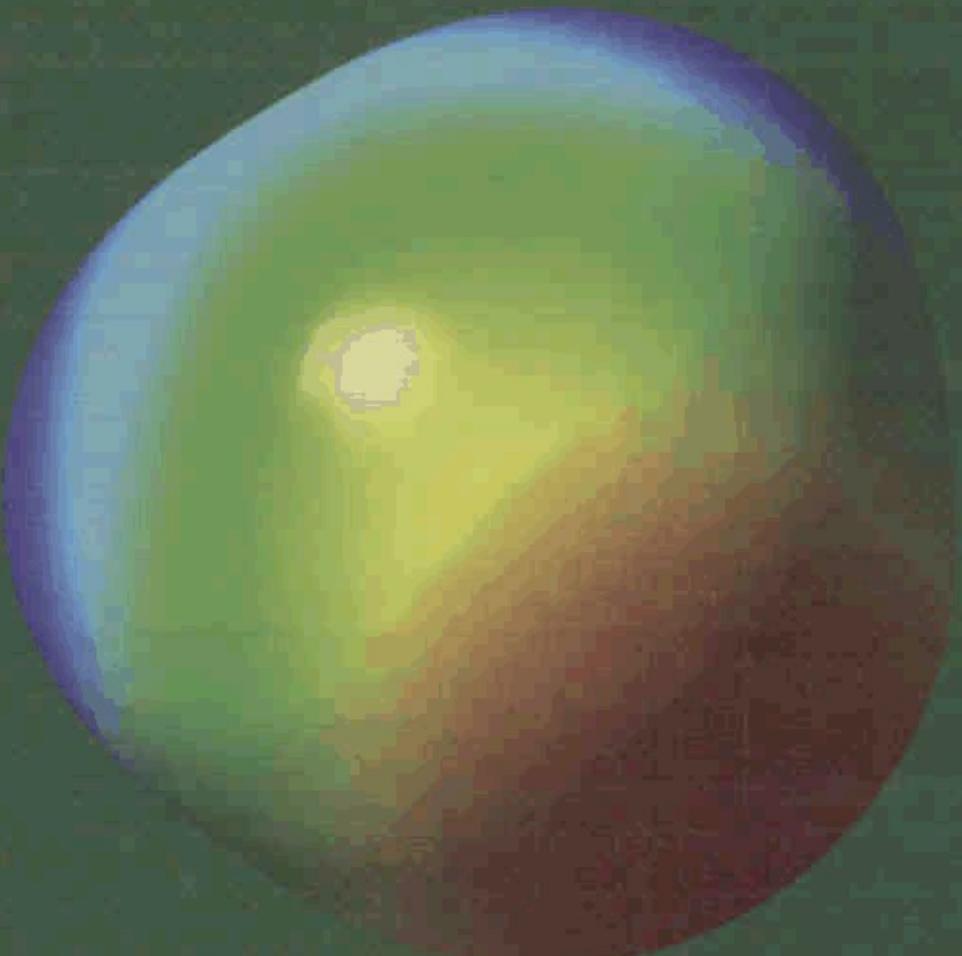


Molecular Models for Fluids

Klaus Lucas



CAMBRIDGE

Contents

Nomenclature	page xi
Preface	xv
1 Introduction	1
1.1 The Macroscopic World	1
1.2 The Microscopic World	9
1.3 Molecular Models	15
1.4 Summary	18
1.5 References	19
2 Foundations	20
2.1 The Macroscopic Framework: Classical Thermodynamics	21
2.1.1 General Relations	21
2.1.2 Heat Capacity	24
2.1.3 Equation of State	24
2.1.4 Fugacity, Activity, Excess Functions	26
2.2 From the Microscopic to the Macroscopic World: Statistical Mechanics	30
2.2.1 Macrostate and Microstate	31
2.2.2 Ensemble Averages	32
2.2.3 Relative Probability of a Microstate	34
2.2.4 Thermodynamic Functions	35
2.2.5 The Semiclassical Approximation	39
2.3 Kinetic Energy of a Molecular System: Classical Mechanics	43
2.3.1 Basic Equations of Classical Mechanics	44
2.3.2 Molecular Degrees of Freedom	47
2.3.3 A Model for Vibration: The Harmonic Oscillator	49
2.3.4 A Model for Rotation: The Rigid Rotator	52
2.3.5 A Model for Internal Rotation	54
2.4 Potential Energy of a Molecular System: Classical Electrostatics	61
2.4.1 Basic Equations of Classical Electrostatics	62
2.4.2 The Multipole Expansion	66
2.4.3 Continuum Models	78

