $b$                         |
| $k_1$                      | first-order rate constant  |
| $k_{+1}$                   | (forward) first-order rate constant  |
| $k_{-1}$                   | (reverse) first-order rate constant  |
| $K_d$                      | dissociation constant  |
| $K_e$                      | equilibrium constant   |
| $l$                        | step length or size, length of sample tube, length of receiver coil                          |
| $L(Z)$                     | lattice correlation function   |
| $\mathcal{L}$              | Laplace transform  |
| LED                        | longitudinal eddy current delay  |
| $M$                        | relaxivity (or permeability)   |
| $M_0$                      | thermal equilibrium magnetisation  |
| MAGROFI                    | magnetisation rotating frame imaging   |
| MGSE                       | Modulated Gradient Spectroscopy <i>see</i> OGSE  |
| MAS                        | magic angle spinning   |
| MMME                       | multiple modulation multiple-echo  |
| MOSY                       | mobility ordered spectroscopy  |
| MRI                        | (nuclear) magnetic resonance imaging   |
| MSD, $\langle R^2 \rangle$ | mean square displacement   |
| MW                         | molecular weight   |
| $M_n$                      | number-average molecular weight  |
| $M_w$                      | weight-average molecular weight  |
| LED                        | longitudinal eddy current delay  |
| $\mathbf{n}$               | outward surface normal   |
| $n$                        | number of spatial dimensions   |
| $n_{\text{avg}}$           | average number concentration of counterions in the spherical shell                           |
| $n(R_{\text{cell}})$       | number concentration of counterions at the outer shell boundary                              |
| NOE                        | nuclear Overhauser effect  |
| NOESY                      | nuclear Overhauser enhancement spectroscopy  |
| $O_D$                      | obstruction factor   |

|                                       |  |
|---------------------------------------|--|
| OGSE                                  | oscillating gradient spin-echo (sequence)  |
| $p$                                   | coherence order ( <i>see also</i> multiple quantum coherences)   |
| $P_b$                                 | bound (fractional) population (of a ligand)  |
| $P_e$                                 | Péclet number  |
| $P_f$                                 | free (fractional) population (of a ligand)   |
| $P_n(x)$                              | Legendre polynomial of order $n$   |
| $\bar{P}(\mathbf{R}, t)$              | average or mean propagator, the probability that a particle will move a distance $\mathbf{R}$ in time $t$    |
| $P(a)$                                | distribution sphere radii  |
| $P(x, y)$                             | joint probability (e.g., $P(D_{ii}, D_{jj})$ , $P(\omega, D)$ )  |
| $P(v)$                                | distribution of velocities   |
| $P(\mathbf{r}_0, \mathbf{r}_1, t), P$ | diffusion propagator, the probability of moving from $\mathbf{r}_0$ to $\mathbf{r}_1$ in time $t$            |
| $P_\phi, P_\phi(\phi, t)$             | probability of phase distribution = phase distribution function  |
| $[P]_{\text{Total}}$                  | total macromolecule concentration  |
| PFG                                   | pulsed field gradient  |
| PGSE                                  | pulsed gradient spin-echo  |
| PGSTE                                 | pulsed gradient stimulated (spin) echo   |
| $\mathbf{q}$                          | dephasing strength of gradients when used for measuring displacement ( <i>see</i> $\mathbf{q}$ , $q$ -space) |
| $\Delta\mathbf{q}$                    | gradient mismatch  |
| $q_{\text{max}}$                      | maximum value of $q$ used in an experiment   |
| $\mathbf{r}$                          | position of a particle (or voxel)  |
| $\Delta\mathbf{r}$                    | sample movement  |
| $\mathbf{r}_0$                        | initial position   |
| $\mathbf{r}_1$                        | finishing position   |
| $r_s$                                 | Stokes radius (effective hydrodynamic radius)  |
| $\mathbf{R}$                          | dynamic displacement (= $\mathbf{r}_1 - \mathbf{r}_0$ )  |
| $R_a$                                 | Rayleigh number  |
| $R_{\text{cell}}$                     | radius of an electroneutral spherical shell  |
| $R_s$                                 | radius of a charged hard sphere  |
| RMS                                   | root mean square   |
| RMSD                                  | root mean square displacement  |
| RTOP                                  | return to origin probability   |
| $\text{RTOP}^0$                       | RTOP in free isotropic solution  |
| $\text{RTOP}^e$                       | dimensionless RTOP enhancement   |
| rf                                    | radio frequency  |
| $S(\mathbf{q})$                       | Fourier transform of $\rho(\mathbf{r}_1)$ , signal in MRI  |

