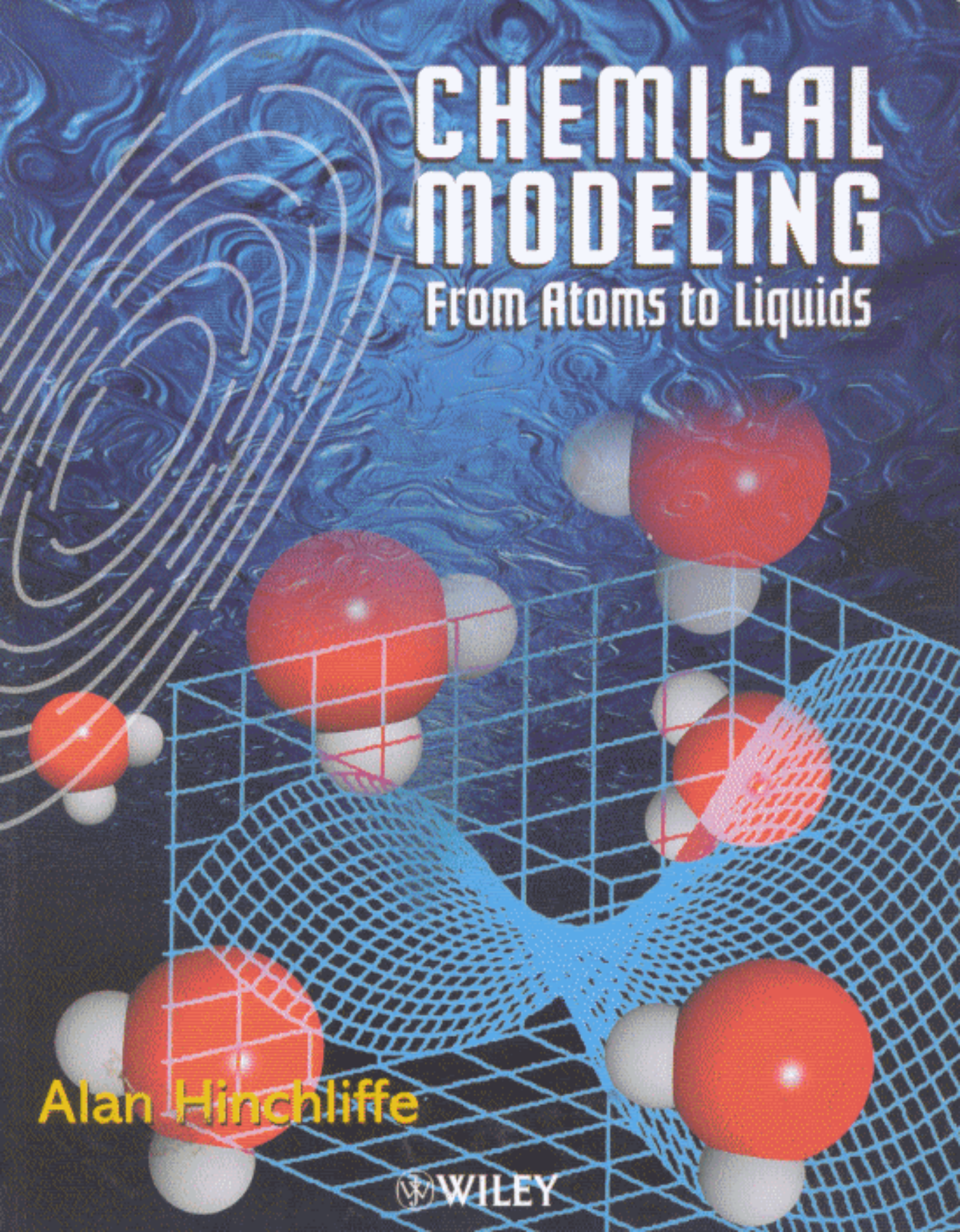




CHEMICAL MODELING

From Atoms to Liquids

Alan Hinchliffe

 WILEY

Contents

Introduction	xiii
Acknowledgments	xv
Software Packages	xvii
1 Describing Macroscopic Systems	1
1.1 The Van der Waals Equation of State	2
1.2 Beattie–Bridgeman Equation of State	4
1.3 Benedict–Webb–Rubin Equation of State	4
1.4 The Virial Equation of State	4
1.5 The Principle of Corresponding States (PCS)	5
2 Thermodynamics	7
2.1 Work, Heat and Heat Capacity	7
2.2 Isothermal and Adiabatic Changes	9
2.3 Systems and States	10
2.4 The Zeroth Law	11
2.5 The First Law	11
2.6 The Enthalpy H	12
2.6.1 Bond Energies and Enthalpies	13
2.7 Entropy and the Second Law	14
2.8 The Third Law	15
2.8.1 Molar Enthalpies of Formation and Molar Entropies	15
2.8.2 Atom and Bond Contributions	16
2.9 Differential Relationships	17
2.10 The Gibbs and the Helmholtz Energies	19
2.11 The Chemical Potential	19
2.12 Applications to Equilibrium	20
3 Résumé of Classical Mechanics	22
3.1 Newton's Laws	22
3.2 Momentum	23
3.3 Energy	24
3.3.1 Work	26
3.4 The Law of Conservation of Energy	26
3.4.1 The Gravitational Field	27
3.5 The Gravitational Potential Energy	30
3.5.1 Relationship Between Force and Mutual Potential Energy	30

3.6	Vibrational Motion	31
3.6.1	Average Values	33
3.7	The Potential Energy	34
3.8	Two Particles, One Spring	35
3.8.1	Summary	37
3.9	Normal Modes of Vibration	37
3.10	Angular Momentum	40
