

Contents

Preface	v
1 Qualitative Description of Liquid Properties	1
1.1 Three Phases of Matter: pVT Behaviour of Pure Materials	2
1.1.1 Critical isotherm	4
1.1.2 Triple point	4
1.1.3 Phase diagram of a pure material (e.g. argon)	5
1.1.4 Phase change from gas to liquid	6
1.1.5 A liquid open to the atmosphere	7
1.2 Melting and Lindemann's Law	8
1.3 Molecular Thermal Movements in the Liquid Phase: Brownian Motion	9
1.4 Qualitative Considerations Continued: Flow Properties of Dense Liquids	12
1.4.1 Ideal liquids and Bernoulli's equation	13
1.4.2 Flow in real liquids: Introduction of viscosity	15
1.4.3 Poiseuille's formula: Viscous flow through a tube	15
1.4.4 Turbulence and Reynolds number	16
1.5 Rigidity of Liquids	17
1.6 Surface Properties	18
1.6.1 Surface free energy and surface tension	18
1.6.2 Surface energy versus surface free energy	20
1.6.3 Contact angle	20
1.6.4 Capillarity	21
1.6.5 Energy for capillary rise	23
1.7 Water and Ice Revisited	24

2	Excluded Volume, Free Volume and Hard Sphere Packing	29
2.1	Excluded Volume and Packing Problems	29
2.2	Accessible Configuration Space	30
2.3	Experiments on Random Packing Models	31
2.4	Origins of Method of Molecular Dynamics	33
2.5	Free-Volume Approximation	36
2.6	Free Volume and Entropically Driven Freezing Transition	36
2.7	Building on Hard Sphere Equation of State	39
2.8	Hard-Particle Fluid Equation of State Using Nearest-Neighbour Correlations	41
2.9	Free Volume Revisited in Hard Sphere Fluid	42
	2.9.1 Statistical geometry of high-density fluid	43
	2.9.2 Chemical potential in terms of statistical geometry	44
2.10	Hard Particles in Low Dimensions	45
	2.10.1 Rods and disks	46
	2.10.2 Hard ellipses	46
2.11	Equation of State of Hard-Body Fluids	47
2.12	Hard Sphere Fluid in Narrow Cylindrical Pores	48
3	Thermodynamics, Equipartition of Energy and Some Scaling Properties	51
3.1	Thermodynamic Functions for a Fluid	51
	3.1.1 Thermodynamic identity and the first principle of thermodynamics	53
	3.1.2 Helmholtz free energy and variational principle	54
	3.1.3 Gibbs free energy	56
3.2	Specific Heats and Compressibilities	56
	3.2.1 Specific heat at constant pressure	57
	3.2.2 Specific heat properties of liquid metals near freezing	58
	3.2.3 Compressibilities, both adiabatic and isothermal	59
3.3	Fluctuation Phenomena	59
	3.3.1 Fluctuations in a perfect gas	60
	3.3.2 Effect of intermolecular forces	61
	3.3.3 Temperature fluctuations	62
3.4	Clausius–Clapeyron Equation and Melting	62
3.5	Free Energy from Partition Function	64

3.6	Principle of Equipartition of Energy	67
3.6.1	Internal energy and other thermodynamic functions of a perfect gas	67
3.6.2	Harmonic oscillator revisited	68
3.7	Thermodynamic and Other Properties of Hard Sphere Fluid . . .	68
3.8	Scaling of Thermodynamic Properties for Inverse-Power Repulsive Potentials	70
3.8.1	Consequence for melting transition	70
Appendix 3.1	Analogues of the Clausius–Clapeyron Equation for Other Phase Transitions	71
A3.1.1	A magnetic system	71
A3.1.2	Higher-order phase transitions	72
Appendix 3.2	Partition Function, Phase Space and Configurational Integral for Inverse Power Repulsive Potentials	73
4	Structure, Forces and Thermodynamics	75
4.1	Pair Distribution Function $g(r)$	75
4.2	Definition of Liquid Structure Factor $S(k)$	76
4.3	Diffraction Scattering from a Liquid	78
4.4	Salient Features of Liquid Structure Factor	79
4.4.1	Long wavelength limit and connection with thermodynamic fluctuations	79
4.4.2	The Hansen–Verlet freezing criterion	80
4.4.3	Relation between the main features of the peak in the structure factor	81
4.4.4	Verlet’s rule related to Lindemann’s melting criterion . .	83
4.5	Internal Energy and Virial Equation of State with Pair Forces . .	84
4.6	Ornstein–Zernike Direct Correlation Function	85
4.6.1	Direct correlation function from Percus–Yevick theory for hard spheres	87
4.6.2	Softness corrections to the hard sphere potential	90
4.6.3	Small angle scattering from liquid argon near triple point	91
4.7	Thermodynamic Consistency and Structural Theories	92
4.7.1	Consistency of virial and fluctuation compressibility: Consequences for $c(r)$	92

