

Index

including tables of notation and short courses

Greek letters

- α volume expansivity, $(dV/dT)/V$, or critical exponent, 277, or constant of spring, of gas entropy, 55, 133, of phonon density of states, 111, of Weiss theory, 251
- α_m magnetisability, $dm/d\mathcal{B}$; α_p , polarisability, $dp/d\mathcal{E}$
- β $1/kT$ or critical exponent, 277
- Γ surface tension
- γ C_p/C_V or classical density of states, 148, or critical exponent, 277
- Δ quantum uncertainty in, 18, or fluctuation in or finite change in
- δ small change in or critical exponent, 277
- ε energy of small system or energy density or binding energy; ε_F , Fermi energy, 126
- ε_0 permittivity of free space
- ζ one particle partition function, 134
- η efficiency, 60, or emf or viscosity
- θ gas scale temperature, 1; θ_D , Debye temperature, 111
- κ thermal conductivity
- λ wavelength or vapour pressure constant, 264, or scaling constant, 279; λ_T , thermal de Broglie wavelength, 132
- μ chemical potential, 114
- μ_B Bohr magneton, 94; μ_N , nuclear magneton, 185
- μ_0 permeability of free space
- ν frequency or one-to-one jump rate, 19; ν_A , attempt frequency, 216
- Ξ grand partition function, 117
- ξ coherence length, 281
- Π Peltier heat, 237
- ρ density or phase space probability density, 144, or one-to-many jump rate, 19; ρ_{ij} , density matrix, 299
- σ electrical conductivity or Stefan–Boltzmann constant, 106, or Thomson heat, 237
- σ_i spin index, 283
- τ relaxation time, 228, or scattering time, 228, or period
- Φ generalised thermodynamic potential, grand potential, 116, or flux

320 *Index*

- ϕ electrostatic potential *or* potential energy *or* quantum basis function *or* number of phases, 274; ϕ_A , activation energy, 213
- χ spin state function
- ψ state function
- Ω dimensionless phase space volume, 145
- ω angular frequency; ω_D , Debye frequency, 110; ω_E , Einstein frequency, 109
- A, phases of argon
 gas, κ , 226
 isotherms, 248; co-existence curve, 278
 latent heat of sublimation, Prob. 14.1
 surface tension, Prob. 8.5
- A, availability, 75
- \mathcal{A} , area
- a , interatomic spacing *or* availability per particle *or* constant in van der Waals' equation, 177
- abnormal statistical representations, 292, 303
- absolute zero, 1
 entropy at, 44
 inaccessibility of, 188
 negative, 35
- absorption coefficient, 107
- accessibility of states
 energy range convention, 19
 ergodic assumption, quantum form, 21, 303; classical form, 144, 148, 288; failure of, 286, 303
 in abnormal representations, 292, 303
- activation, thermal, 213; typical value of ϕ_A , 217
 in phase transitions, 262, 265
- adiabatic invariance, quantum principle of, 43
- adiabatic process, 7; reversible, 58
 demagnetisation, 96, 187, Prob. 15.5
 expansion, 54, 82, Probs. 5.3, 8.4
- adsorption of He on solid, Prob. 12.6
- advanced potentials, 296
- Al, lattice mode spectrum, heat capacity, 110
- alloys, 269, 270, 272
- anomaly, *see* heat capacity
- antiferromagnetism, 277
- antisymmetric fermion states, 122
- approach to equilibrium, 20, 302; classical picture, 144, 149, 294
 Boltzmann transport equation, 230
 entropy increase, 39, 58; in classical statistics, 149; related rules for directions of changes, for F , 69, for G , 74, for A , 76; and coarse graining, 297, 304; in fluctuations, 306
 non-equilibrium thermodynamics, 238;
 Onsager reciprocal relations, 241
 relaxation times, 228
 rules for directions of change, for F , 69; for G , 74; for A , 76
 scattering rates and occupation number, 218
 thermal activation, 213
 transport properties, Chap. 17
- approximate energy states, 15, 304
- Arrhenius plot, 217
- astronomical thermodynamics
 3 K background radiation, Prob. 10.2
 existence of free radicals in space, 135
 virial theorem and galaxies, 156, Prob. 14.2
- atmosphere, composition, Prob. 13.2;
 variation of μ with height, Prob. 11.2
- attempt frequency, ν_A , 216; in droplet formation, 267
- attractive forces, 153; in collisions, 227;
 needed for liquefaction, 175; in equation of state, 176; in B_2 , 159, 178
- availability, A , 75, Prob. 7.5
 and equilibrium conditions, 76
 and fluctuation distributions, 205
 in phase transitions, 260
- averages, 13
- Avogadro's number, N_A , 52
- B_J , Brillouin function, 186
- B_n , virial coefficient, 159, 164
- \mathcal{B} , magnetic field; \mathcal{B}_c , \mathcal{B}_{c1} , \mathcal{B}_{c2} , critical fields of a superconductor, 191, 193; ℓ , reduced \mathcal{B} in scaling law, 280
- b , van der Waals' constant, 177; *or* reduced \mathcal{B} in critical point theory, 284
- band theory of electron transport in metals, 229
- basis function, 298
- big bang, Prob. 10.2
- binary mixtures, phases of, 268, Prob. 18.5
- binding energy of pair of molecules, e , 155
- Birkhoff, measure theory, 291
- black body radiation, *see* radiation
- Bloch wall, 262
- blurring of states, by uncertainty principle, 18; by external perturbation, 295
- Bohr magneton, μ_B , 94, 185; nuclear magneton, μ_N , 185
- Bohr–Sommerfeld quantum condition, 143
- Boltzmann, Maxwell–Boltzmann speed distribution, 51
- Boltzmann–Gibbs definition of \mathcal{S} , 39
- Boltzmann's constant, k , 53
 in definitions of T and S , 28, 38
see also Stefan–Boltzmann constant, σ , 106
- Boltzmann's distribution, 32
 and fluctuations, 200, 202
 calculations of state functions from, 86
 classical form of, 149
 connection with scattering rates, 218