3.11	Circular Motion	41
4	Modeling Simple Solids (i)	43
4.1	The Laws of Electrostatics	43
4.2	The Electrostatic Field	45
4.3	The Mutual Electrostatic Potential Energy U_{AB} of Q_A and Q_B	46
4.4	The Electrostatic Potential $\phi(\mathbf{R})$	47
4.5	Relationships between $\mathbf{E}$, $\mathbf{F}$, ϕ and U	48
4.6	Mutual Potential Energy of an Array of Point Charges	48
4.7	The Binding Energy of a Crystal	51
4.8	A Simple Ionic Solid	53
4.9	Better Pair Potentials	55
4.10	The Binding Energy of a Van der Waals Solid	56
5	Introduction to Quantum Mechanics	58
5.1	Particles and Waves	58
5.2	Particle Aspects of Radiation	59
5.3	Wave Aspects of Matter and the de Broglie Hypothesis	61
5.4	The Probabilistic Nature of some Experiments	62
5.5	Wave Particle Duality	63
5.6	Linear Operators	64
5.7	Observations	66
5.7.1	Postulate 1	67
5.7.2	Postulate 2	67
5.7.3	Postulate 3	67
5.7.4	Postulate 4	67
5.7.5	Postulate 5: The Commutation Relations	68
5.7.6	Postulate 6: The Schrödinger Representation	69
5.7.7	Angular Momentum	69
5.7.8	Postulate 7: Spin	70
5.8	Time Dependence	71
5.9	Free Particles	73
5.10	Particles in Potential Wells	74
5.10.1	The Correspondence Principle	77
5.10.2	The Two-dimensional Well	79
5.10.3	The Three-dimensional Well	84
5.10.4	The Finite Well	85
5.11	Unbound States	87
5.12	A Major Failure of the Classical Model	87
5.12.1	The Quantum Mechanical Treatment	88
5.12.2	The Vibrational Spectrum of HCl	90

