NMR STUDIES OF TRANSLATIONAL MOTION

Translational motion in solution, either diffusion or fluid flow, is at the heart of chemical and biochemical reactivity. Nuclear magnetic resonance (NMR) provides a powerful non-invasive technique for studying the phenomena using magnetic field gradient methods. Describing the physical basis of measurement techniques, with particular emphasis on diffusion, balancing theory with experimental observations and assuming little mathematical knowledge, this is a strong, yet accessible, introduction to the field. A detailed discussion of magnetic field gradient methods applied to magnetic resonance imaging (MRI) is included, alongside extensive referencing throughout, providing a timely, definitive book to the subject, ideal for researchers in the fields of physics, chemistry and biology.

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Cambridge Molecular Science

As we enter the twenty-first century, chemistry has positioned itself as the central science. Its subject matter, atoms and the bonds between them, is now central to many of the life sciences on the one hand, as biological chemistry brings the subject to the atomic level, and to condensed matter and molecular physics on the other. Developments in quantum chemistry and in statistical mechanics have also created a fruitful overlap with mathematics and theoretical physics. Consequently, boundaries between chemistry and other traditional sciences are fading and the term *Molecular Science* now describes this vibrant area of research.

Molecular science has made giant strides in recent years. Bolstered both by instrumental and by theoretical developments, it covers the temporal scale down to femtoseconds, a time scale sufficient to define atomic dynamics with precision, and the spatial scale down to a small fraction of an Angstrom. This has led to a very sophisticated level of understanding of the properties of small molecule systems, but there has also been a remarkable series of developments in more complex systems. These include protein engineering; surfaces and interfaces; polymers; colloids; and biophysical chemistry. This series provides a vehicle for the publication of advanced textbooks and monographs introducing and reviewing these exciting developments.

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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.[1–6] A tabulation of many of the commonly used NMR acronyms can be found elsewhere.[7]

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[8–21] 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[22,23] 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 (*see also* D^{app})
a_M	relaxation length
a_{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 ith 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

$\mathbf{D}$	self-diffusion tensor
$\mathbf{D}^{lab}$	diffusion tensor in the laboratory axes frame (x', y', z')
$\mathbf{D}_\omega$	diffusion coefficient spectrum or tensor
D_κ	fractional diffusion coefficient
D_ω	frequency-dependent diffusion coefficient
D^∞	effective or long-time self-diffusion coefficient
D^*	asymptotic dispersion coefficient
$D(t)$	(measuring time-dependent) diffusion coefficient obtained in the SGP limit
$\mathbf{D}(t)$	time-dependent diffusion tensor
D^0	infinite dilution (or short time) self-diffusion coefficient
D_{anion}	anion diffusion coefficient
D_{cation}	cation diffusion coefficient
d_f	dimension of the fractal space
d_w	random walk dimension
D^{app}, $D^{app}(t)$ or $D^{app}(\Delta)$	'apparent diffusion coefficient' obtained by simplistically applying the free diffusion solution to the analysis of a more complicated system
D^{eff}	synonymous with D^∞
D^*_{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
$\mathbf{D}_M$	mutual diffusion tensor
D_M	mutual diffusion coefficient
DOSY	diffusion ordered spectroscopy
$\mathbf{D}^{pr}$	self-diffusion tensor in the principal axes frame (x, y, z)
DQ	double quantum
d_s	spectral dimension
DCNMR	*see* 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_{Diff})

E_{dc}	pulsed electric field
E_{Diff}	spin-echo attenuation due to diffusion
$E(g_1)$	spin-echo attenuation due to B_1 gradients (normally synonymous with E_{Diff})
$E(\mathbf{q}, \infty)$	long–time diffusive attenuation
E_{phase}	signal attenuation due to the phase-twist or residual phase-twist
E_{poly}	spin-echo attenuation in a polydisperse system
E_{Relax}	spin-echo attenuation due to relaxation
ENMR	electrophoretic NMR
F	Perrin factor
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^{app}	initial guess of gradient strength
g_e	encoding gradient
g_{eff}	effective gradient
$\mathbf{g}_{int}$	magnetic gradient arising from internal susceptibility differences (*see* 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
$\Im$	tortuosity
$\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$	unit coordinate vectors
IMFG	internal magnetic field gradient (*see* 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 (*see* $\mathbf{k}$, 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 *see* 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_{avg}	average number concentration of counterions in the spherical shell
$n(R_{cell})$	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 (*see also* 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
$[P]_{Total}$	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 (*see* $\mathbf{q}$, q-space)
$\Delta\mathbf{q}$	gradient mismatch
q_{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_{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
$RTOP^0$	RTOP in free isotropic solution
$RTOP^e$	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_{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_{RD}	radiation damping time constant
T_S	singlet relaxation time
TOCSY	total correlation spectroscopy
$\mathbf{u}$	fluctuating part of velocity
v	velocity
v	kinematic viscosity
v^+	velocity of cationic species
v^-	velocity of anionic species
v_{max}	maximum measurable velocity (*see* 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 (*see also* 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, θ, ϕ)	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

α	thermal expansion
α	time-independent scaling constant
$\Gamma(\Delta)$	time-dependent function characteristic of a geometry
γ	(chemical) activity coefficient
γ	gyromagnetic ratio
γ_{eff}	effective gyromagnetic ratio
δ	duration of the gradient pulse
δ_h	hydration/solvation (grams of solvent/grams of solute)
δ_{nm}	Kronecker delta
Δ	difference
Δ	timescale of the diffusion measurement
Δ_{CPMG}	effective diffusion time (i.e., effective Δ) in a CPMG measurement
Δ^{eff}	effective diffusion time (i.e., effective Δ) in an OGSE experiment
η	magic (gradient) ratio
η	viscosity
η_F	filling factor
Θ	Spectral function
θ	occupation probability
θ_a	exponent of anomalous diffusion
κ	$= 2/d_w$
κ	thermal diffusivity
κ	exponent characterising the time dependence of the mean square displacement
Λ	conductivity
Λ_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
λ	separation between adjacent sites
μ	drift velocity
μ_0	permittivity constant (magnetic permeability)
σ	length of oscillating gradient pulse
σ	standard error
τ	a delay in a pulse sequence or discretisation time
τ_b	lifetime of a ligand in the bound state
τ_c	reorientational correlation time
τ_e	extracellular (external to the pore) lifetime
τ_f	lifetime of a ligand in the free state
τ_i	intracellular (internal to the pore) lifetime
τ_J	time between jumps
τ_m	mixing time
τ_v	velocity correlation time
ν	frequency (with respect to spectrometer reference frequency)
ν_l	step rate
$\Delta\nu$	linewidth
$\Delta\nu_{1/2}$	linewidth at half-height
ξ	dimensionless variable ($= D\Delta/a^2$) for characterising restricted diffusion
Φ_{Flow}	change in phase of a spin-echo signal due to flow
ϕ	phase angle (phase of spins)
ϕ	porosity
ϕ	volume fraction
$\langle\phi^2\rangle$	mean square phase distribution
ω	frequency (rad s^{-1})