

Contents

Preface	xi
Units, Fundamental Constants, and Symbols	xiii
About the Companion Website	xix
1 The Realm of Nanoscience and Molecular Engineering	1
1.1 Nanoscience and Molecular Engineering	1
1.1.1 Trial-and-Error Approach and Deductive Rational Engineering	4
1.1.2 Combined Deductive Rational Engineering	5
1.1.3 Perception of Our World – Apparent Unique Behaviors in Small Systems	6
1.2 Properties in Lower Dimensionalities	7
1.2.1 Flatland – The Uniqueness of Lower Dimensionality	8
1.3 Mechanical System Responses	10
1.3.1 Bulk Rheological Responses	10
1.3.2 Molecular Perspective of Mechanical Systems	12
1.4 Driving Forces and Responses in Thermal Transport	16
1.4.1 Classical Thermal Transport	16
1.4.2 Thermal Conductivity Based on Classical Mechanics and Statistics	18
1.4.3 Size Effect on Thermal Energy Transfer	24
1.5 Electronic Transport of Lower Dimensional Systems	27
1.5.1 Drude Model – Microscopic Model for Macroscopic Electron Transport	29
1.5.2 Characteristic Length Scales for Electron Transport	31
1.5.3 One-dimensional Electron Transport	34
1.6 Acoustic Transport and Dimensionality	38
1.7 Critical Molecular Response Times in Nanoconstrained Systems	40
1.7.1 Longitudinal Response to Stress – Maxwell Model	42
1.7.2 Shear Response to Stress	45
1.7.3 Dissipative Two-Dimensional Shear Response	47
1.8 Miniaturization, Scaling, and System Constraints	50
1.8.1 Phenomenological Shortcoming of the Scaling Analysis	51
1.8.1.1 Terminal Velocity of Liquid Droplets and Solid Particles	51
1.8.1.2 Interfacial Constraints and Nanocomposite Membrane Permeability	54

1.8.2	Dimensional Constraints and Thermal Conductivity	60
1.9	Organization and Outlook for Nanoscience and Nanotechnology	64
1.9.1	Classification of Nanoscience and Nanotechnology	65
	Study Problems to Chapter 1	68
2	Interfacial and Size-Constraint Systems	79
2.1	Overview	79
2.2	VdW Molecular Interactions	80
2.2.1	VdW Interactions in Gases	80
2.2.2	VdW Interactions in Liquids	86
2.3	Interfacial Effects on Liquids and VdW Solids	90
2.3.1	Simplistic Perspective Bulk and Surface Binding Energy	92
2.3.2	Interfacial Effect on VdW Liquid Structures	94
2.3.2.1	Molecular Perspective of the Bulk Cohesion Energy	97
2.3.2.2	Molecular Perspective of the Adhesion Energy	100
2.3.3	Free Surface Effects on VdW Solids	105
2.4	Interfacial Effects on Spin-Coated Polymer Films	111
2.4.1	Bulk Mechanical Response, Polymer Mobility, and the Glass Transition	111
2.4.2	Polymer Chain Entanglement and Melt Viscosity	115
2.4.3	Interfacial Constraint on the Glass Transition in Thin Films	118
2.5	Size and Interfacial Constraints in Metal Nanoclusters	123
2.5.1	Size Effect on Cohesion Energy and Surface Energy in Quasicrystals	126
2.6	Two-Dimensional Systems and Surface Energy	131
2.6.1	Surface Energy of Graphite	132
2.6.2	Surface Energy of Graphite's Ultimate Nanostructure – Graphene	136
	Study Problems to Chapter 2	139
3	Size-Constrained Condensed Fluid Molecular Systems	147
3.1	Molecules and Phase Properties	147
3.1.1	Molecules and Molecular Interactions	147
3.1.2	Molecular Interactions and VdW EOS	149
3.1.3	Gas Bulk Critical and Molecular Properties	155
3.2	Metastable Liquid Phenomena	163
3.2.1	Metastable Liquids and Cavitation	163
3.2.2	Homogeneous Nucleation Process of Vapor Bubbles	167
3.2.3	Free Energy of Bubble Nucleation	167
3.2.4	Probability of Bubble Nucleation and Liquid Tensile Strength	171
3.3	Hydraulic Transport in Capillaries and Boundary Conditions	175
3.3.1	Bending Stresses on Vascular Plants and Drought Embolism	176
3.3.2	Water Transport – Darcy's Law	179
3.3.3	Poiseuille Flow in Capillaries – Slip Boundary Condition	185
3.3.4	Molecular Conformations at Interfaces and Apparent Slip	194
3.3.5	Surface Roughness and Heterogeneous Slip	197