2.5 Molecular Properties: Quantum Mechanics	92
2.5.1 Duality of Particle and Wave: The Wavefunction	93
2.5.2 The Schrödinger Equation	95
2.5.3 Energy Levels of a Molecule	98
2.5.4 Electronic Structure of Molecules	106
2.5.5 Intermolecular Interactions	118
2.6 Experiments in Silico: Computer Simulation	127
2.6.1 The Monte Carlo Method	129
2.6.2 Molecular Dynamics	140
2.6.3 Effects Due to Small Numbers of Molecules	142
2.7 Summary	143
2.8 References	145
3 The Ideal Gas	147
3.1 Definition and Significance	147
3.2 The Canonical Partition Function	148
3.3 Factorization of the Molecular Partition Function	149
3.4 The Equation of State	152
3.5 Mixing Properties	155
3.6 Individual Contributions to the Thermodynamic Functions	158
3.6.1 Translation	158
3.6.2 Electronic Energy	160
3.6.3 External Rotation	162
3.6.4 Vibration	166
3.6.5 Internal Rotation	174
3.6.6 Corrections	180
3.7 Equilibrium Constant	184
3.8 Summary	189
3.9 References	190
4 Excess Function Models	191
4.1 General Properties	192
4.1.1 Repulsive and Attractive Contribution	192
4.1.2 Nonrandomness	194
4.2 Intermolecular Potential Energy	198
4.2.1 Simplified Liquid Models	198
4.2.2 The Free Segment Approximation	200
4.2.3 Group Interaction Models	203
4.2.4 Surface Charge Interaction Models	205
4.3 Simple Model Molecules	214
4.3.1 The Partition Function	214
4.3.2 The Excess Free Energy	217
4.3.3 Local Compositions	220
4.4 Complex Model Molecules	226
4.4.1 Size and Shape Effects	228
4.4.2 Surface Effects	232
4.4.3 Predictive Models	242

4.5 Summary	257
4.6 References	258
5 Equation of State Models	260
5.1 General Properties	261
5.1.1 The Low-Density Limit	261
5.1.2 The Low-Density Expansion	261
5.1.3 The Hard Body Limit	266
5.2 Intermolecular Potential Energy	266
5.2.1 The Pairwise Additivity Approximation	268
5.2.2 The Rigid Molecule Approximation	269
5.2.3 Spherical Interaction Models	270
5.2.4 Nonspherical Interaction Models	274
5.3 The Statistical Virial Equation	283
5.3.1 Pure Gases	283
5.3.2 Gas Mixtures	290
5.3.3 Nonspherical Interactions	295
5.4 Conformal Potential Models	297
5.4.1 Correlation Functions	299
5.4.2 Thermodynamic Functions	301
5.4.3 The Pair Correlation Function	303
5.4.4 Conformal Potentials	306
5.5 Perturbation Models	313
5.5.1 The λ -Expansion	313
5.5.2 The Hard Body Reference	315
5.5.3 The Conformal Potential Reference	320
5.5.4 Generalized van der Waals Models	327
5.6 Summary	335
5.7 References	336
Appendix 1. Fundamental Constants and Atomic Units	339
Appendix 2. Stirling's Formula	341
Appendix 3. Relative Probability of a Microstate	343
Appendix 4. Spherical Harmonics, Rotation Matrices, and Clebsch–Gordan Coefficients	351
Appendix 5. Higher-Order Perturbation Terms for the Intermolecular Potential Energy of Simple Molecules	353
Appendix 6. Rules for Integration	357
Appendix 7. Internal Rotation Contributions	359
Appendix 8. Quasichemical Approximation for the Degeneracy in a Lattice	363
Appendix 9. Off-Lattice Formulation of the Quasichemical Approximation	365
Appendix 10. Combinatorial Contribution to the Excess Entropy in a Lattice	371

x • Contents

Appendix 11. Integration Variables for Three-Body Interactions	379
Appendix 12. Multipole Perturbation Terms for the High-Temperature Expansion	381
Index	383