

Understanding Nanomaterials

Second Edition

Malkiat S. Johal
Lewis E. Johnson



CRC Press
Taylor & Francis Group
Boca Raton London New York

CRC Press is an imprint of the
Taylor & Francis Group, an **Informa** business

Detailed Contents

Series Preface	xv	Chapter 2		
Preface to the Second Edition	xvii	Thermodynamics and Nanoscience		17
Preface to the First Edition	xix	2.1 TERMINOLOGY IN THERMODYNAMICS	17	
Acknowledgments	xxi	2.1.1 The system and surroundings	17	
Authors	xxiii	2.1.2 Some thermodynamic variables	18	
		2.1.3 Reversible and irreversible		
		changes		20
Chapter 1		2.2 TEMPERATURE AND NANOMATERIALS	21	
A Brief Introduction to Nanoscience	1	2.2.1 Thermodynamics and size effects	21	
1.1 THE SCOPE OF NANOSCIENCE	1	2.2.2 Melting temperatures		
1.2 THE NEED FOR NANOSCIENCE EDUCATION	3	of nanomaterials		22
1.3 THE NANOSCALE DIMENSION	5	2.3 THE FIRST LAW OF THERMODYNAMICS	29	
1.4 DIMENSIONALITY AND ITS IMPLICATIONS	8	2.3.1 Work	29	
1.5 SELF-ASSEMBLY	9	2.3.2 Heat exchange and heat capacity	36	
1.6 SUPRAMOLECULAR SCIENCE	11	2.3.3 The first law in terms of work		
1.7 OVERVIEW OF THE TEXT	12	and heat		36
1.8 SOURCES OF INFORMATION		2.3.4 Enthalpy		38
ON NANOSCIENCE	13	2.4 THE ENTROPY STATE FUNCTION:		
END OF CHAPTER QUESTIONS	14	THE SECOND AND THIRD LAWS	39	
		2.4.1 The classical interpretation		
		of entropy		39
		2.4.2 The statistical interpretation		
		of entropy		41

2.5	THE GIBBS ENERGY STATE FUNCTION	44	3.4	BIMOLECULAR BINDING KINETICS	81
2.5.1	The direction of spontaneous change	44	3.4.1	Kinetics of reversible binding	81
2.5.2	The Gibbs energy and surface tension	47	3.4.2	The Scatchard and Hill equations: Cooperativity of binding	84
2.5.3	Multicomponent systems and chemical potential	49	3.5	SOLUTION KINETICS AND DIFFUSION CONTROL	86
2.6	PHYSICAL AND CHEMICAL EQUILIBRIA	50	3.5.1	Some basic physics of diffusion of nanomaterials in solution	87
2.6.1	The equilibrium constant	50	3.5.2	Kinetics of diffusion control	89
2.6.2	Heterogeneous equilibria	51		END OF CHAPTER QUESTIONS	92
2.6.3	The relationship between Gibbs energy and the equilibrium constant	52		REFERENCES AND RECOMMENDED READING	94
2.6.4	Temperature dependence of the equilibrium constant	54	Chapter 4		
2.6.5	Phase equilibria in bulk materials	55	Quantum Effects at the Nanoscale		95
2.6.6	Phase equilibria in nanoparticles	57	4.1	QUANTUM CONFINEMENT IN NANOMATERIALS	96
	END OF CHAPTER QUESTIONS	60	4.2	BASIC INTRODUCTION TO QUANTUM MECHANICS	97
	CITED REFERENCES	61	4.2.1	Electromagnetic radiation	97
	REFERENCES AND RECOMMENDED READING	61	4.2.2	Matter waves and the uncertainty principle	98
Chapter 3		63	4.2.3	Bound systems and quantization	99
Kinetics and Transport in Nanoscience			4.2.4	The wavefunction	101
3.1	RATES OF CHEMICAL REACTIONS	63	4.2.5	The Schrödinger equation	102
3.1.1	The rate of reaction	63	4.3	CONFINEMENT OF ELECTRONS IN BOXES	104
3.1.2	Rate laws and reaction orders	65	4.3.1	The one-dimensional model	104
3.1.3	A note on reversible reactions	70	4.3.2	The two- and three-dimensional models and the concept of degeneracy	113
3.1.4	Integrated rate laws	71	4.4	NANOSCALE CONFINEMENT ON RINGS AND SPHERES	118
3.2	THEORETICAL MODELS FOR REACTION RATES	74	4.4.1	The particle on a ring model	119
3.2.1	Temperature dependence of the rate constant	74	4.4.2	The particle in a sphere model	121
3.2.2	Collision theory	75	4.5	QUANTIZATION OF VIBRATION AND ROTATION	122
3.2.3	Catalysis	77	4.5.1	Quantization of vibrational motion: The harmonic oscillator	122
3.3	MODELING SIMPLE MECHANISMS	79	4.5.2	Quantization of rotational motion: The rigid rotator	125

