

Contents

1 Thermal processes and diffusion	1
1.1 Boltzmann, Einstein, and molecules	1
1.2 Statistical physics and ensembles	2
1.2.1 Temperature and entropy	2
1.2.2 The Boltzmann distribution and partition function	7
1.2.3 Partition function, free energy, and entropy of an ideal monatomic gas	8
1.2.4 Ensembles and averages	10
1.2.5 Fluctuations, ergodicity, and the autocorrelation function	11
1.3 Thermal energy and self-diffusion	13
1.3.1 Fick's law	13
1.3.2 Brownian motion: the Einstein derivation	14
1.3.3 The probabilistic description	15
1.3.4 Relationship of diffusion to velocity autocorrelation function	20
1.3.5 The diffusion tensor	21
1.3.6 The Smoluchowski equation	22
1.3.7 The Langevin equation	22
1.3.8 Correlation and the fluctuating force	24
1.3.9 Ornstein–Uhlenbeck process	26
1.3.10 Diffusion in a harmonic potential	26
References	27
2 Flow and dispersion	29
2.1 Flow	30
2.1.1 Eulerian and Lagrangian descriptions	30
2.1.2 Substantive derivative and fluid dynamics	32
2.1.3 Navier–Stokes, inertia, and the Reynolds number	33
2.1.4 Stress and strain tensors	34
2.1.5 Navier–Stokes solutions and lattice Boltzmann	36
2.1.6 Conditional probability and average propagators for flow	39
2.2 Non-Newtonian fluids and viscoelasticity	41
2.2.1 Strain fields used in rheology	42
2.2.2 Linear viscoelasticity	44
2.2.3 Non-linear viscoelasticity	47
2.3 Dispersion	49
2.3.1 Stationary random flow and pseudo-diffusion	49

2.3.2	Porous medium characteristics	50	4.2.3	Quantum view of nutation	115
2.3.3	The dispersion tensor	53	4.2.4	Classical descriptions of resonant reorientation	118
2.3.4	Taylor dispersion in pipe flow	58	4.2.5	Semi-classical description	120
2.3.5	The velocity autocorrelation function and dispersion spectrum	60	4.2.6	Relaxation and the Bloch equations	121
2.3.6	Non-local dispersion	61	4.3	Signal detection	123
References		63	4.3.1	Free precession and Faraday detection	123
3	Quantum description of nuclear ensembles	65	4.3.2	Fourier transformation and the spectrum	126
3.1	Quantum mechanics and nuclear spin	66	4.3.3	Digital Fourier transformation	128
3.1.1	Four key ideas in quantum mechanics	67	4.4	Intrinsic spin interactions	129
3.1.2	Representation of angular momentum	71	4.4.1	Resolution in NMR	129
3.2	Spin ensembles and the density matrix	77	4.4.2	Chemical shift	131
3.2.1	Spin- $\frac{1}{2}$ ensembles	79	4.4.3	Scalar coupling	131
3.2.2	Density matrix properties	81	4.4.4	Quadrupole coupling	134
3.2.3	Evolution and the quantum Liouville equation	82	4.4.5	Internuclear dipolar interactions	136
3.2.4	Pure states, mixed states and quantum coherence	82	4.5	Fluctuations, spin relaxation, and motional averaging	138
3.3	Tensor bases for the density matrix	83	4.5.1	Spin-lattice relaxation	139
3.3.1	Liouville space for spin- $\frac{1}{2}$	83	4.5.2	Spin-spin relaxation	140
3.3.2	Liouville space for $I > \frac{1}{2}$	85	4.5.3	Motional averaging	142
3.3.3	Product operator Liouville space for two coupled spin- $\frac{1}{2}$ nuclei	87	4.6	Pulse sequences	144
3.3.4	Spherical tensors	89	4.6.1	Basic spin manipulation	144
3.4	The spin Hamiltonian	94	4.6.2	Echoes	149
3.4.1	The i -spin Hamiltonian	95	4.6.3	Multiple pulse line-narrowing	160
3.4.2	The Hamiltonian in terms of tensor products	96	4.6.4	Multiquantum pathways	163
3.4.3	Precession diagrams for $I = 1/2$ and $I = 1$	98	4.6.5	Multidimensional NMR	169
3.4.4	Spherical tensor precession for coupled spin- $\frac{1}{2}$	100	References		173
3.5	The thermal equilibrium density matrix	100	5	Magnetic field gradients and spin translation	177
3.5.1	The Boltzmann form of the density matrix	100	5.1	Gradient fields and Maxwell's equations	178
3.5.2	Nuclear spins in thermal equilibrium—the high temperature approximation	101	5.2	Phase evolution of spin isochromats	180
3.5.3	Higher terms in the expansion—breakdown of the high temperature approximation	103	5.2.1	Magnetisation phase	180
3.5.4	A closer look at thermal equilibrium	103	5.2.2	Spin isochromats in an inhomogeneous field	181
References		104	5.2.3	Phase evolution in the presence of a field gradient	181
4	Introductory magnetic resonance	107	5.3	Magnetic resonance imaging	184
4.1	Introductory remarks	108	5.3.1	Spatial Fourier relations	184
4.1.1	The NMR orchestra	108	5.3.2	Trajectories in k-space	185
4.1.2	Coherence and the spin echo	108	5.3.3	Selective excitation	188
4.2	Resonant excitation	109	5.4	Translational motion encoding	191
4.2.1	The rotating frame transformation	110	5.4.1	Time-varying gradients and phase factors	193
4.2.2	The resonant radiofrequency field	111	5.4.2	Coherent spin motion: velocity, acceleration, and jerk	196
			5.4.3	The Carr-Purcell analysis of diffusion effects	197
			5.4.4	The Bloch-Torrey equation for diffusion and flow	202
			5.5	Pulsed gradient spin-echo NMR: diffusion and flow	204
			5.5.1	The Stejskal-Tanner experiment	204
			5.5.2	The role of background gradients	211