4.7.2	A route to thermodynamic consistency in liquid-structure theory	93
4.8	Liquid–Vapour Critical Point	95
4.8.1	Critical constants for insulating fluids and expanded alkali metals	95
4.8.2	Ornstein–Zernike theory and critical exponents	98
4.8.3	Scaling relations	99
4.8.4	X-ray critical scattering from fluids	100
4.9	Fluids at Equilibrium in a Porous Medium	101
Appendix 4.1	Inhomogeneous Monatomic Fluids	102
A4.1.1	Equilibrium conditions	103
A4.1.2	Direct correlation function	105
A4.1.3	Hypernetted-chain approximation in liquid-structure theory	106
Appendix 4.2	The Dieterici Equation of State	107
Appendix 4.3	Force Equation and Born–Green Theory of Liquid Structure	108
5	Diffusion	111
5.1	Background: Magnitude of Diffusion Coefficients in Gases	111
5.1.1	Practical consequences of “slow” diffusion in dense liquids	113
5.2	Fick’s Law and Diffusion Equation	114
5.2.1	Examples of diffusion across a thin film	115
5.3	Solute Diffusion at High Dilution in Water and in Non-aqueous Solvents	116
5.3.1	Stokes–Einstein and semiempirical estimates of solute diffusion	116
5.4	Summary of Techniques, Including Computer Simulation, for Determining	118
5.4.1	Incoherent neutron scattering	119
5.4.2	Dynamic light scattering	121
5.4.3	Nuclear magnetic resonance	122
5.4.4	Computer simulation of mean square displacement	123
5.5	Velocity Autocorrelation Function in Pure Dense Liquids	125
5.5.1	Frequency spectrum and long-time tails	126
5.5.2	The Nernst–Einstein relation	129

5.6	Models of Velocity Autocorrelation Function	131
5.6.1	The Zwanzig model	132
5.6.2	Wallace's independent atom model	134
5.6.3	Generalisation of Stokes–Einstein relation	135
6	Viscosity	137
6.1	Hydrodynamic Variables	137
6.2	Stresses in a Newtonian Fluid and the Navier–Stokes Equation	139
6.2.1	Viscosity stress tensor	139
6.2.2	Bulk and shear viscosity	141
6.2.3	The Navier–Stokes equation	141
6.2.4	Viscous dissipation	142
6.3	Laminar Flow and the Measurement of Shear Viscosity	143
6.3.1	Oscillating disk viscometer	145
6.3.2	Couette viscometer	145
6.3.3	Hydrodynamic lubrication	146
6.4	Creeping Flow Past an Obstacle	146
6.4.1	Stokes' law revisited	147
6.4.2	The viscosity of suspensions	149
6.4.3	Percolation	150
6.5	Vorticity	150
6.5.1	Vorticity diffusion	151
6.5.2	The Magnus force	152
6.6	Models of Viscosity	152
6.6.1	Shear and bulk viscosity of hard sphere fluid	153
6.6.2	Temperature dependence of shear viscosity	155
6.6.3	Green–Kubo formulae for viscosity	156
6.6.4	Computer simulation of shear viscosity in a Lennard–Jones fluid	157
6.7	Transverse Currents and Sound Propagation in Isothermal Conditions	157
6.7.1	Linearised Navier–Stokes equation	157
6.7.2	Bulk viscosity	159
6.7.3	Brillouin light scattering	160
6.8	Microscopic Density Fluctuations and Inelastic Scattering	160
6.8.1	Inelastic neutron scattering from liquids	161
6.8.2	Inelastic photon scattering from liquids	165

6.8.3	Fast sound in water	167
Appendix 6.1	Kinetic Calculation of Shear Viscosity for Hard Spheres	168
7	Heat Transport	171
7.1	Fourier's Law	171
7.2	Studies of Heat Conduction by Molecular Dynamics	174
7.2.1	Green-Kubo formula	175
7.2.2	Non-equilibrium methods	176
7.2.3	Transient time correlation formula	176
7.3	Electronic Contribution to Heat Conduction in Liquid Metals . .	178
7.4	Thermodynamics with Mass Motion and Entropy Production . .	180
7.4.1	Thermodynamic relations	180
7.4.2	Entropy production	181
7.4.3	Constitutive relations	182
7.5	The Effect of Heat Flow on Sound Wave Propagation	183
7.5.1	Hydrodynamic modes	183
7.5.2	Light scattering	185
7.5.3	Sound propagation in the critical region	186
7.6	Binary Fluids	187
7.6.1	Thermodiffusion	187
7.6.2	Hydrodynamic modes	189
7.7	Superfluid Helium	189
7.7.1	Transport properties of superfluid ^4He	191
7.7.2	Inelastic neutron scattering from superfluid ^4He	193
Appendix 7.1	Kinetic Theory of Thermal and Electrical Conductivity	196
Appendix 7.2	Hydrodynamics of Superfluid Helium in the Two-Fluid Model	198
8	Chemical Short-Range Order: Molten Salts and Some Metal Alloys	201
8.1	Classical One-Component Plasma: Static and Dynamic Screening	201
8.1.1	Debye screening	202
8.1.2	Dynamic screening and plasma excitation	204
8.1.3	Structure and dynamics of the strongly coupled OCP . .	204