4.6	QUANTUM MECHANICAL TUNNELING	128	5.4.2	Conjugation in organic molecules	170
4.6.1	Implications of finite energy barriers	128	5.4.3	Solvatochromism	173
4.6.2	Implications for the quantum mechanical harmonic oscillator	129	5.4.4	Aggregation and electronic structure	175
4.7	SUMMARY	130	5.4.5	π - π stacking interactions	176
	END OF CHAPTER QUESTIONS	131		END OF CHAPTER QUESTIONS	178
	REFERENCES AND RECOMMENDED READING	132		REFERENCES AND RECOMMENDED READING	180
Chapter 5					
Intermolecular Interactions and Self-Assembly					
5.1	INTERMOLECULAR FORCES AND SELF-ASSEMBLY	133	6.1	SPECTROSCOPIC METHODS	181
5.1.1	Ion-ion interactions	135	6.1.1	Interactions between light and matter	183
5.1.2	Ion-dipole interactions	137	6.1.2	UV-visible spectroscopy	188
5.1.3	Dipole-dipole interactions	140	6.1.3	The absorption of visible light by a nanofilm	192
5.1.4	Interactions involving induced dipoles	142	6.1.4	Molecular fluorescence spectroscopy	194
5.1.5	Dielectric screening	145	6.1.5	Vibrational spectroscopy methods	197
5.1.6	Dispersion forces	148	6.2	LIGHT SCATTERING METHODS	201
5.1.7	Overlap repulsion	149	6.2.1	Scattering and absorption	201
5.1.8	Total intermolecular potentials	152	6.2.2	Rayleigh and Raman scattering	202
5.1.9	Hydrogen bonds	154	6.2.3	Raman spectroscopy	203
5.1.10	The hydrophobic effect	154	6.2.4	Light scattering by nanoparticles	204
5.2	ELECTROSTATIC FORCES BETWEEN SURFACES: THE ELECTRICAL DOUBLE LAYER	156	6.2.5	Determining particle size using scattered light	204
5.2.1	The electrical double layer	157	6.2.6	Dynamic light scattering	207
5.2.2	The Debye length	159	6.3	X-RAY SPECTROSCOPY	211
5.2.3	Interactions between charged surfaces in a liquid	160	6.3.1	Absorption	212
5.3	INTERMOLECULAR FORCES AND AGGREGATION	162	6.3.2	Fluorescence	212
5.4	SIMPLE MODELS DESCRIBING ELECTRONIC STRUCTURE	164	6.3.3	Diffraction	213
5.4.1	Applications of the particle-in-a-box model	164		END OF CHAPTER QUESTIONS	214
	REFERENCES AND RECOMMENDED READING	164		REFERENCES AND RECOMMENDED READING	215

Chapter 7			
Fundamentals of Surface Nanoscience	217		
7.1 FUNDAMENTALS OF SURFACE SCIENCE	218	8.3 ELLIPSOMETRY	265
7.1.1 Surface energy of solids and liquids	218	8.3.1 Basic principles of electromagnetic theory and polarized light	266
7.1.2 Surface free energy of adsorbed monolayers	219	8.3.2 Basic principles of ellipsometry	270
7.1.3 Contact angles and wetting phenomena	223	8.3.3 Obtaining the thickness of films: Optical parameters Del (Δ) and Psi (Ψ)	273
7.1.4 Nanomaterials and superhydrophobic surfaces	225	8.3.4 The ellipsometer	275
7.2 ADSORPTION PHENOMENA: SELF-ASSEMBLED MONOLAYERS	230	8.4 OTHER TECHNIQUES FOR MEASURING THICKNESS AND REFRACTIVE INDEX	278
7.2.1 Simple adsorption isotherms	235	8.4.1 Reflection phenomena at interfaces	278
7.2.2 Other useful adsorption isotherms	240	8.4.2 Surface plasmon resonance	280
8.4.3 Dual polarization interferometry	284		
7.3 SURFACTANT CHEMISTRY	241	8.5 SURFACE-SENSITIVE SPECTROSCOPIC METHODS	290
7.3.1 Micelle and microemulsion formation	243	8.5.1 Attenuated total reflection	290
7.3.2 The determination of surface excess: The CMC and the cross-sectional area per molecule	246	8.5.2 IR spectroscopy	292
END OF CHAPTER QUESTIONS	250	8.5.3 Reflection absorption	292
REFERENCES AND RECOMMENDED READING	254	8.5.4 IR spectroscopy	293
		8.6 NONLINEAR SPECTROSCOPIC METHODS	294
		8.6.1 Surface-enhanced Raman spectroscopy	294
		8.6.2 An introduction to nonlinear optics	294
		8.6.3 Second-harmonic generation	300
		8.6.4 Sum-frequency generation spectroscopy	304
Chapter 8			
Surface Characterization and Imaging Methods	255	8.7 IMAGING NANOSTRUCTURES	308
8.1 SURFACE TENSIOMETRY: THE SURFACE TENSIOMETER	255	8.7.1 Imaging ellipsometry	308
8.2 QUARTZ CRYSTAL MICROBALANCE	259	8.7.2 Scanning probe methods	311
8.2.1 The piezoelectric effect	259	8.7.3 Transmission electron microscopy	317
8.2.2 QCM principles	261	8.7.4 Near-field scanning optical microscopy	323
8.2.3 QCM and dissipation (D)	263	END OF CHAPTER QUESTIONS	329
8.2.4 Modern QCM-D setup	264	REFERENCES AND RECOMMENDED READING	332