5.5.3 Echo schemes to reduce the effect of background gradients	212	6.5.2 Regimes of interest	280
5.5.4 More efficient encoding schemes	215	6.5.3 Alternative non-dimensional parameters	282
5.5.5 Using pulsed gradients to measure the diffusion tensor	220	6.6 Pulsed gradient spin-echo NMR for bounded molecules	283
5.6 Pulsed gradient spin-echo NMR: general motion	221	6.6.1 Diffusion in a harmonic potential	284
5.6.1 Narrow gradient pulse approximation and q -space	222	6.6.2 Diffusion and exchange between two sites	285
5.6.2 Low q limit	226	6.6.3 Dimensional restriction: randomly distributed pipes and sheets	286
5.6.3 The meaning of k-space and q-space for time-varying gradients	227	6.6.4 Curvilinear diffusion	289
5.7 Finite gradient pulses and generalised motion	228	6.6.5 Anisotropic diffusion in oriented liquid crystals	292
5.7.1 Multiple propagator approach	228	6.6.6 Diffusion in fractal geometries	294
5.7.2 Generalised gradients and the frequency domain	234	6.7 Frequency-domain measurements and restricted motion	295
5.8 Phase effects of RF pulses and homospoiling	242	6.7.1 Spectral densities for free and restricted diffusion	297
5.8.1 Rules for RF pulses	242	6.7.2 Spectral analysis of flow	301
5.8.2 The spin echo and stimulated echo	244	References	303
5.9 Diffusion in the radiofrequency field	245	7 Restricted displacements and diffraction phenomena	309
5.9.1 How RF field gradients work	245	7.1 PGSE NMR ‘diffraction’ in pores	310
5.9.2 Measurement of diffusion and flow	247	7.1.1 A historical precursor: rectangular boundaries	311
5.9.3 Advantages and disadvantages of RF gradients	248	7.1.2 Diffusive diffraction in an enclosed pore	312
References	248	7.1.3 The pore density assumption revisited	316
6 Restricted diffusion	252	7.1.4 Diffusive diffraction in a matrix of enclosing pores	317
6.1 Apparent and effective diffusion coefficients	253	7.1.5 ‘Long-narrow’ PGSE NMR: direct imaging of the structure factor by diffusive diffraction	318
6.2 Time-dependent mean-squared displacement	254	7.2 Finite time diffraction in planar, cylindrical and spherical pores	322
6.2.1 Tortuosity and the long-time limit	254	7.2.1 Finite Δ : the exact treatment	322
6.2.2 The short-time limit for restricted diffusion	256	7.2.2 Parallel plane pore	323
6.2.3 Interpolation of short- and long-time limits for restricted diffusion	259	7.2.3 Cylindrical pore	325
6.2.4 $D_{\text{eff}}(t)$ and calculation of the apparent diffusion coefficient for any gradient waveform	259	7.2.4 Spherical pore	328
6.2.5 The definition of the asymptotic limit	260	7.2.5 Finite width gradient pulses and relaxation effects	329
6.3 Spin relaxation in microscopically inhomogeneous media	261	7.3 Interconnected pores	331
6.3.1 Exchange between sites	262	7.3.1 Eigenmodes of the interconnected pore space	332
6.3.2 Relaxation sinks and normal modes: wall relaxation and the Brownstein–Tarr relations	266	7.3.2 Pore equilibration model	335
6.4 Diffusion in local inhomogeneous fields	269	7.3.3 ‘Long-narrow’ PGSE NMR and interconnected pores	342
6.4.1 Calculating the local field	270	7.4 Applications of q -space diffraction	343
6.4.2 Effect of molecular diffusion and the Anderson–Weiss treatment	270	7.4.1 Emulsions and capsules	343
6.4.3 Measuring relaxation in porous media.	273	7.4.2 Biology and medicine	344
6.4.4 Decay due to diffusion in the internal field	274	7.4.3 Pulsed gradient spin-echo ESR	345
6.4.5 q -space analysis of internal field correlations	276	7.5 Flow diffraction	347
6.5 Restricted diffusion for spin echoes with steady gradients	278	7.6 Related issues	348
6.5.1 Characteristic length scales	279	7.6.1 Frequency-domain modulated gradient NMR and diffusive diffraction	348
		7.6.2 Return to origin probability	349
		References	350

