Contents

Preface to the Third Edition  XIII
Preface to the First Edition  XV

1  Introduction  1

2  Complexity and Entropy  5
2.1  Introduction  5
2.2  Counting Microscopic States  5
2.3  Multiplicity and Entropy of Macroscopic Physical States  9
2.4  Multiplicity and Entropy of a Spin System  10
2.4.1  Multiplicity of a Spin System  10
2.4.2  Entropy of Spin System  11
2.4.2.1  Entropy and Fluctuations About Equilibrium  12
2.4.2.2  Entropy and Temperature  12
2.5  Multiplicity and Entropy of an Einstein Solid  14
2.5.1  Multiplicity of an Einstein Solid  15
2.5.2  Entropy of the Einstein Solid  15
2.6  Multiplicity and Entropy of an Ideal Gas  16
2.6.1  Multiplicity of an Ideal Gas  17
2.6.2  Entropy of an Ideal Gas  18
2.7  Problems  19

3  Thermodynamics  21
3.1  Introduction  21
3.2  Energy Conservation  23
3.3  Entropy  24
3.3.1  Carnot Engine  24
3.3.2  The Third Law  28
3.4  Fundamental Equation of Thermodynamics  29
3.5  Thermodynamic Potentials  32
3.5.1  Internal Energy  33
3.5.2  Enthalpy  34
3.5.3  Helmholtz Free Energy  35
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5.4</td>
<td>Gibbs Free Energy</td>
<td>37</td>
</tr>
<tr>
<td>3.5.5</td>
<td>Grand Potential</td>
<td>38</td>
</tr>
<tr>
<td>3.6</td>
<td>Response Functions</td>
<td>40</td>
</tr>
<tr>
<td>3.6.1</td>
<td>Thermal Response Functions (Heat Capacity)</td>
<td>40</td>
</tr>
<tr>
<td>3.6.2</td>
<td>Mechanical Response Functions</td>
<td>42</td>
</tr>
<tr>
<td>3.7</td>
<td>Stability of the Equilibrium State</td>
<td>45</td>
</tr>
<tr>
<td>3.7.1</td>
<td>Conditions for Local Equilibrium in a PVT System</td>
<td>45</td>
</tr>
<tr>
<td>3.7.2</td>
<td>Conditions for Local Stability in a PVT System</td>
<td>46</td>
</tr>
<tr>
<td>3.7.3</td>
<td>Implications of the Stability Requirements for the Free Energies</td>
<td>50</td>
</tr>
<tr>
<td>3.7.4</td>
<td>Correlations Between Fluctuations</td>
<td>52</td>
</tr>
<tr>
<td>3.8</td>
<td>Cooling and Liquefaction of Gases</td>
<td>55</td>
</tr>
<tr>
<td>3.9</td>
<td>Osmotic Pressure in Dilute Solutions</td>
<td>58</td>
</tr>
<tr>
<td>3.10</td>
<td>The Thermodynamics of Chemical Reactions</td>
<td>61</td>
</tr>
<tr>
<td>3.10.1</td>
<td>The Affinity</td>
<td>62</td>
</tr>
<tr>
<td>3.11</td>
<td>Problems</td>
<td>67</td>
</tr>
</tbody>
</table>

4 The Thermodynamics of Phase Transitions 75

4.1 Introduction 75
4.2 Coexistence of Phases: Gibbs Phase Rule 76
4.3 Classification of Phase Transitions 77
4.4 Classical Pure PVT Systems 79
4.4.1 Phase Diagrams 79
4.4.2 Coexistence Curves: Clausius–Clapeyron Equation 80
4.4.3 Liquid–Vapor Coexistence Region 83
4.4.3.1 Lever Rule 84
4.4.3.2 Law of Corresponding States 84
4.4.3.3 Response Functions in the Coexistence Region 85
4.4.4 The van der Waals Equation 87
4.4.5 Steam Engines – The Rankine Cycle 90
4.5 Binary Mixtures 93
4.5.1 Equilibrium Conditions 94
4.6 The Helium Liquids 96
4.6.1 Liquid He⁴ 97
4.6.1.1 Thermomechanical Effect 97
4.6.2 Liquid He³ 99
4.6.3 Liquid He³–He⁴ Mixtures 100
4.7 Superconductors 101
4.8 Ginzburg–Landau Theory 104
4.8.1 Theoretical Background 105
4.8.2 Applications of Ginzburg–Landau Theory 108
4.8.2.1 Superfluids 108
4.8.2.2 The Curie Point 108
4.8.2.3 Superconductors 109
4.9 Critical Exponents 110
4.9.1 Definition of Critical Exponents 110
4.9.2 The Critical Exponents for Pure PVT Systems 111
4.9.3 The Critical Exponents for the Curie Point 113
4.9.4 The Critical Exponents for Mean Field Theories 114
4.10 Problems 116