- Boltzmann's distribution (*continued*)
 for independent particles, 132
 quasi-Boltzmann distribution, 207, Prob. 16.6
see also Gibbs' distribution and short course on *Temperature, Boltzmann Factors and Elementary Kinetic Theory*
- Boltzmann's H , 39; H -theorem, quantum, 39, 305; classical, 297
- Boltzmann's transport equation, 230;
 linearised, 230
- bond forces, 155
- Born, Yvon–Born–Green high density equation, 166
- Born–Oppenheimer approximation in molecular motion, 89
- Born–von Kármán calculation of lattice heat capacity, 109
- Bose condensation, 131, Prob. 12.5
- Bose–Einstein distribution, 124
- bosons, 122; reservoir, 131; boson scattering, 220
- boundary conditions, for standing waves, 102; in molecular dynamics, 172
- Boyle's law, 52, 62; Boyle temperature, T_B , 160, 169, 247, Prob. 14.4
- Bragg–Williams theory of order–disorder transformation, Prob. 18.6
- Brillouin and Maxwell's demon, 308
- Brillouin function in paramagnetics, 186, Prob. 15.4; in ferromagnetics, 252
- bulk modulus, K , Probs. 5.4, 10.6; ratio of adiabatic and isothermal, 82
- C , heat capacity, 1, *or* electrical capacitance
- c , speed of molecule, light or phonon, *or* number of constituents, 274
- caloric theory of heat, 2
- canonical state, 32; *see also* grand canonical state, 117
 entropy, S , 40
 fluctuations, 200
 heat capacity, 35
 partition function, Z , and F , 93
- canonical variables, 146; in equipartition, 151; practical, 291
- capacitor, voltage fluctuations of, Prob. 13.4
- CO gas, heat capacity, 91
- Carnot engine, 60, 62; Carnot's principle, 60
- cause and effect, 296
- cavitation in liquids, Prob. 18.4
- cell potentials, 197, Prob. 7.4
 and heat of reaction, 83
- Celsius temperature scale, 1
- chain rule in differentiation, 79
- charged systems, energies of, 181–5;
 electrochemical potential, 128, 194
- Chemical Thermodynamics: short course**
Chapters 1–12 (omitting 2.5, 2.6, 2.7, 3.4, 3.5, 12.4, 12.5) and sections 15.6, 16.6, 16.7, 18.1, 18.2, 18.8
 chemical thermodynamics
 absolute reaction rate theory, 216
- Chemical thermodynamics (continued)**
 chemical equilibrium in terms of G , 74; in terms of μ , 115
 dissociation potential, Prob. 7.4
 Gibbs–Duhem relation, 117
 Gibbs–Helmholtz relation for cell, 84;
 electrode potentials, 197
 heat of reaction and H , 74, 83, Probs. 6.6, 7.4
 law of mass action and equilibrium
 constant, K , 134
 phase rule, 272
 third law and absolute entropy, 44, 65
 chemical potential, μ , 114
 and G , 116
 derivatives, from Gibbs–Duhem relation, 117
 for charged particles, 128, 194; for uncondensed gas, 133, Prob. 11.1; for gas under gravity, Prob. 11.2
 in absence of reservoir, 129
 in cell, 196
 in chemical reactions, 115; law of mass action, 134
 in expression for dE , 115
 in Gibbs' distribution, 117
 in Maxwell relations, 116
 in phase rule, 272
 variation with T , for fermions, 127, 129, Prob. 12.5; for bosons, 130
- Clausius' inequality, 40, 58
- Clausius–Clapeyron equation, 81; in phase diagrams, Probs. 18.1, 18.2
- Clausius statement of second law, 9, 59
- Clausius' virial theorem, 155
- classical limit of statistical mechanics,
 Chaps. 13, 14
 approach to equilibrium in, 144, 149, 294
 conditions for, 142
 entropy, S_{cl} , 149; of gas, Prob. 13.5
 equipartition theorem, 149
 ergodic assumption, 148, 289
 for vibrator and rotator, 87, 91
 forms of the fundamental results in, 149
 H -theorem, 297
 partition function, Z_{cl} , 149, 162
 problem of time-reversal symmetry in, 293
 theory of radiation, ultraviolet catastrophe, 105
- Classical Thermodynamics: short course**
Chapters 1, 5–8, 11, omitting 5.2, 5.3, 11.4
 close packing, 98; random, 173
- CMN thermometer, 189
- cluster, cluster integral, 164
- coarse graining, classical, 297; quantum, 304
- coefficients, virial, B_n , 162, 164; B_2 , 159, 168
- coexistence curve in P - V diagram, 278; and law of corresponding states, 168
- coexistence line in phase diagram, 247
- coherence length, ξ , 281
- coldness as $1/T$, 28, 35, 59
- collective modes
 and third law, 45