Chapter 9			
Introduction to Functional Nanomaterials			
9.1 NANOSCALE MACHINES	335	9.7 GRAPHENE	376
9.2 CHARGE TRANSFER	338	9.8 NANOFRAMEWORKS	378
9.2.1 The Marcus model of charge transfer	339	END OF CHAPTER QUESTIONS	379
9.2.2 Band theory	340	CITED REFERENCES	380
9.2.3 Solar cells and light-emitting diodes	344	REFERENCES AND RECOMMENDED READING	382
9.2.4 Field-effect transistors	347		
9.3 EXCITATION TRANSFER	348	Chapter 10	
9.3.1 Functional dye assemblies	348	Fabrication, Properties, and Applications of Thin Films	383
9.3.2 Photorelaxation	351	10.1 LANGMUIR-BLODGETT FILMS	383
9.3.3 Resonant energy transfer	353	10.1.1 Langmuir films	384
9.3.4 Formation and properties of excitons	353	10.1.2 Langmuir–Blodgett films	386
9.4 QUANTUM DOTS	358	10.2 POLYELECTROLYTES	389
9.4.1 Optical properties of quantum dots	359	10.2.1 Electrostatic self-assembly	390
9.4.2 Synthesis of quantum dots	360	10.2.2 Charge reversal and interpenetration	392
9.4.3 In vivo imaging with quantum dots	362	10.2.3 Multilayer formation	395
9.4.4 Photodynamic therapy	364	10.3 MODEL PHOSPHOLIPID BILAYER FORMATION AND CHARACTERIZATION	396
9.5 NANOWIRES	364	10.3.1 Black lipid membranes	397
9.5.1 Quantum effects on conductivity of nanowires	366	10.3.2 Solid supported lipid bilayers	398
9.5.2 Electron transport in nanowires	367	10.3.3 Polymer cushioned phospholipid bilayers	402
9.5.3 Nanowire synthesis	369	10.3.4 Fluorescence recovery after photobleaching	403
9.5.4 Summary	369	10.3.5 Fluorescence resonant energy transfer	404
9.6 CARBON NANOTUBES	370	10.3.6 Fluorescence interference contrast microscopy	405
9.6.1 Carbon nanotube structure	371	10.3.7 Solvent assisted lipid bilayer formation	406
9.6.2 Some properties of nanotubes	372	10.4 SELF-ASSEMBLED MONOLAYERS	407
9.6.3 Methods for growing nanotubes	373	10.4.1 Thiols on gold	407
9.6.4 Catalyst-induced growth mechanism	375	10.4.2 Silanes on glass	409

10.5	POLED AMORPHOUS FILMS	411	10.7.5	Arrays of supported bilayers and microfluidic platforms	425
	10.5.1 Spin-coating	411	10.7.6	Summary	428
	10.5.2 Poling	411			
10.6	PATTERNING	413	10.8	NANOSCALE HYBRID PHOTONICS	428
	10.6.1 Optical and electron beam lithography	414	10.8.1	The electro-optic effect	429
	10.6.2 Soft lithography	416	10.8.2	Organic-inorganic hybrid electro-optics	430
	10.6.3 Nanosphere lithography	416			
	10.6.4 Patterning using AFM	417	END OF CHAPTER QUESTIONS		432
	10.6.5 Summary	420	CITED REFERENCES		433
10.7	DNA AND LIPID MICROARRAYS	420		REFERENCES AND RECOMMENDED READING	434
	10.7.1 Using a DNA microarray	420			
	10.7.2 Array fabrication	421			
	10.7.3 Optimization of DNA microarrays	423	Glossary		435
	10.7.4 Applications of DNA microarrays	424	Index		459