8 Double wavevector encoding	354
8.1 Double PGSE NMR	355
8.1.1 The double scattering process	355
8.1.2 Compensated and uncompensated sequences	356
8.2 Double PGSE NMR and dispersion	356
8.2.1 Propagator and ensemble descriptions	356
8.2.2 Dispersion measurement and the low- q limit	358
8.2.3 Reversible and irreversible dispersion	362
8.3 Phase cycling for double PGSE NMR	363
8.3.1 Characterising the coherences	364
8.3.2 Coherence selection	365
8.4 Non-local dispersion tensor	367
8.4.1 The pulse sequence for velocity and displacement encoding	367
8.4.2 Non-local dispersion for porous media flow	372
8.4.3 Non-local dispersion for pipe flow	373
8.5 Restricted diffusion and double wavevector encoding with long mixing time	375
8.5.1 Correlated and uncorrelated phase encoding	375
8.5.2 The propagator description $\tau_m \gg a^2/D$	376
8.5.3 Local anisotropy, global isotropy	378
8.6 Restricted diffusion and double wavevector encoding with infinitesimal mixing	383
8.6.1 The Mitra paradox	384
8.6.2 Propagator description, $\tau_m \ll a^2/D$	385
8.7 Restricted diffusion and double wavevector encoding with finite mixing time	389
8.7.1 First-order expression for restricted isotropic geometries with general pulse timings	389
8.7.2 Isotropic fluid with unrestricted diffusion and finite width gradient pulse effects	391
8.8 Diffusive diffraction with double PGSE NMR	391
8.8.1 Diffractograms with signed amplitude	392
8.8.2 Unravelling structure in polydisperse systems	394
References	395
9 Multidimensional PGSE NMR	397
9.1 Fourier or Laplace?	398
9.1.1 An example from PGSE NMR	398
9.1.2 Forward and inverse	398
9.2 Inverse Laplace transformations	400
9.2.1 Analytic and numerical inverse Laplace transformations	400
9.2.2 Regularised non-negative least squares in 1-D	402