322 *Index*

- collective modes (*continued*)
 phonons, 108
 spin waves, 257
- collision cross-section, 225; temperature dependence, 227
- collision time and relaxation time, 228
- commutation of differential operators, 79
- compressibility, and density fluctuations, 206; at critical point, 247, 258
- computation of equation of state, 170
- condensation of vapours, 258–268; nuclei, 263
- condensed gases, Chap. 12; condition, 132
 Fermi gas, 127, 128, Probs. 12.4, 12.5
 Bose gas, Bose condensation, 131, Prob. 12.5
- conditional probability, 14
- conductivity, electrical, σ , of metal, 228, 233
 variation with frequency, Prob. 17.3
- conductivity, thermal, κ
 of gas, 224
 of metal, 235; Wiedemann–Franz law, 236
- configuration space, integral, 163
- configurational entropy, 42, 98
- constants of the motion, external, 289;
 hidden internal, 291
- constraints, 3, 56, 289
 importance in fluctuations, 200, 207
- contact potential, 197, Prob. 15.7
- contents, variable, Chap. 11
- cooling, by
 adiabatic demagnetisation, 96, 186, Prob. 15.5; nuclear 190
 adiabatic expansion, of monatomic gas, 54; in general, Prob. 8.4
 refrigerator, 61; dilution refrigerator, Prob. 18.5
 Joule expansion, 161
 Joule–Kelvin expansion, 161
- coordination number, solids, 98; fluids, 173
- correlated fluctuations, 206, Probs. 16.2, 16.5
- corresponding states, law of, 167, Prob. 14.5
 for hard spheres, 175
 quantum form of, Prob. 14.6
- cosmic background radiation, Prob. 10.2
- Coulomb forces, 155
- coupling constant between spins, 251, 283;
 renormalised, 284
- covalent bond forces, 155
- Cr Br₃, ferromagnetic, 280
- critical droplet, 263
- critical fields of superconductors, 191, 193
- critical point behaviour, 250, 277, 279
 critical exponents, 275; universality, 277;
 relations between, 279, Prob. 18.8
 critical isotherm, 247, 255, 276
 critical opalescence, 281
 critical point, 247, 252, 255, 276
 critical temperature, T_c , 247, 252, 276; and
 law of corresponding states, 169
 local ordering in, 281
 of alloy, Prob. 18.6; of ferromagnetic, 252,
 255, 276, 281; of fluid, 168, 169, 258,
 278; of superconductor, 192, 280
- critical point behaviour (*continued*)
 scaling laws in, 277, Probs. 18.7, 18.8
- critical point mean field theories
 Bragg–Williams theory of order–disorder
 transformation, Prob. 18.6
 Landau theory, Prob. 18.7
 van der Waals’ theory of fluid, 257; T_c , P_c
 and V_c , 258, Prob. 18.3; co-existence
 curve, Prob. 18.3
 values of critical exponents for, Prob. 18.7
 Weiss theory of ferromagnetism, 251, 255;
 T_c , 252; Curie–Weiss susceptibility, 256
- critical point precise theories
 Ising model and Onsager’s solution in 2-
 D, 282
 renormalisation theory, 283; successful
 predictions of, 284
- cross section, collision, 225; temperature
 dependence, 227
- cryogenics
 dilution refrigerator, Prob. 18.5
 cooling by adiabatic demagnetisation, 96,
 186, Prob. 15.5; nuclear, 190
 cooling by Joule–Kelvin expansion, 161
 superinsulation, Prob. 10.3
 thermodynamics of refrigeration, 61
- crystal field, 96, 188
- Cu, solid
 electrical and thermal conductivities,
 232
 lattice, zero point energy of, Prob. 10.4
 nuclear demagnetisation of, 190
 nuclear spins, and third law, 44; and
 negative T , 36
- Cu–Mg, phase diagram, 272
- Curie’s law, 95, 186, Prob. 15.4; Curie–Weiss
 law, 256
- Curie temperature, 249, 252, 276
- d , number of dimensions
- Daniell cell, 83, 196
- de Boer, calculation of T_c for ³He, Prob. 14.6
- de Broglie wavelength, 49; thermal, λ_T , 132,
 142, Prob. 12.5
- Debye, permittivity at high frequency,
 Prob. 17.4
- Debye, theory of lattice heat capacity, 109
 T^3 law, 110; for potassium, Prob. 12.4
 temperature, θ_D , 111
- decimation, 283
- degenerate gases, 127, 131; condition, 132
- degenerate quantum states, 15
- degrees of freedom, mechanical
 in equipartition theorem, 150
 in phase space, 146
 of lattice, 109; of molecule, 89
- degrees of freedom, thermodynamic
 and constants of motion, 290
 in phase rule, 273
- demagnetisation, cooling by, 96, 186,
 Prob. 15.5
- demon, Maxwell’s, 307