8.2	Macroscopic Properties of Molten Salts	205
8.2.1	Selected macroscopic data for chlorides	206
8.2.2	Melting parameters	207
8.2.3	Alkali halide vapours and critical behaviour of ionic fluids	208
8.3	Structural Functions for Multicomponent Fluids	209
8.3.1	Number-concentration structure factors	210
8.4	Coulomb Ordering in Monohalides and Dihalides	212
8.4.1	Alkali halides	212
8.4.2	Noble-metal halides	213
8.4.3	Fluorite-type superionic conductors	214
8.4.4	Tetrahedral-network structure in $ZnCl_2$	214
8.5	Structure of Trivalent-Metal Halides	216
8.5.1	Octahedral-network formation in lanthanide chlorides	217
8.5.2	Ionic-to-molecular melting in $AlCl_3$ and $FeCl_3$	217
8.5.3	Liquid haloaluminates	218
8.5.4	Molecular-to-molecular melting in $GaCl_3$ and $SbCl_3$	218
8.6	Transport and Dynamics in Molten Salts	219
8.6.1	Ionic transport	219
8.6.2	Viscosity	221
8.6.3	Dynamics of density fluctuations	223
8.7	Chemical Short-Range Order in Liquid Alloys	224
8.7.1	The CsAu compound	224
8.7.2	Other alkali-based alloys with chemical short-range order	225
9	Bonds, Rings and Chains	227
9.1	Outline	227
9.2	Elemental Molecular Liquids	228
9.2.1	Nitrogen	228
9.2.2	Phase diagram of carbon: Especially liquid-liquid transformation	229
9.2.3	Selenium and sulphur: Especially liquid-liquid transitions	231
9.2.4	Structure of liquid boron	232
9.3	Orientational Pair Correlation Function from Diffraction Experiments	234

9.3.1	Use of generalised rotation matrices	235
9.3.2	Example of orientational structure in water	236
9.4	Polymers	238
9.4.1	The isolated polymer molecule	238
9.4.2	Polymer solutions	239
9.4.3	Polymer blends	242
9.4.4	Polymeric materials	243
9.5	Liquid Crystal Phases	244
9.5.1	Smectic phase	245
9.5.2	Nematic phase	245
9.5.3	Cholesteric phase	246
9.6	Nematic Liquid Crystals and their Phase Transitions	247
9.6.1	Landau–de Gennes theory	248
9.6.2	Molecular mean-field theory of isotropic-nematic transition	250
9.6.3	The isotropic-nematic-smecticA transition	251
9.6.4	Model potentials for molecular liquid and liquid crystals	252
Appendix 9.1	Melting and Orientational Disorder	253
Appendix 9.2	Crystallisation from Solution	254
10	Supercooling and the Glassy State	255
10.1	Macroscopic Characteristics of a Glass	255
10.2	Kinetics of Nucleation and Phase Changes	259
10.2.1	Homogeneous nucleation and crystal growth	259
10.2.2	The critical cooling rate for glass formation	261
10.2.3	Superheating and vapour condensation	261
10.3	The Structure of Amorphous Solids	262
10.3.1	Network and modified-network glasses	263
10.3.2	Molten and amorphous semiconductors	264
10.4	Thermodynamic Aspects and Free Energy Landscape	266
10.4.1	A topographic view of supercooled liquids	267
10.5	Atomic Motions in the Glassy State	269
10.5.1	Relaxation processes	269
10.5.2	Strong and fragile liquids	271
10.5.3	Annealing and aging	273
10.5.4	Anharmonicity and boson peaks	274