|                            |   |
|----------------------------|---|
| $ S(\mathbf{q}) ^2$        | power spectrum of $\rho(\mathbf{r}_0)$ , elastic incoherent structure factor or form factor |
| $ S_0(\mathbf{q}) ^2$      | average pore structure factor   |
| SE                         | spin-echo (sequence) (or Hahn echo (sequence))  |
| SGP                        | short gradient pulse approximation  |
| SGSE                       | steady gradient spin-echo   |
| $S_p$                      | surface area of a pore  |
| $S_p/V_p$                  | surface (area)-to-volume ratio of a pore  |
| STE                        | stimulated echo (sequence)  |
| STRAFI                     | stray-field imaging   |
| $t_e$                      | delay for eddy current dissipation  |
| $t_{\text{echo}}$          | time at which echo formation occurs   |
| $T$                        | temperature   |
| $T$                        | total time for image acquisition  |
| $T_1$                      | spin–lattice relaxation time  |
| $T_2$                      | spin–spin relaxation time   |
| $T_2^{ZQC}$                | transverse relaxation time of a zero-quantum coherence                                      |
| $t_r$                      | reptation time  |
| $T_{\text{RD}}$            | radiation damping time constant   |
| $T_s$                      | singlet relaxation time   |
| TOCSY                      | total correlation spectroscopy  |
| $\mathbf{u}$               | fluctuating part of velocity  |
| $v$                        | velocity  |
| $\nu$                      | kinematic viscosity   |
| $v^+$                      | velocity of cationic species  |
| $v^-$                      | velocity of anionic species   |
| $v_{\text{max}}$           | maximum measurable velocity ( <i>see</i> NMR Imaging – max measurable flow rate)            |
| $v_0$                      | constant velocity   |
| $V$                        | total volume (of a system)  |
| $V_h$                      | partial specific volume of a solvent  |
| $V_p$                      | volume of a pore  |
| $V_s$                      | partial specific volume of a solute   |
| $\mathbf{v}$               | (local) spin velocity ( <i>see also</i> Lagrangian velocity field)                          |
| $\mathbf{v}_i(t)$          | velocity of a particle in the barycentric reference frame                                   |
| $\bar{\mathbf{V}}$         | average velocity  |
| $\langle v \rangle$        | average velocity  |
| $\langle v^2 \rangle$      | mean square velocity  |
| $\langle v(0)v(t) \rangle$ | velocity auto-correlation function  |



|                               |  |
|-------------------------------|--|
| WATERGATE                     | a gradient-based water suppression technique   |
| $x, y, z$                     | Cartesian coordinates (primes can be used to denote the laboratory frame, if required) |
| $(r, \theta, \phi)$           | spherical polar coordinates  |
| $z_0$                         | initial position for a one-dimensional motion  |
| $z_1$                         | finishing position for a one-dimensional motion  |
| $Z$                           | one dimensional dynamic displacement ( $= z_1 - z_0$ )                                 |
| $\langle Z \rangle$           | average displacement   |
| $\langle Z_u^2 \rangle$       | positional variance  |
| $Z_u(t)$                      | displacement fluctuation   |
| $\langle Z^n(\Delta) \rangle$ | moments of the average propagator ( $\bar{P}(Z, \Delta)$ )                             |

### Greek

|                        |   |
|------------------------|---|
| $\alpha$               | thermal expansion   |
| $\alpha$               | time-independent scaling constant   |
| $\Gamma(\Delta)$       | time-dependent function characteristic of a geometry                        |
| $\gamma$               | (chemical) activity coefficient   |
| $\gamma$               | gyromagnetic ratio  |
| $\gamma_{\text{eff}}$  | effective gyromagnetic ratio  |
| $\delta$               | duration of the gradient pulse  |
| $\delta_h$             | hydration/solvation (grams of solvent/grams of solute)                      |
| $\delta_{nm}$          | Kronecker delta   |
| $\Delta$               | difference  |
| $\Delta$               | timescale of the diffusion measurement                                      |
| $\Delta_{\text{CPMG}}$ | effective diffusion time (i.e., effective $\Delta$ ) in a CPMG measurement  |
| $\Delta^{\text{eff}}$  | effective diffusion time (i.e., effective $\Delta$ ) in an OGSE experiment  |
| $\eta$                 | magic (gradient) ratio  |
| $\eta$                 | viscosity   |
| $\eta_F$               | filling factor  |
| $\Theta$               | Spectral function   |
| $\theta$               | occupation probability  |
| $\theta_a$             | exponent of anomalous diffusion   |
| $\kappa$               | $= 2/d_w$   |
| $\kappa$               | thermal diffusivity   |
| $\kappa$               | exponent characterising the time dependence of the mean square displacement |
| $\Lambda$              | conductivity  |
| $\Lambda_q$            | pitch of a magnetisation helix due to a pulse of area ' $2\pi q$ '          |

|   |  |
|---|--|
| $\rho(\mathbf{r}_0), \rho(\mathbf{r}_0, 0)$ | equilibrium spin density   |
| $\lambda$                                   | separation between adjacent sites  |
| $\mu$                                       | drift velocity   |
| $\mu_0$                                     | permittivity constant (magnetic permeability)                                      |
| $\sigma$                                    | length of oscillating gradient pulse   |
| $\sigma$                                    | standard error   |
| $\tau$                                      | a delay in a pulse sequence or discretisation time                                 |
| $\tau_b$                                    | lifetime of a ligand in the bound state  |
| $\tau_c$                                    | reorientational correlation time   |
| $\tau_e$                                    | extracellular (external to the pore) lifetime                                      |
| $\tau_f$                                    | lifetime of a ligand in the free state   |
| $\tau_i$                                    | intracellular (internal to the pore) lifetime                                      |
| $\tau_j$                                    | time between jumps   |
| $\tau_m$                                    | mixing time  |
| $\tau_v$                                    | velocity correlation time  |
| $\nu$                                       | frequency (with respect to spectrometer reference frequency)                       |
| $\nu_l$                                     | step rate  |
| $\Delta\nu$                                 | linewidth  |
| $\Delta\nu_{1/2}$                           | linewidth at half-height   |
| $\xi$                                       | dimensionless variable ( $= D\Delta/a^2$ ) for characterising restricted diffusion |
| $\Phi_{\text{Flow}}$                        | change in phase of a spin-echo signal due to flow                                  |
| $\phi$                                      | phase angle (phase of spins)   |
| $\phi$                                      | porosity   |
| $\phi$                                      | volume fraction  |
| $\langle\phi^2\rangle$                      | mean square phase distribution   |
| $\omega$                                    | frequency ( $\text{rad s}^{-1}$ )  |