- dense systems, 165–73; random close packing in, 173
- density matrix, $\hat{\rho}_{ij}$, 299
 approach to equilibrium, 305
 coarse graining, 304
 diagonal and off-diagonal terms, 299
 equation of motion, 301
 equilibrium, 301
 time reversibility, 303
- density of black body radiation, 82, 106
- density of modes
 in k space, 103
 in frequency, photons, 105; phonons, 109
- density of occupation, f , 124, 125
- density of probability in phase space, $\tilde{\rho}$, 144, 145
- density of states in energy, g , 16, Prob. 4.3
 calculation of functions of state, 96
 classical, γ , 148
 double, 200
 exponential behaviour of, 17, 31
 of electrons, 127, Prob. 12.4
 of reservoir, 31, 117
- departure from local equilibrium, 230; in metal, 233
- derivatives, partial, 78
- detailed balance, 23
- diagrams, for cluster integrals, 163
- diamagnetism, atomic, Prob. 15.3;
 fluctuations in, 208
 in superconductors, 191
- diatomic gases, heat capacities, 89, Probs. 9.3, 9.4
 o- and p-H₂, Prob. 12.9
- diesel engine, Prob. 6.3
- differentials of thermodynamic potentials, 67, 70
- diffusion, in fluids, 175; in gas, Prob. 17.1
- dilution refrigerator, Prob. 18.5
- dimensionality in phase transitions, 282
- dimensionless units in phase space, 144, 145
- dipole interactions, 155, 169
- Dirac, Fermi–Dirac particles and
 distribution, 122, 125; calculation of scattering rates, 218
- disconnected parts of phase space, 289
- discontinuous media, 108
- disorder and entropy, 38
- dispersion of waves, 102; phonons, 108
- dissipation, 6; and fluctuations, 210, 212
see also transport properties
- dissociation of molecules, 89, 216
- dissociation voltage, 83, 197, Prob. 7.4
- distillation column, 270
- distribution
 Boltzmann or canonical, 32
 ensemble v. fluctuation, 22
 Fermi–Dirac and Bose–Einstein, 124
 Gaussian, 34
 Gibbs, grand-canonical, 118
 microcanonical, 23
 of energy, 29, 34; of velocity, 50, 51; of fluctuations, 199–209
- distribution (*continued*)
 radial, 157; many-body, 165
- distribution function, 4, 13
- Domb, scaling laws, 277
- droplet nucleation, 263, 265
- Duhem, Gibbs–Duhem relation between intensive variables, 117
- Dulong and Petit’s law, 109
- dynamical computation of equation of state, 170
- E , internal energy, 6
- \mathcal{E} , electric field
- ϵ , emissivity, 107; or energy of molecule
- effective field, in Weiss theory, 254; near T_c , 283
- effective Hamiltonian, in decimation, 283
- efficiency, heat engine, 60; diesel engine, Prob. 6.3; heat pump, 61
- Ehrenfests, coarse graining, 297
- Einstein, Bose–Einstein particles and
 distribution, 122, 124; lattice heat capacity, 109; scattering rate and occupation number, 218; view of thermodynamics, 288
- elastic and inelastic scattering, 220, 231
- electric field, \mathcal{E}
 and driving force for electrons, 128, 196, Prob. 15.7
 energy of, work done by, 181
- electric polarisability, α_p , Langevin theory, Prob. 15.1; high frequency, Prob. 17.4; fluctuations, 208, Prob. 16.2
- electrical conductivity, σ , of metal, 228, 233
 variation with frequency, Prob. 17.3
- electrical noise, 212, Probs. 13.4, 16.7, 16.8
- electrocaloric effect, Prob. 15.2
- electrochemical potential, 128, 194
- electrolysis, 84, Prob. 7.4; electrode potentials, 197
- electromagnetic radiation, *see* radiation
- electromotive force, emf, η , of cell, 196, Prob. 7.4; thermal, η_s , 235, 237
- electrons
 in atoms, excitations quenched, 89;
 diamagnetism, Prob. 15.3;
 paramagnetism, 94, 185
 in metals, free electron model, heat capacity, 127, Prob. 12.4; transport properties, 233–238; paramagnetism of conduction electrons, Prob. 12.3
 in semiconductors, 135, Prob. 11.4; holes, 135; in superconductors, 190
- emission
 black body, 106
 emissivity, ϵ , 107, Prob. 10.3
 spectrum, 107
 spontaneous and stimulated, 218
- endothermic reaction, 74
- energy
 activation, ϕ_A , 213, 217
 exchange, 252, 254
 Fermi, ϵ_F , 126

324 *Index*

- energy (*continued*)
 kinetic, and equipartition, 151; and the virial, 156
 magnetic atom, 185, Prob. 15.3
 lattice, thermal, 107; zero point, binding, Probs. 10.4, 14.1
 molecule, 89, Prob. 12.9
 potential, of thermodynamic system, 68, 117; interatomic, 154; of imperfect gas, Prob. 14.3
 process energy, 72
 uncertainty, 18, 140
 zero point, 15, Probs. 10.4, 14.1
- energy, internal, E , 6, 57
 accessibility range, δE , 19
 distribution, 29, 34, 204
 expressions for dE , 64, 115
 of field, self and mutual, 181–5
 of gas, monatomic, 50; molecular, 89; Fermi, 128, Prob. 12.4
 of oscillator, 87
 of paramagnetic salt, 95, Prob. 9.2; of ferromagnetic, 254
 of rotator, 91
 of solid lattice, 109
 statistical calculation of, 86, 93
see also thermodynamic potentials
- energy density of radiation, 82, 91; frequency distribution, 105, 106
- energy states, approximate, 15; exact, 15, 303
- engineering thermodynamics
 diesel engine, Prob. 6.3
 flow processes, process energy, 72
 heat engines, 59
 heat pumps, 61, Prob. 6.2
see also cryogenics
- ensemble, 11; classical, 144
 and density matrix, 299
- entropy decreasing, 293
 Onsager, 242
 probabilities 11, 18, 144; and fluctuation distribution, 22, 199
- enthalpy, H , 67
 and C_p , 73
 and flow processes, 72; Joule Kelvin expansion, 73, 161
 and heat of reaction, 74, 84
 and latent heat, 74
- entropy, equilibrium, S , 40; classical
 definition, 149
 additivity of, 38, 42, 58
 and μ , 114
 and fluctuations, 204
 and heat flow, 44, 59, 65; particle heat, 115
 and P , 64
 and thermodynamic driving forces, 238
 as function of state, 42
 at $T=0$, third law, 44
 canonical, 40; microcanonical, 41; grand canonical, 118
 configurational, 42, 98
- entropy, equilibrium (*continued*)
 conservation in reversible processes, 40, 58
 entrained, S^* , 240
 increase of, second law, 39, 57, Prob. 6.5; in non-equilibrium thermodynamics 238; *see also* \tilde{S}
 large system approximation for, 41, 118
 measurement of, 65
 natural variables for, 64
 of mixing, 136, Prob. 12.7
 of monatomic gas, 55, 133; Gibbs' paradox, Prob. 13.5; of binary phases, 271; of oscillator, 88; of paramagnetic, 96, 186; of Fermi gas, 128; of superconductor, 193; of ferromagnetic, 253
 statistical calculation of, 86, 93, 96, 118
 units of, 38, 63
- entropy, general non-equilibrium, \tilde{S} , Chap. 4
 as measure of disorder, 38
 effects of measurement and entropy of observer on, 307
 Gibbs–Boltzmann definition, 39; classical form, 149; density matrix form, 306
 increase of, 39, 58; classical picture, 149; H -theorem, 39, 305; classical form, 297; in fluctuations, Maxwell's demon, 306; need for coarse graining, 297, 303; problem of time reversal symmetry, 293, 303
- equal area rule, in mean field theories of phase transitions, 256, 258; proof, 260
- equation of state, Chap. 14
 and law of corresponding states, 167, 278
 and virial, 158
 dense systems, 165–73
 direct computation of, 170
 hard sphere, 175; modified hard sphere, 177
 in phase transitions, 246, 257; near critical point, 276, 279
 of ideal monatomic gas, 51, 133; of argon, 246; of ferromagnetic, 254, 279
 van der Waals, 177, 257
- equilibrium, thermal, 5; *see also* approach to equilibrium
 canonical and microcanonical, 23, 32, 41; grand canonical, 117
 chemical, 74; equilibrium constant, 134; Prob. 12.8
 conditions for, 72, 74, 76
 density matrix, 301
 energy distribution, 29, 34, 204
 fluctuations, Chap. 16
 local, departure from, 230, 233
 of phases, 74
 of two large systems in contact, 29
 principle of equal probability in, 23, 145, 148, 301
 principle of random phases in, 301
 equilibrium radiation, 82, 93, 103; *see also* radiation
 equipartition of energy, classical theorem of, 149