5 Equilibrium Statistical Mechanics i – Canonical Ensemble 121
5.1 Introduction 121
5.2 Probability Density Operator-Canonical Ensemble 123
5.2.1 Energy Fluctuations 124
5.3 Semiclassical Ideal Gas of Indistinguishable Particles 125
5.3.1 Approximations to the Partition Function for Semiclassical Ideal Gases 126
5.3.2 Maxwell–Boltzmann Distribution 129
5.4 Interacting Classical Fluids 131
5.4.1 Density Correlations and the Radial Distribution Function 132
5.4.2 Magnetization Density Correlations 134
5.5 Heat Capacity of a Debye Solid 135
5.6 Order–Disorder Transitions on Spin Lattices 139
5.6.1 Exact Solution for a One-Dimensional Lattice 140
5.6.2 Mean Field Theory for a $d$-Dimensional Lattice 142
5.6.3 Mean Field Theory of Spatial Correlation Functions 145
5.6.4 Exact Solution to Ising Lattice for $d = 2$ 146
5.7 Scaling 148
5.7.1 Homogeneous Functions 148
5.7.2 Widom Scaling 149
5.7.3 Kadanoff Scaling 152
5.8 Microscopic Calculation of Critical Exponents 155
5.8.1 General Theory 156
5.8.2 Application to Triangular Lattice 158
5.8.3 The $S^4$ Model 161
5.9 Problems 163

6 Equilibrium Statistical Mechanics ii –
Grand Canonical Ensemble 167
6.1 Introduction 167
6.2 The Grand Canonical Ensemble 168
6.2.1 Particle Number Fluctuations 169
6.2.2 Ideal Classical Gas 170
6.3 Virial Expansion for Interacting Classical Fluids 172
6.3.1 Virial Expansion and Cluster Functions 172
6.3.2 The Second Virial Coefficient, $B_2(T)$ 174
6.3.2.1 Square-Well Potential 175
6.3.2.2 Lennard-Jones 6–12 Potential 176
6.4 Black Body Radiation 178
6.5 Ideal Quantum Gases 181
8.3 Linearized Hydrodynamic Equations 260
  8.3.1 Linearization of the Hydrodynamic Equations 260
  8.3.2 Transverse Hydrodynamic Modes 264
  8.3.3 Longitudinal Hydrodynamic Modes 265
  8.3.4 Dynamic Correlation Function and Spectral Density 267
8.4 Light Scattering 268
  8.4.1 Scattered Electric Field 270
  8.4.2 Intensity of Scattered Light 272
8.5 Hydrodynamics of Mixtures 274
  8.5.1 Entropy Production in Multicomponent Systems 275
  8.5.2 Fick's Law for Diffusion 277
  8.5.3 Thermal Diffusion 279
8.6 Thermoelectricity 280
  8.6.1 The Peltier Effect 280
  8.6.2 The Seebeck Effect 282
  8.6.3 Thomson Heat 284
8.7 Superfluid Hydrodynamics 284
  8.7.1 Superfluid Hydrodynamic Equations 284
8.8 Problems 291

9 Transport Coefficients 295
  9.1 Introduction 295
  9.2 Elementary Transport Theory 295
  9.2.1 The Mean Free Path 296
  9.2.2 The Collision Frequency 296
  9.2.3 Tracer Particle Current 298
  9.2.4 Transport of Molecular Properties 300
  9.2.5 The Rate of Reaction 301
  9.3 The Boltzmann Equation 303
  9.3.1 Derivation of the Boltzmann Equation 304
  9.4 Linearized Boltzmann Equation 304
  9.4.1 Kinetic Equations for a Two-Component Gas 305
  9.4.2 Collision Operators 306
  9.5 Coefficient of Self-Diffusion 308
  9.5.1 Derivation of the Diffusion Equation 308
  9.5.2 Eigenfrequencies of the Lorentz–Boltzmann Equation 309
  9.6 Coefficients of Viscosity and Thermal Conductivity 311
  9.6.1 Derivation of the Hydrodynamic Equations 311
  9.6.2 Eigenfrequencies of the Boltzmann Equation 315
  9.6.3 Shear Viscosity and Thermal Conductivity 317
  9.7 Computation of Transport Coefficients 318
  9.7.1 Sonine Polynomials 319
  9.7.2 Diffusion Coefficient 319
  9.7.3 Thermal Conductivity 321
Appendix E  Scattering Theory   389

Appendix F  Useful Mathematics and Information  395
F.1     Series Expansions  395
F.2     Reversion of Series  395
F.3     Derivatives  395
F.4     Integrals  395

References  397

Index  403