3.4	Nanoconduit Flow – BL Model and Nanocapillaries	201
3.4.1	BL Model	201
3.4.2	Nanoconduit Flow Through Carbon Nanotubes	205
3.5	Membrane Transport	211
3.5.1	Osmosis	211
3.5.2	Water Purification and Desalination – RO	216
3.5.3	Transport Mechanisms Through Solvent Swollen Polymer Membranes	218
3.5.3.1	Solution-Diffusion (SD) Model	219
3.5.3.2	Pore-Flow (PF) Model	233
3.5.4	Polymer Membranes and Nanoporous Transport	233
	Study Problems to Chapter 3	240
4	First Steps Toward Quantum Mechanics	249
4.1	Thermal Emission: From Boltzmann to Quantum Distribution Law	249
4.1.1	Blackbody Radiator	250
4.1.2	Rayleigh and Jeans – Standing Wave Model	253
4.1.3	Quantum Distribution Law – Planck's Law	256
4.1.4	Principle Distribution Laws in Nature	258
4.1.5	Microsystems and the Chemical Potential	263
4.2	First View into Quantum Mechanics	266
4.2.1	Photoelectric Effects	266
4.2.2	Wave-Particle Duality	268
4.2.3	The Franck-Hertz Experiment	271
4.3	Atom Structure and a Simple Model	272
4.3.1	The Electron	272
4.3.2	Hydrogen Emission Spectrum	274
4.3.3	Bohr Model of the Atom	276
4.3.4	Wave-Particle Duality and Dispersion Relation	278
4.4	Wave and Particle Interferences and Probability	281
4.4.1	Single-Slit Interference	281
4.4.2	Double-Slit Interference	283
4.4.3	Screen Intensity and Probability	285
4.4.4	Uncertainty Principle and Macroscopicity	285
4.5	Quantum Wave Theory, Quantum Constraints and Uncertainty	288
4.5.1	One-Dimensional Schrödinger Wave Equation	289
4.5.2	Particle in One-Dimensional Box	291
4.5.2.1	General Solution of the One-Dimensional Well	291
4.5.2.2	Energy Level of the One-Dimensional Well	292
4.5.2.3	Final Wave Function Solution of the One-Dimensional Well	293
4.5.2.4	Quantum Well Structures	294
4.5.3	Hydrogen Atom: Electron Wave Function and Energies	295
4.5.4	Quantum Entanglement and Quantum Computing	298