- equipartition of energy (*continued*)
 in oscillator, 87; in molecule, 91,
 Prob. 13.4; in galvanometer, Prob. 13.4;
 in capacitor, Probs. 13.4, 16.8
 ergodic assumption, 21, 303; classical form,
 148, 289
 and fluctuation distribution, 22
 quasi-ergodic trajectories, 291
 evaporation, 80, 247; droplet, 265
 eutectic point, 270
 exact energy states, 303
 exchange energy, in ferromagnetism, 252
 exchange principle, quantum, 121
 excluded volume, 177; density dependence,
 178
 exclusion principle, Pauli, 123
 exothermic reaction, 74, Prob. 7.4
 expansion of
 gases, isothermal, 54; adiabatic, 54,
 Prob. 5.3; Joule, 54, 160, Prob. 14.4;
 Joule–Kelvin, 73, 161, Prob. 8.3
 solids, low T , 82; Grüneisen theory,
 Prob. 10.6
 fluids, effect on transport, 175
 expansion of equation of state, virial, 162
 expectation value, quantum-statistical, 299,
 302; in fluctuations, 201
 extensive variables, 57; Gibbs' paradox,
 Prob. 13.5
 external fields, 181, 184
 Eyring, absolute rate of chemical reaction,
 216

 F , Helmholtz free energy, 67
 \mathcal{F} , field energy, 181–5
 f , distribution function *or* force *or* mean
 occupation *or* pair function *or* number
 of degrees of freedom
 Fermi, golden rule and master equation, 19,
 304
 Fermi–Dirac distribution, 125, 126
 entropy, 128
 Fermi energy, ϵ_F , 126, Prob. 12.4
 fluctuations, Prob. 16.1
 paramagnetism of conduction electrons,
 Prob. 12.3
 variation of μ with T , 127, 129, Prob. 12.5
 fermions, 122
 interacting, Prob. 11.4
 reservoir, 128
 scattering, 220, 231, 233
 ferromagnetism, 249, 251, 254
 critical point behaviour, 260, 276; theory
 of, 253, 283
 domains, 262; hysteresis, 256, 262
 equation of state and phase diagram, 255,
 260
 Weiss internal field theory, 251, 254; E , S
 and C_m , 253; Curie–Weiss susceptibility,
 256; defects of, 257
 field energy, 6, 181–5
 fine grained probability, 297, 303

 first law of thermodynamics, 8, 57
 first order phase transitions, 250, 254–68
 flow of heat, 7, 26; and particles, 114, 230,
 238
 flow processes and H , 72
 fluctuations, equilibrium distribution of, 4,
 Chap. 16; general principles, 199
 accuracy of Gaussian distribution,
 Prob. 16.3
 and ensemble distribution, 22, 199
 and Onsager reciprocal relations, 242
 behaviour of S in, 306
 correlated, 206, Probs. 16.2, 16.5
 difficult cases, 200, 208; P , 200, 207; T , S
 and μ , 201, 306
 from Boltzmann distribution, 200, 202;
 from S , 204; from A , 205; from response
 functions, 203
 magnitude, 34, 206
 near critical point, 280
 of E , 29, 34, 204; of magnetisation, 202,
 207; of V at fixed P , T , 205; of V in
 thermal isolation, Prob. 16.4; of
 polarisation, 208, Prob. 16.2; of mirror,
 Prob. 13.4; of voltage, 212, Probs. 13.4,
 16.7; of Fermi occupation, Prob. 16.1; of
 vacancy concentration, Prob. 16.6
 power spectrum, 209; fluctuation–
 dissipation theorem, 210, 212; thermal
 noise, 210, Probs. 13.4, 16.7, 16.8
 quantum fluctuations, 201
 quasi-Boltzmann, 207
 fluid
 diffusion and viscosity of, 175
 hard sphere, 173; modified hard sphere,
 175
 negative pressures in, Prob. 18.4
 structure, 173
 flux lines in superconductors, 193
 forces, dissipative, 6; intermolecular, 153,
 Chap. 14; noise forces, 210, Prob. 16.9
 forces, thermodynamic driving, 230, 238
 Franz, Wiedemann–Franz law, 236
 free electron model of metal, 127, Prob. 12.4;
 transport, 227, 233–8
 free energy, Helmholtz, F , 67, 68
 and fluctuations, 207
 and Z , 93; calculation of functions of
 state, 93
 minimisation of, 72
 of ideal monatomic gas, 17, Prob. 7.1; of
 molecule, 135; of paramagnetic, 94; of
 vacancy, 98; of superconductor, 193; of
 oscillator, Prob. 9.1; of rubber model,
 Prob. 9.6
 singularity at critical point, 279, Prob. 18.7
 see also Gibbs function, G , 74; availability,
 A , 75; grand potential Φ_F , 116, 118
 free path, mean, l , 224
 frequency, Debye, ω_D , 110; Einstein, ω_E ,
 109; attempt, ν_A , 216
 frequency density of modes, g_{ω} , photons,
 105; phonons, 109

