## Contents

	Pi	reface	page xv
	Ac	cknowledgements	xvii
Pa	rt I	Bulk water	1
1.	Un	iqueness of water	3
	1.1	Introduction	3
	1.2	Molecular structure	4
	1.3	Six unique features	7
	1.4	Modeling of water	9
	1.5	Conclusion	10
2.	And	omalies of water	13
	2.1	Anomalous properties	13
		2.1.1 Density maximum	13
		2.1.2 Isobaric specific heat (C <sub>P</sub> )	15
		2.1.3 Isothermal compressibility ( $\kappa_T$ )	15
		2.1.4 Coefficient of thermal expansion (α <sub>P</sub> )	16
		2.1.5 Dynamic anomalies present at low temperature	17
	2.2	Translational and orientational order	19
	2.3	Temperature-density range of water anomalies	21
	2.4	Conclusion	22
	App	pendix 2.A Microscopic expressions of specific heat, isothermal	
		compressibility, and coefficient of thermal expansion	23
	App	pendix 2.B Quantification of spatial order in water	24
3.	Dyr	namics of water: molecular motions and hydrogen-bond-breaking	
	kine	etics	27
	3.1	Introduction	27
	3.2	Timescales of translational and rotational motion	28

viii Contents

	3.3	Jump reorientation motion in water	30
	3.4	Effects of temperature on water motion	33
	3.5	Translational diffusion	35
	3.6	Hydrogen-bond lifetime dynamics	36
	3.7	Vibrational dynamics of the O-H bond	39
	3.8	Dielectric relaxation	40
	3.9	Solvation dynamics	42
	3.10	Ionic conductivity of rigid ions in water	45
	3.11	Electron transfer reactions in water	47
	3.12	Motion becomes collective at low temperature	49
	3.13		50
	App	endix 3.A Rotational time correlation functions	51
	App	endix 3.B Quantification of hydrogen-bond	
		lifetime dynamics	58
4.	Inhe	erent structures of liquid water	61
	4.1	Introduction	61
	4.2	Transition between inherent structures of water	66
	4.3	Connected water cluster moves during transition	67
	4.4	HB network restructuring	67
	4.5	Coordination number fluctuation in inherent structure and	
		corresponding dynamics in parent liquid	68
	4.6	Low-energy excitations in liquid water	69
	4.7	Conclusion	69
5.	The	pH of water	71
	5.1	Introduction	71
	5.2	Temperature and pressure dependence of pH	73
	5.3	Mechanism of autoionization	74
	5.4	pH of blood	75
	5.5	Food and blood pH	76
	5.6	pH of seawater	77
	5.7	Conclusion	77
Da	rt II	Water in biology	70
La			79
6.		logical water	81
	6.1	Introduction	81
	6.2	Relaxation measurements	83
	6.3	Unique characteristics of biological water	83
	6.4	Phenomenological models and simple theories	84
	6.5	Protein-glass transition and hydration-layer dynamics	88

Contents	ix

	6.6	Protein aggregation and biological water	90
	6.7	Conclusion	90
	App	endix 6.A The dynamic exchange model	91
7.	An o	essential chemical for life processes: water in biological functions	97
	7.1	Introduction	97
	7.2	Role of water in enzyme kinetics	99
	7.3	Role of water in drug-DNA intercalation	101
	7.4	Role of water in the biological function of RNA	105
	7.5	Water-mediated molecular recognition	107
	7.6	Protein folding and protein association: role of biological water	109
	7.7	Role of water in beta-amyloid aggregation in Alzheimer disease	109
		7.7.1 Role of water in the early stages of oligomer formation	110
		7.7.2 Role of water in the late stages of fibril growth	111
	7.8	Role of water in photosynthesis	112
	7.9	Conclusion	114
8.	Hyd	ration of proteins	117
	8.1	Introduction	117
	8.2	What is the thickness of the hydration shell?	118
	8.3	How structured is the water in the hydration shell of a protein?	121
	8.4	Orientational arrangement of water molecules at the surface	123
	8.5	Dynamics of the protein hydration shell: experimental studies	124
		8.5.1 Dielectric spectrum	124
		8.5.2 Nuclear magnetic resonance studies	126
		8.5.3 Quasi-elastic neutron-scattering experiments	127
		8.5.4 Vibrational spectroscopy	128
		8.5.5 Solvation dynamics	129
	8.6	Conclusion	131
	App	endix 8.A Orientation of water molecules in the hydration layer	132
9.		erstanding the protein hydration layer: lessons from	
	com	puter simulations	135
	9.1	Introduction	135
	9.2	Molecular motion in the hydration layer	136
	9.3	Hydrogen-bond lifetime dynamics	140
	9.4	Computer simulation of solvation dynamics	142
	9.5	Dielectric relaxation	143
	9.6	Explanation of anomalous dynamics in the hydration layer	144
	9.7	Protein-glass transition at 200 K: role of water dynamics	144