5.13	The Variation Theorem	92
5.13.1	The Linear Variation Method	94
6	Electric Multipoles, Polarizabilities and Intermolecular Forces	96
6.1	Electrostatic Charge Distributions	96
6.1.1	Electric Multipoles	96
6.2	Continuous Charge Distributions	102
6.3	The Electrostatic Potential	103
6.4	Dielectric Polarization and Polarizabilities	107
6.5	Dispersion Energy	110
6.5.1	Short Range Interactions	110
6.6	The Pair Potential	111
7	Some Statistical Ideas	112
7.1	Statistics	113
7.1.1	Averages, Probabilities and Standard Deviations	113
7.1.2	Two Dice	117
7.2	Enumeration	118
7.3	The Binary Alloy	119
7.3.1	Enumeration	120
7.4	Sharpness of the Multiplicity Function	123
7.5	The Boltzmann Distribution (i)	125
7.5.1	The Boltzmann Distribution (ii)	127
7.6	The Partition Function	131
7.6.1	Degeneracies	131
7.6.2	Safety in Numbers	131
8	Applications of the Boltzmann Distribution	135
8.1	The Two-level Quantum System	136
8.1.1	The Internal Energy	138
8.1.2	The Heat Capacity	139
8.2	The Maxwell-Boltzmann Distribution of Velocities and Speeds	140
9	Modeling Simple Solids (ii)	147
9.1	Young's Modulus	147
9.2	Young's Modulus for a Crystalline Solid	151
9.3	The Melting Point of a Simple Solid	153
9.3.1	A Consequence of the Zero Point Energy	155
9.4	The Dulong-Petit Rule	156
9.5	When Do we Need to Use Quantum Mechanics?	160
9.5.1	The de Broglie Criterion	160
9.5.2	The Boltzmann Criterion	160
10	Molecular Mechanics	161
10.1	Implementation of Molecular Mechanics	164
10.1.1	A Contribution from each Chemical Bond	164
10.1.2	A Contribution from each Bending Mode	164
10.1.3	A Contribution from each Dihedral Motion	165

10.1.4	An Electrostatic Contribution	165
10.1.5	Non-bonded Interactions	165
10.1.6	Conjugated Systems	166
10.2	An MM Calculation	166
10.3	Features of PE Surfaces	170
10.3.1	Multiple Minima	170
10.3.2	Local and Global Minima	171
10.3.3	Saddle Points	171
10.4	Locating Stationary Points	173
10.5	Gradient Methods	174
10.6	Steepest Descents	175
10.7	Second Derivative Methods	175
10.8	Characterization of Stationary Points	177
10.9	Proteins and Docking	177
10.9.1	The Effect of pH	180
10.10	Protein Docking	180
10.11	Molecular Properties	180
10.12	The Effect of Solvents	181
11	Molecular Dynamics and Monte Carlo Techniques	185
11.1	Molecular Dynamics	185
11.1.2	Collection of Statistics	188
11.1.3	Heating	188
11.1.4	Periodic Boundary Conditions	189
11.2	The Monte Carlo Method	190
12	The Ideal Monatomic Gas	193
12.1	The Classical Treatment	193
12.2	The Quantum Treatment	196
13	Quantum Gases	198
13.1	Rayleigh Counting	200
13.2	The Maxwell-Boltzmann Distribution of Atomic Kinetic Energies	203
13.3	Black Body Radiation	205
13.4	Modeling Metals	208
13.5	Indistinguishability	211
13.6	The Effect of Spin	215
13.7	Fermions and Bosons	217
13.8	Origins of the Bose and Fermi Factors	218
14	Introduction to Statistical Thermodynamics	221
14.1	Non-interacting Particles	222
14.2	The Molecular Partition Function q	223
14.2.1	q_{trans}	224
14.2.2	q_{rot}	226
14.2.3	q_{vib}	229
14.2.4	q_{el}	230
14.3	The Statistical Entropy	231