326 *Index*

- function of state, 57
 statistical calculations of, Chap. 9, 118
 fundamental results, Chaps. 2, 3, 4, 6;
 classical forms, 149; reviewed, Chap. 19
 future and past, 294
- G , Gibbs function, 67
 g , density of states in energy, 16, *or*
 acceleration of gravity *or* radial
 distribution function, 157, *or* Landé
 factor, 185, *or* departure from
 equilibrium occupation, 230; $g_{i, \nu}$, density
 of modes in frequency, 105
 galaxy, and virial theorem, 156, Prob. 14.2
 gas
 condensed, Fermi, 127, 128; Bose, 131
 hard sphere, 173, Prob. 14.7; modified
 hard sphere, 175, Prob. 14.7; van der
 Waals, 177
 imperfect, B_2 , 159, 168; Boyle temperature,
 T_B , 160, 169; Joule expansion, 160,
 Prob. 14.4; Joule–Kelvin expansion,
 161; potential energy, Prob. 14.3
 molecular, heat capacity, C , 89, Prob. 12.9;
 law of mass action, 134
 polar, Probs. 15.1, 16.2, 17.4
 gas, ideal uncondensed monatomic, Chap. 5,
 133
 C_V and C_p , 54
 Carnot cycle, 62
 chemical potential, μ , 133, Prob. 11.1;
 under gravity, Prob. 11.2
 energy, E , 48, 50
 entropy, S , 55, 133; Gibbs' paradox,
 Prob. 13.5
 equation of state, 51, 133
 expansion, isothermal and adiabatic, 54,
 Prob. 5.3; Joule, 54; Joule–Kelvin, 73,
 Prob. 8.3
 fluctuations of, 206, 207
 free energy, F , 72, Prob. 7.1
 gas constant, R , 62
 grand potential, Φ , 133
 in gravitational field, 151, Probs. 11.2, 13.2
 mixtures, entropy of mixing, 136,
 Probs. 11.1, 12.7
 pressure, P , 51, 133; partial, Prob. 11.1
 quantum states, 48
 thermal conductivity, 224; diffusion,
 Prob. 17; viscosity, Prob. 17.2
 thermodynamic properties, 54, 62,
 Probs. 8.1, 8.2, 8.3
 velocity distributions in, 50, 51
 velocity of sound in, Prob. 5.4
 gas scale temperature, θ , 1, 52, 61, Prob. 8.2
 Gaussian distribution, 34; of fluctuations, 34,
 203–9, Prob. 16.3
 ghost cells, 172
 Gibbs–Boltzmann definition of \tilde{S} , 39
 Gibbs distribution, 117; for Fermi and Bose
 gases, 124
 Gibbs–Duhem relation between intensive
 variables, 117
 Gibbs ensembles, 11, 144; canonical, 32;
 microcanonical, 23; grand canonical,
 117
 Gibbs function, G , 67, 74
 in phase and chemical equilibrium, 74
 and μ , 116
 and fluctuations, 207
 Gibbs–Helmholtz relation for cell, 84
 Gibbs' paradox, Prob. 13.5
 Gibbs phase rule, 272
 glass, 5, 45, 289
 golden rule, 19
 grand canonical state, 117
 entropy S_G , 118
 fluctuations, Prob. 16.1
 Gibbs distribution, 118
 Partition function, Ξ , 118; uncondensed
 gas, 133
 potential, Φ_f or Φ , 116, 118, Prob. 11.3
 gravity, gas under, and μ , Prob. 11.2; and
 Maxwell–Boltzmann distribution, 151,
 Prob. 13.2
 Green, Yvon–Born–Green high density
 equation, 166
 greenhouse effect, 107
 growth point, on solid, 99
 Grüneisen theory of thermal expansion of
 solid, Prob. 10.6
- H , enthalpy, 67, *or* Boltzmann's H , 39, *or*
 heat flux density
 \mathcal{H} , Hamiltonian, 146
 h , Planck's constant; $h = h/2\pi$
 H_2 , heat capacity, 91, Probs. 9.3, 12.9; law of
 corresponding states, 169
 H_2O , triple point, Prob. 18.1; melting
 pressure, 81, Prob. 8.7; surface tension,
 Prob. 8.6; law of corresponding states,
 169
 halogen molecules, 91
 Hamiltonian, \mathcal{H} , classical, 146; quantum,
 301
 in electric and magnetic systems, 182, 184
 magnetic, renormalised, 283
 operators which do not commute with,
 201, 300, 302
 symmetry under exchange of identical
 particles, 122
 Hamilton's equations of motion in phase
 space, 146; and constants of motion,
 290
 hard core forces, 153; radius, 155; collision
 cross section, 225
 hard ferromagnetic, 256, 262
 hard sphere fluid, 173; partition function,
 Prob. 14.7; modified, 175, 257
 harmonic oscillator, 15, 87
 ^3He , calculation of T_c , Prob. 14.6
 ^4He , liquid surface, Prob. 10.5; storage,
 Prob. 10.3; Bose condensation, 131,
 Prob. 12.5; adsorption, Prob. 12.6;
 ionisation, Prob. 12.8; liquefier, 162; B_2 ,
 Prob. 14.4; law of corresponding states,