10.6	Supercooled and Glassy Materials	274
10.6.1	Hard sphere statistics on the amorphous branch	274
10.6.2	Supercooled water	276
10.6.3	Metallic glasses	277
10.6.4	Superionic glasses	278
10.6.5	Glassy polymers	279
11	Non-Newtonian Fluids	283
11.1	Introduction to Non-Newtonian Flow Behaviour	283
11.1.1	Linear visco-elasticity	285
11.2	Viscosity in Uniaxial Liquid	287
11.3	Flow Birefringence and Flow Alignment	290
11.4	Non-Newtonian Behaviour in Polymeric Liquids	291
11.4.1	Reptation in concentrated polymer systems	292
11.4.2	Macroscopic flow phenomena in polymeric liquids	293
11.5	Flow in Nematic Liquid Crystals	294
11.5.1	Curvature elasticity and the Freedericksz transition	295
11.5.2	Macroscopic flow and disclinations in nematics	297
11.6	Colloidal Dispersions and Suspensions	300
11.6.1	Flow properties of colloidal dispersions	301
11.6.2	The rheology of field-responsive suspensions	304
11.7	Surfactant Systems	305
12	Turbulence	309
12.1	Introduction	309
12.2	Instabilities in Fluids	311
12.2.1	The Rayleigh–Taylor instability	311
12.2.2	Thermal convection and the Rayleigh–Bénard instability	312
12.2.3	The Kelvin–Helmholtz instability	314
12.3	Evolution of Bénard Convection with Increasing Rayleigh Number	316
12.4	Energy Cascade in Homogeneous Turbulence	319
12.4.1	Energy cascade and Kolmogorov microscales	320
12.4.2	Kinetic energy spectrum	322
12.4.3	Energy spectra from renormalisation group approach	324
12.5	Diffusion in Homogeneous Turbulence	324

12.5.1	Time and length scales in diffusion	324
12.5.2	Stochastic modelling of turbulent diffusion	325
12.5.3	Eddy diffusivity	327
12.6	Turbulent Shear Flows	328
12.6.1	Length scales of momentum transport	328
12.6.2	Reynolds stresses	329
12.6.3	Lattice Boltzmann computing	331
12.7	Turbulence in Compressible Fluids	332
12.8	Turbulent Behaviour of Non-Newtonian Fluids	333
Appendix 12.1	Navier–Stokes Equation: Analogy with Maxwell’s Equations	335
Appendix 12.2	Series Solution of Navier–Stokes Equation	337
13	Liquid–Vapour Interface	339
13.1	Background and Empirical Correlations	339
13.1.1	Relation between surface tension and bulk properties: Organic liquids near 298 K	340
13.2	Definition of a Surface and its Thermodynamic Properties	342
13.2.1	Gibbs surface	342
13.2.2	Surface tension	343
13.2.3	Surface entropy	344
13.3	Phenomenology	345
13.3.1	Free energy from inhomogeneity	346
13.3.2	Density gradient contribution to free energy	347
13.3.3	Extension to binary alloys and surface segregation	347
13.4	Microscopic Theories: Direct Correlation Function	348
13.4.1	Density profile and surface tension	349
13.4.2	Density gradient expansion: Pressure through interface	350
13.4.3	Critical behaviour of surface tension	351
13.4.4	Application to nucleation theory	352
13.5	Microscopic Theories: Two-Particle Distribution Function	355
13.5.1	Tangential pressure deficit and surface tension	355
13.5.2	The Fowler approximation: Relation of surface tension to shear viscosity	356
13.5.3	Computer studies: Role of interatomic forces in condensed rare-gas elements	357

13.6	Interfacial Dynamics	357
13.6.1	Surface waves	357
13.6.2	Capillary waves and surface fluctuations	359
13.6.3	Interface reflectivity and diffuse interface in a critical fluid mixture	360
13.7	Interfacial Transport and Rheology	361
14	Quantum Fluids	365
14.1	Ideal Fermi and Bose Gases	365
14.1.1	The Fermi surface	366
14.1.2	Bose–Einstein condensation	367
14.2	Boson Fluids	368
14.2.1	The weakly interacting Bose gas (WIBG)	368
14.2.2	Superfluid liquid ^4He	370
14.2.3	Bose–Einstein condensates	373
14.3	Normal Fermion Fluids	375
14.3.1	Liquid ^3He in the normal state	375
14.3.2	Electron fluids	379
14.3.3	Wigner crystallisation	383
14.4	BCS Superconductivity and Superfluidity in Fermion Fluids	384
14.4.1	The superconducting state	384
14.4.2	Flux quantisation and Josephson effects	386
14.4.3	Superfluidity in liquid ^3He	388
14.5	Electron Theory of Liquid Metals	389
14.5.1	Interatomic forces from liquid structure factor $S(k)$	390
14.5.2	Diffractive scattering from two-component plasmas	391
14.5.3	Transport coefficients	393
14.6	Liquid Hydrogen Plasmas and the Giant Planets	395
14.6.1	Exploring the phase diagram of hydrogen	395
14.6.2	Hydrogen–helium mixtures and the constitution of giant planets	396
Appendix 14.1	Density Profiles in the Perturbed Electron Gas	397
	References	399
	Index	419