9.8 I	ree-energy barrier for escape of water molecules from	
		146
9.9	Conclusion A. & Schenger Street of T. A. & Schenger	146
Water	in and around DNA and RNA	151
10.1	Introduction: the unique role of water in stabilizing	
	DNA and RNA	151
10.2	Hydration of different constituents	152
10.3	Groove structure and water dynamics	153
10.4	Translational and rotational dynamics of water molecules in the	
	grooves	153
10.5	Solvation dynamics	155
10.6		156
10.7	Correlation between diffusion and entropy: Adam-Gibbs	
	relation steading along its value to alone 1.3	157
10.8	Sequence dependence of DNA hydration: spine of hydration	
	in AT minor groove	159
10.9	Effects of nanoconfinement and surface-specific interactions	161
10.10	Water around RNA	161
	10.10.1 Structure of water around RNA	162
		162
10.11	Conclusion	162
Apper	ndix 10.A Hydrogen-bonding pattern around DNA	163
		167
		167
11.2		1.00
11.2		168
		169
		170
		174
	- Checintumia roluginos	174
		177
		177
12.2		
12.2		179
		179
		180
12.5	Transport of small molecules across the bilaver	181
	Water 10.1 10.2 10.3 10.4 10.5 10.6 10.7 10.8 10.9 10.10 10.11 Apper Protei 11.1 11.2 11.3 11.4 11.5 11.6 Water 12.1 12.2 12.3 12.4 12.5	protein hydration layer  9.9 Conclusion  Water in and around DNA and RNA  10.1 Introduction: the unique role of water in stabilizing DNA and RNA  10.2 Hydration of different constituents  10.3 Groove structure and water dynamics  10.4 Translational and rotational dynamics of water molecules in the grooves  10.5 Solvation dynamics  10.6 Entropy of groove water and dynamics  10.7 Correlation between diffusion and entropy: Adam–Gibbs relation  10.8 Sequence dependence of DNA hydration: spine of hydration in AT minor groove  10.9 Effects of nanoconfinement and surface-specific interactions  10.10 Water around RNA  10.10.1 Structure of water around RNA  10.10.2 Dynamics of water around RNA  10.11 Conclusion  Appendix 10.A Hydrogen-bonding pattern around DNA  Protein–DNA interaction: the role of water as a facilitator  11.1 Introduction  11.2 Structural analysis of protein–DNA complex: classification of hydration water  11.3 Dynamics of water around a protein–DNA complex  11.4 Role of water in thermodynamics of protein–DNA interactions  11.5 Protein diffusion along DNA  11.6 Conclusion  Water surrounding lipid bilayers: its role as a lubricant  12.1 Introduction  12.2 Hydration of different constituents: phospholipids and buried proteins  12.3 Rugged energy landscape for water motion  12.4 Translational and rotational dynamics of water

Contents	XI

	12.7	Transport of large molecules across the bilayer	18
	12.8	Electrostatic potential across the membrane	184
	12.9	Conclusion	18:
13.	The r	role of water in biochemical selection and protein synthesis	18
	13.1	Introduction	18
	13.2	Role of water in kinetic proofreading	188
		13.2.1 Brief analysis of the Hopefield-Ninio approach	
		to kinetic proofreading	190
		13.2.2 Analysis of experimental results in the light of the	
		Hopfield-Ninio formulation	190
		13.2.3 Aminoacylation of tRNA during protein synthesis	192
		13.2.4 tRNA selection in ribosome	194
		13.2.5 DNA replication	196
	13.3	Water as a lubricant of life	196
	13.4	Conclusion	197
Part	III	Water in complex chemical systems	199
14.	The h	ydrophilic effect	201
	14.1	Introduction	201
	14.2	Water near ions	202
	14.3	Water near an extended hydrophilic surface	204
	14.4	Aqueous hydrophilic binary mixtures	207
		14.4.1 Water–urea binary mixture	208
		14.4.2 Water–guanidinium hydrochloride	
		binary mixture	209
	14.5	Aqueous salt solutions	209
		14.5.1 Ionic conductivity	209
		14.5.2 Viscosity	211
	14.6	Conclusion	212
15.	The hydrophobic effect		
	15.1	Introduction	215
	15.2	Hydrophobic hydration	217
	15.3	Temperature dependence of hydrophobicity: enthalpy	
		versus entropy stabilizations	219
	15.4	Hydropathy scale	220
	15.5	Pair hydrophobicity and potential of mean force between two	
		hydrophobic solutes	221
	15.6	Biological applications of potential of mean force	223
		15.6.1 Protein folding	224
		The state of the s	