- ⁴He (*continued*)
169; phase diagram, liquid at $T=0$, Prob. 18.2
- ³He/⁴He mixtures, phase diagram and dilution refrigerator, Prob. 18.5
- heat capacity, C , 1
anomaly, Bose gas, 131, Prob. 12.5; at critical points of ferromagnetic, 254, 276; of fluid, 277; of superconductor, 192, 280; Schottky, 96
 C_p and enthalpy, 73
 $C_p - C_v$, 54, 82
negative, 35
of ideal monatomic gas, 54; of oscillator, 87; of rigid rotator, 91; of diatomic gas, 89; of O-H₂ and p-H₂, Prob. 12.9; of paramagnetic salt, 94; of lattice, 107; of radiation, 106; of electron gas, 128, Prob. 12.4; of superconductor, 193, Prob. 15.6; of ferromagnetic, 254, 276
- heat engines, 59, 62
- heat flow, 7
conservation of heat, 8
direction of, 26
meaning in presence of current, 115, 236, Prob. 17.7
particle heat, 115
Peltier, Π , and Thomson σ , 237
pure, sources and sinks, 59
reversible, and S , 7, 44, 59, 65; microscopic expression, 43
- heat pump, 61, Prob. 6.2
- heat of reaction, and H , 74, 84; from cell voltages, 83
- Heisenberg, uncertainty principle, 18, 140; exchange interaction, 252
- Helmholtz, free energy F , *see* free energy; Gibbs-Helmholtz relation for cell, 84
- hidden constants of motion, 291
- high density limit, 165
- high field magnets, 194
- higher order transition, *see* critical point behaviour
- homogeneous systems, 57, 116
- H -theorem, quantum, 39, 305; classical, 297
- hypernetted chain, 166
- hysteresis, ferromagnetic, 256, 262
- I , electric current *or* nuclear spin *or* moment of inertia *or* value of integral *or* number of intensive variables, 274
- ideal gas, *see* gas
- ideal gas scale temperature, θ , 1, 53, 59, 62, Prob. 8.2
- identifiable and non identifiable objects, 120
- imperfect gas, B_2 , 159, 168; Boyle temperature, T_B , 160, 169, 247; Joule expansion, 160; Joule-Kelvin expansion, 161; potential energy, Prob. 14.3
- inaccessibility of absolute zero, 188
- independence, statistical, 14
- independent systems, microsystems, 97; partition function, 97, 135, 163; *see also* independent systems (*continued*)
modes, particle states
- independent variables in thermodynamics, 79
- indistinguishable particles, Chap. 12; *see* particle
- inelastic scattering rates, 220
- information and entropy, 307
- inhomogeneous systems, 68
- instability and phase transitions, 247, 251
- integral, configuration, 163; cluster, 164
- intensive and extensive variables, 57
- interactions, necessary to establish equilibrium, 15; importance at low T , 45; strongly interacting systems, 87, 97, Chaps. 14, 18
- intermolecular forces, 153, 156, 176
- internal energy, E , *see* energy, internal
- internal field, 181, 184; in ferromagnetism, 251, 283
- internal motions of molecule, 90; partition function, 135
- interstitial site occupation, Prob. 9.5
- inversion temperature, Joule-Kelvin, T_i , 161, Prob. 14.4; for van der Waals gas, 178
- ionisation probability, He, Prob. 12.5
- irreducible cluster, 164
- irreversible processes, 7 and ΔS , 40, 58; and thermodynamic potentials, 72, 74, 76; in non-equilibrium thermodynamics, 238
- irreversibility, origin of, 293, 304
- isentropic process, 58; isenthalpic process, 73
- Ising model of phase transition, 282
- isotherms, argon, 246; magnetic 254, 279; van der Waals, 177, 257
- J , current density *or* total angular momentum quantum number *or* exchange interaction constant, 283
- Jeans, Rayleigh-Jeans classical theory of temperature radiation, 105
- Johnson noise, 212, Probs. 16.7, 16.8
- joint probability, 14
- joint states, 25
- Jones, Lennard-Jones potential, 154
- Joule, experiments on energy conservation, 6; Joule expansion, 54, 160, Prob. 14.4; Joule-Kelvin expansion, 73, 161, 178, Probs. 8.3, 14.4
- jump rates, one-to-one and one-to-many, 18-20, 304; and occupation, 218
- K , bulk modulus, $-VdP/dV$, *or* equilibrium constant, 137, *or* molecular rotation quantum number *or* kinetic energy *or* reduced interaction constant, 28
- K, solid potassium, heat capacity below 3 K, Prob. 12.4
- K, unit of temperature, 1
- k , Boltzmann's constant, 53, *or* $|k|$
- \mathbf{k} , propagation vector of wave, 102
- Kadanoff, criterion for critical point, 282