14.4	The Canonical Partition Function	232
14.5	Distinguishable Non-interacting Particles	232
14.6	Indistinguishable Non-interacting Particles	233
14.7	Thermodynamic Quantities from Partition Functions	235
14.7.1	The Internal Energy U	235
14.7.2	The Entropy S	236
14.7.3	The Sackur–Tetrode Equation	236
14.7.4	Residual Entropy	237
14.7.5	Other Thermodynamic Quantities	238
14.8	Equation of State for Gas Reactions	238
14.9	Equilibrium Constants	239
15	Modeling Atoms	241
15.1	The Old Quantum Theory	241
15.2	The One-electron Atom	242
15.2.1	General Features of the Bound States	243
15.3	Normalized Hydrogen Atom Wavefunctions	244
15.3.1	Visualization	244
15.4	The Physical Significance of l and m_l ; the Stern–Gerlach Experiment	253
15.5	Many-electron Atoms	255
15.6	The Pauli Principle	258
15.7	The Hartree–Fock Model	258
15.8	The Periodic Table	262
16	Diatomics	263
16.1	Some Useful Jargon	266
16.2	Potential Energy Curves	267
16.3	Visualization of the LCAO MOs	267
16.4	Density Differences	271
16.5	Notation	271
16.6	The Next Steps, H_2 , H_2^- and He_2	272
16.7	The HF–LCAO Model	273
16.7.1	Contour Plots for F_2 at 141.2 pm	275
16.8	Bond Orders and Population Analysis	278
16.9	Slater Orbitals	281
17	Quantum Modeling of Larger Systems	284
17.1	Implementation of Molecular HF–LCAO Theory	285
17.1.1	Gaussian Orbitals	291
17.1.2	A Modern Implementation	294
17.2	Koopmans’ Theorem	297
17.3	Geometry Optimization	298
17.3.1	The Floating Spherical Gaussian Orbital (FSGO) Model	298
17.3.2	General Comments on Geometry Optimization	300
17.4	Lower Levels of Calculation	300
17.5	The Hückel π -electron Model	302
17.5.1	Applications	305
17.5.2	Heteroatoms	305

17.6	Zero Differential Overlap (ZDO) π -electron Theories	306
17.7	All-valence Electron ZDO Theories	308
17.8	Pseudopotential Models	309
17.9	Thermodynamic Properties	310
17.10	Including the Solvent (The Self-Consistent Reaction Field)	314
18	Describing Electron Correlation	318
18.1	Configuration Interaction	319
18.2	Perturbation Theory	322
18.3	The MP n method for Treating Electron Correlation	326
18.4	Density Functional Theory	327
19	The Band Theory of Solids	332
19.1	Drude's Model of a Metal	332
19.2	Ohm's Law	334
19.3	Pauli's Free Electron Model	335
19.3.1	Conductivity	335
19.3.2	The Wavevector	337
19.4	The Band Theory	340
19.5	The Kronig-Penney Model (1930)	340
19.6	Semiconductors	343
19.6.1	Doped Semiconductors	344
20	Modeling Polymeric Materials	346
20.1	Size and Shape	348
20.2	Early Models for Polymer Chains	349
20.2.1	The Freely Jointed Chain	351
20.2.2	The Freely Rotating Chain	351
20.3	Barriers to Internal Rotation	352
20.4	Molecular Dynamics Simulations	353
20.5	The Elasticity of Rubber	353
21	Modeling Liquids	358
21.1	The Radial Distribution Function	358
21.2	The Internal Energy of a Liquid	361
21.3	The Virial Equation of State	362
21.4	Computer Simulation	364
21.4.1	The Pair Potential	365
21.4.2	Pairwise Additivity	366
21.4.3	Model Pair Potentials	368
21.4.4	Site-site Intermolecular Potentials	369
21.5	Classical and Quantum Liquids	370
Appendix: A	Mathematical Toolkit	371
A.1	Taylor's Theorem	371
A.2	Partial Differentiation	371
A.2.1	First Partial Derivatives	371
A.2.2	Total Derivatives	372

A.3	Scalars and Vectors	372
A.3.1	Vector Addition and Scalar Multiplication	372
A.3.2	Coordinate Systems	373
A.3.3	Cartesian Components of a Vector	375
A.3.4	The Dot (or Scalar) Product	375
A.3.5	The Cross (or Vector) Product	376
A.4	Scalar and Vector Fields	376
A.5	Vector Calculus	377
A.5.1	Differentiation of Fields	377
A.5.2	The Gradient	378
A.5.3	The Laplacian	378
A.6	Volume Integrals of Scalar Fields	379
A.7	Line Integrals	380
A.8	Matrices and Determinants	382
A.8.1	Determinants	382
A.8.2	Properties of Determinants	383
A.8.3	Evaluation of Determinants	383
A.8.4	Matrices	384
A.8.5	The Transpose of a Matrix	384
A.8.6	The Hermitian Transpose of a Matrix	385
A.8.7	Algebra of Matrices	385
A.8.8	The Inverse Matrix	386
A.8.9	Matrix Eigenvalues and Eigenvectors	387
	Suggestions for Further Reading	389
	Index	391