9.2.3 Regularised non-negative least squares in 2-D	404
9.2.4 Testing using known distributions and pearling effects	406
9.3 Multi-dimensional Fourier–Fourier methods	407
9.3.1 VEXSY	407
9.3.2 SERPENT	411
9.3.3 POXSY	412
9.3.4 Two-dimensional propagators	413
9.3.5 Inhomogeneous field exchange	414
9.4 Fourier–Laplace methods	416
9.4.1 Diffusion-resolved spectroscopy	417
9.4.2 Propagator-resolved T_2	419
9.5 Multidimensional Laplace–Laplace correlation methods	421
9.5.1 Relaxation-relaxation	421
9.5.2 Negative peaks and coupled eigenmodes	423
9.5.3 Diffusion–relaxation	425
9.5.4 Diffusion-local field and relaxation-local field	427
9.5.5 DDCOSY	430
9.6 Multidimensional Laplace–Laplace exchange methods	433
9.6.1 DEXSY	434
9.6.2 Relaxation exchange spectroscopy	437
9.6.3 Symmetry and peak amplitude sign in exchange and correlation spectroscopy	439
9.7 Diffusion tensor measurement	440
9.7.1 Frame transformation	440
9.7.2 Echo experiment for diffusion tensor	442
9.7.3 Choice of diffusion gradient directions	443
9.7.4 Diagonalisation and diffusion matrix parameters	444
9.7.5 Diffusion tensor imaging	445
9.7.6 Cancelling the effect of imaging gradients	446
9.7.7 Extracting and displaying the information content	447
References	447
10 Velocimetry	451
10.1 Imaging the propagator	452
10.1.1 Pulse sequence	452
10.1.2 Data processing	453
10.1.3 Velocity resolution limit	455
10.1.4 Velocity null experiments	456
10.2 Single-step phase encoding for velocity	457
10.2.1 Reference phase processing	458
10.2.2 Fourier analysis	459
10.2.3 Choice of method	460
10.3 Fast encoding and real-time velocimetry	461
10.3.1 Flow timescale	461

10.3.2	Velocimetry timescale	461
10.3.3	Echo planar imaging	463
10.3.4	Rapid acquisition relaxation enhanced imaging	466
10.3.5	FLASH	469
10.3.6	SPRITE	470
10.4	Velocimetry applications in materials science, biology, and medicine	474
10.4.1	Porous media flow	474
10.4.2	Inertial flow and turbulence	475
10.4.3	Rheo-NMR	476
10.4.4	Electro-osmotic and electrophoretic flow	481
10.4.5	Biology	483
10.4.6	Granular flow	483
10.5	Potential artifacts	484
	References	485
11	Translational dynamics and quantum coherence	491
11.1	Diffusion measurement using multiple-quantum coherences	492
11.1.1	Use of dipolar couplings	492
11.1.2	Use of the quadrupole interaction	496
11.1.3	Scalar couplings and heteronuclear states	499
11.2	Singlet states and time extension	504
11.2.1	Product states, singlet-triplet states, and symmetry	505
11.2.2	Sequence for translation measurement	507
11.2.3	Measurement of diffusion via the singlet state	509
11.3	Intermolecular quantum coherence	510
11.3.1	The quantum description	512
11.3.2	Multi-echo and CRAZED phenomena	515
11.3.3	Experimental verification of multiple echo effect	519
11.3.4	Probing structure via intermolecular coherences	520
	References	521
12	Tricks of the trade	524
12.1	Instrumental limits	524
12.1.1	The diffusion baseline	524
12.1.2	Test samples	525
12.1.3	Non-Gaussian displacements	526
12.2	Conquering artifacts	526
12.2.1	Real-time monitoring	526
12.2.2	Sample movement	526
12.2.3	Eddy currents	528
12.2.4	Pulse mismatch	530
12.2.5	Small is beautiful	531
12.2.6	Fringe field diffusometry	532

12.3	Pulse-sequence compensation	533
12.3.1	Eddy current fields	533
12.3.2	Convection compensation	534
12.3.3	Gradient pulse mismatch compensation	535
12.3.4	Varying q	538
12.4	Final thoughts	538
	References	539

Index