xii Contents

		15.6.2 Hydrophobic association	227
		15.6.3 Pattern formation in chiral molecules	227
	15.7	Hydrophobic collapse of polymers	227
		15.7.1 The Flory–Huggins theory	228
	15.8	Molecular-level understanding of hydrophobic interaction	230
	15.9	Hydrophobic force law	234
	15.10	Hydrophobicity at different length scales	234
	15.11	Conclusion	235
	Apper	ndix 15.A Pratt-Chandler theory	236
	15.A.	1 Cavity distribution functions	237
	15.A.:	2 Theory for A–W and A–A pair correlations	239
16.		mphiphilic effect: the diverse but intimate world of aqueous	
	binary	y mixtures — white the AMI of	243
	16.1	Introduction: the role of aqueous mixtures in chemistry	
		and biology	243
	16.2	Non-ideality of amphiphilic binary mixtures	245
	16.3	Water–DMSO binary mixture	245
	16.4	Water-alcohol binary mixture	249
		16.4.1 Aqueous methanol solution	250
		16.4.2 Aqueous ethanol solution	250
		16.4.3 Water–tertiary butyl alcohol	250
	16.5	Water-acetone binary mixture	252
	16.6	Water-dioxane binary mixture	252
	16.7	Liquid-liquid structural transformation in aqueous	
		binary mixtures: a generic phenomenon for amphiphilic solutes	253
	16.8	Theoretical development	254
	16.9	Biological applications	256
	16.10	Conclusion	258
17.	Water	r in and around micelles, reverse micelles, and microemulsions	261
	17.1	Introduction: different self-assemblies in water	261
	17.2	Structure of micelles and reverse micelles	262
		17.2.1 Micelles	262
		17.2.2 Reverse micelles	263
	17.3	Dynamics of water surrounding micelles	265
	17.4	Free-energy landscape of hydrogen-bond arrangements at the surface	266
	17.5	Reverse micelles and microemulsions: dynamics of water	268
	17.6	Orientational dynamics	269
	17.7	Core-shell model	270

The second secon	111
Contents	XIII

	17.8	Distance-dependent relaxation near the core of the reverse	
		micelle: propagation of surface-induced frustration	273
	17.9	Ising model description of the dynamics	273
	17.10	Conclusion	274
18.	Water	in a carbon nanotube: nature abhors a vacuum	277
	18.1	Introduction	277
	18.2	Type and structures of carbon nanotubes	277
	18.3	Structure of water inside a carbon nanotube	278
	18.4	Dynamics and transport of water	279
		18.4.1 Translational motion of water inside a CNT	279
		18.4.2 Rotation of water molecules within a CNT	280
	18.5	Nanotubes as a filtration device	282
	18.6	Conclusion	283
Danie	TV7 A	dyamond topics on water	285
rari	IV P	dvanced topics on water	203
19.	The e	ntropy of water	287
	19.1	Introduction	287
	19.2	Relation between entropy and diffusion	291
		19.2.1 Diffusion–entropy scaling relation:	
		the Rosenfeld relation	291
		19.2.2 The Adam–Gibbs relation	293
	19.3	Calculation of the entropy of water	295
		19.3.1 From structure	296
		19.3.2 From dynamics	297
	19.4	Entropy from cell theory	298
	19.5	Entropy of water in confined systems (reverse micelles, carbon	
		nanotubes, grooves of DNA)	299
	19.6	Conclusion	300
	Appe	ndix 19.A Entropy for translational degree of freedom of	
		an ideal gas (Sackur-Terode equation)	301
		ndix 19.B Entropy for vibrational degree of freedom	302
	Appe	ndix 19.C Entropy for rotational degree of freedom	303
20.	The fi	reezing of water into ice	305
	20.1	Introduction	305
	20.2	Phase diagram of water and ice	306
	20.3	Ice formation in micro-droplets	307
	20.4	A lesson from the freezing of interacting spheres and	
		the difference from water	308
	20.5	The freezing of water	308

xiv Contents

	20.6	Nucleation of an embryo	309
	20.7	The freezing of water in computer simulations	310
	20.8	Mechanism of ice formation	311
	20.9	Freezing inside nanotubes	314
	20.10	Conclusion	315
21.	Super	critical water	317
	21.1	Introduction	317
	21.2	Inhomogeneous density fluctuation in supercritical fluids	318
	21.3	Crossing the Widom line	320
	21.4	Spectroscopic studies of supercritical fluids	320
	21.5	Conclusion	322
22.	Appro	paches to understand water anomalies	323
	22.1	Introduction	323
	22.2	Reason for density maximum	327
	22.3	Reason for large isobaric specific heat of water	327
	22.4	Percolation model of water	327
	22.5	Hydrogen-bond network rearrangement dynamics	330
		22.5.1 Energy landscape view of hydrogen-bond	
		rearrangement dynamics	331
		22.5.2 Depolarized Raman scattering profile	333
	22.6	Low-temperature anomalies	334
	22.7	Conclusion	341
	Epilog	g.	345
	Index		349

The color plates will be found between pages 78 and 79.