4.5.4.1	Quantum Entanglement	298
4.5.4.2	Quantum Computing	299
	Study Problems to Chapter 4	302
5	Electron Transport and Electronic Structure of Molecules	309
5.1	Electron Transport in One-Dimensional Quantum Wire	309
5.1.1	Quantum Wire Energy Components	310
5.1.2	Electron Scattering versus Ballistic Transport	312
5.1.3	Single-Mode Quantum Wire	314
5.1.4	Multimode Quantum and Quantum Conductance	315
5.2	Electron Tunneling	318
5.2.1	Finite 1D Potential Well	319
5.2.1.1	Schrödinger Solutions Within Boundaries Encompassing Finite Particle Box	320
5.2.1.2	Schrödinger Solutions Within Finite Particle Box	321
5.2.2	Tunneling Effect: Tunnel Current	321
5.2.2.1	Schrödinger Solutions for a Constant and Narrow Tunnel Barrier	322
5.2.2.2	Tunnel Current: The Transmission Probability and Approximation	323
5.2.2.3	Transmission Coefficient versus Subband Mode	324
5.2.2.4	Tunnel Current: The Work Function of a Vacuum Gap	324
5.2.3	Scanning Tunneling Microscopy	326
5.3	Single Electron Device Technology	329
5.3.1	Energy Discretization of Nanoparticles	330
5.3.2	Single Electron Box	332
5.3.3	Single Electron Transistor	335
5.4	Electrons, Energy States, and Distribution in Atoms	340
5.4.1	Hydrogen Atom: Solution of the Schrödinger Equation	341
5.4.2	Probability and Electron Distribution	342
5.4.3	Electron Orbital Shape – Angular Momentum	345
5.4.4	Energy Degeneracies, Spin-Orbit Coupling, and Fine Structure	346
5.4.5	Relativistic Effects	349
5.5	Electron Distribution and Bonding in Molecules	350
5.5.1	σ -Bonding	351
5.5.2	From σ to π -Bonding	355
5.5.3	Hybrid Molecular Orbitals	357
5.6	Mobile Electrons	358
5.6.1	Delocalized π Electrons	359
5.6.2	HOMO-LUMO Levels and Chromophores	362
5.6.3	Conjugated Polymers as LED and PV Materials	366
5.6.3.1	OLED Material	367
5.6.3.2	Organic Photovoltaic Material	369
	Study Problems to Chapter 5	371

6	Electronic Structure of Matter	377
6.1	Electronic States and Transport in Condensed Material Phases	377
6.1.1	Density of States	377
6.1.2	Electronic Bands and Bandgap	383
6.1.3	Semiconductor Bandgap Engineering	386
6.2	Background on Doped Inorganic Semiconductors	389
6.2.1	Semiconductor Bandgap Engineering	389
6.2.2	Doped Semiconductors	391
6.2.3	Semiconductor p-n Junction	394
6.2.4	The Depletion Layer in the p-n Junction and External Bias	398
6.3	Photovoltaic Cells	403
6.3.1	p-n Junctions and Photovoltaics Basics	403
6.3.2	Solar Cell Efficiency	412
6.3.3	Photovoltaics Beyond Crystalline Silicon	417
	Study Problems to Chapter 6	417
7	Molecular Modes and Energetic Properties	423
7.1	Molecular Modes	423
7.2	Bond Vibrations in Molecules	426
7.2.1	The Quantum Harmonic Oscillator	426
7.2.2	Infrared Spectrum of Diatomic Molecules in Light of the Quantum Harmonic Oscillator	430
7.2.3	Dissociation Energy and Ground-State Electronic Energy of Diatomic Molecules	431
7.2.4	Stiffness of Vibrating Bonds and Vibrational Bond Temperature	436
7.3	Rotational Molecular Mode in Diatomic Molecules	436
7.3.1	Molecular Rigid Rotor	436
7.3.2	Nonrigid Diatomic Rotor	440
7.3.3	Rotational and Vibrational Energies	443
7.4	Polyatomic Molecules	444
7.4.1	Vibrational Modes of Polyatomic Molecules	445
7.4.2	Rotational Modes of Polyatomic Molecules	447
7.5	Lattice Vibrations – Phonons	448
7.5.1	Harmonic Potential and Energies in Bulk Systems	448
7.5.2	Phonon Dispersion	449
7.5.2.1	1D Monospecies Chain	449
7.5.2.2	Systems with Multiple Atoms or Molecules in the Unit Cell	451
7.5.2.3	Phonons and Heat Conduction	455
7.5.3	The Acoustic Phonon Model Based on Debye	456
7.5.3.1	Preamble – Einstein’s Solid Model	456
7.5.3.2	Debye Model	459
7.5.4	Thermal Conduction in Nano-constrained Systems	460
	Study Problems to Chapter 7	463

Appendix	467
A.1 Acoustic Wave Equation	467
A.2 Homogeneous Second-Order Differential Equation	468
A.3 Solution of the 1D Wave Equation in Cartesian Coordinates	470
A.4 Solution to the Schrödinger Wave Equation for Hydrogen	472
Index	475