328 *Index*

- Kelvin, Lord (William Thomson), Joule -
Kelvin expansion, 73, 161; statement of
second law, 60; unit of T , 1, 63; vapour
pressure over curved surface, 265; *see*
also Thomson
- kinetic theory
detailed balance, 23
master equation, 20, 304
of gas, pressure, 51; thermal conductivity,
 κ , 224; diffusion, Prob. 17.1; viscosity,
Prob. 17.2
of metals, conductivity σ , 228, 233;
thermal conductivity, κ , 235;
thermopower, 234
of noise forces, Langevin equation, 211
of nucleation in phase transitions, 265
of thermal activation, 213; chemical
reaction rates, 216
of transport, mean free path method, 224;
relaxation time approximation, 228;
Boltzmann equation, 230
relation to thermodynamics, 9
scattering rates, 220
- Kirkwood equation of state for dense
systems, 165
- k space, 103; k vector, 102
density of modes in, 103
- L , latent heat, 1, *or* length *or* angular
momentum *or* inductance *or* Onsager
coefficient, 239
- l , mean free path, 224
- Landé factor, 185
- Landau, theory of phase transitions,
Prob. 18.7; blurring of trajectories, 295
- Landau, theory of phase transitions,
Prob. 18.7; blurring of trajectories, 295
- Langevin, theory of polar molecules,
Prob. 15.1; response to noise forces, 211,
Prob. 16.9
- large systems,
density of states, 17, 31; joint states of, 25
entropy approximation, 41, 118
fluctuations, 200, 203-9
statistical calculations on, 96
temperature of, heat flow between, 25, 26,
29
third law, 45
- latent heat, L , 1, 250
absence, in higher order transitions, 250;
in ferromagnetic first order transition,
257
and enthalpy, 74
and vapour pressure, 80
of sublimation, and zero point energy,
Prob. 14.1
- lattice, heat capacity, 107; binding energy,
Prob. 14.1
- law, *see also* principle
Boyle's, 52, 62
Curie's, 95, 186; Curie-Weiss, 256
Dulong and Petit's, 109
- law (*continued*)
first law of thermodynamics, conservation
of energy, 8, 57
of conservation of heat, 8
of corresponding states, 167, Probs. 14.5,
14.6
of increase of entropy, *see* entropy
of mass action, 134
second law of thermodynamics, 9, 28, 57-
60
Stefan's, 83, 106
third law of thermodynamics, 44
Wiedemann-Franz, 236
- Lennard-Jones 6-12 potential, 154, 159, 162,
Prob. 14.1
- Liouville's theorem, 147, Prob. 13.1
- liquefaction, 247, 257-68; absence for hard
spheres, 175
- liquefier, He, 162
- liquid, *see* fluid
- local equilibrium, departure from, 230, 233
- Lorenz ratio, $\kappa/\sigma T$, 236
- M , quantum multiplicity, 38, *or* magnetic
moment of large system *or* z -component
of angular momentum
- \mathcal{M} , magnetisation; \mathcal{m} , reduced
magnetisation,
- m , mass *or* magnetic moment of a particle;
 m_0 , magnitude of permanent magnetic
dipole
- macroscopic observables, method of, 304
- macroscopic occupation in Bose gas, 129
- macrostate, 18
- magnet, superconducting high field, 194
- magnetic
energy of atom or ion, 185, Prob. 15.3
fields \mathcal{H} , \mathcal{H}_E , \mathcal{H}_M , 184; effect on time
reversal symmetry, 243
field energy, work, 184
- magnetism
diamagnetism, Prob. 15.3; of
superconductor, 191
ferromagnetism, 251, 254, 276; internal
energy and heat capacity, 253, 276;
equation of state, 255, 260; hysteresis,
256, 262; Curie-Weiss law, 256; critical
behaviour, 276, 279
paramagnetism, 94, 185; adiabatic
demagnetisation, 96, 186; Curie's law,
95, 186; fluctuations, 202, 207
- magneto-caloric effect, 186
- magneton, Bohr, μ_B , 94, 185; nuclear, μ_N ,
185
- many-body effects *see* interactions
- many-body distribution functions, 165
- mass action, law of, 134
- master equation, 20, 304
- matrix mechanics, 298; matrix element, 19,
299; density matrix, 299
- Maxwell
demon and entropy decrease, 307
distribution of molecular velocity, 50;

- Maxwell (*continued*)
 Maxwell–Boltzmann distribution, 51
 mean free path correction, 227
 relations between functions of state, 80, 81–5; involving μ , 116
 Mayer, virial expansion, 162; diagrams, 163
 mean field theories, *see* critical point theories
 mean free path, l , 224; estimates of, 225;
 Maxwell correction, 227; and transport properties, 224, Probs. 17.1, 17.2
 mean value, 13
 measure theory, 291
 measurement, effect on \bar{S} , 307
 Meissner effect in superconductors, 192
 melting, 248; melting pressure of ice, 81, Prob. 8.7
 membrane, semi-permeable, 113, 136, Probs. 11.1, 12.7
 memory and direction of time, 296
 metals
 conductivity, electrical, 228, 233; thermal, 235; Wiedmann–Franz law, 236
 free electron model, 127; electronic heat capacity, 128, Prob. 12.4; paramagnetism, Prob. 12.3
 scattering of electrons, 231
 superconductors, 190
 thermoelectricity, 234, 236, 239
 work function, W , 196; contact potential, 197, Prob. 15.7
 metastable states, in thermally activated process, 213; in phase transitions, 248, 256, 263, 265, 270
 Mg–Cu, phase diagram, 272
 microcanonical state, 23; entropy, 41; fluctuations, 200
 microstates, 4, 18; exact, 303
 microstructure of ensemble, 295, 297; of density matrix, 305
 microsystems, independent, 97
 minimisation of F , 72; of A , 76
 mirror, fluctuations of, Prob. 13.4
 mixed phase regions, 247, 258, 270
 mixing, entropy of, 136, Prob. 12.7; in binary alloys, 271, Prob. 18.6
 mixtures, of gases, Prob. 11.1; phase separation in, 268, Prob. 18.5
 modes, of molecular motion, 89; of waves in box, 48, 92, 103; k -space density, 103; photons, 105; lattice waves, 108; spin waves, 45
 modified hard sphere fluid, 175
 molecular dynamics, computation of thermal properties, 170
 molecular heat capacity, 92, Probs. 5.3, 9.4, 12.9, 13.4
 momentum, canonical, 146
 Monte Carlo method, computation of thermal properties, 170
 mutual field energies, 182, 184
 N , total number of atoms, systems, etc; N_A , Avogadro's number, 52; N_V , N_C ,
 N (*continued*)
 numbers of independent variables and restrictive conditions, 274
 ρ , density of states (alternative to g)
 n , integer *or* occupation number *or* number density
 Nambu formalism, 86, 302
 natural variables, for S , 64, 97; for F , 67, 93; for thermodynamic potentials, 67, 70; including μ , 70, 116
 negative C , 35; P , Prob. 18.4; T , 35
 Nernst theorem (the third law), 44
 neutron spectroscopy and phonons, 109
 Ni, spontaneous magnetisation, 253
 noise, electrical, 212, Probs. 13.4, 16.7, 16.8; mechanical, Prob. 16.9
 non-commuting variables, fluctuations, 201; and density matrix, 300, 302
 non-condensed gases, Chap. 5, 131, 142, Prob. 13.5
 non-equilibrium distributions in transport, 230, 233
 non-equilibrium thermodynamics, 238, 241, Prob. 17.7
 non-randomising perturbations, 21, 306
 nuclear spin, 36, 44, 185; magneton, μ_N , 185; demagnetisation, 190
 nucleation, barrier, 263; rate of, 265
 Nyquist's formula for resistor noise, 212; mechanical equivalent, Prob. 16.9
 observables, quantum, 86, 199, 302; expectation value, 201, 299
 macroscopic, method of, 304
 off-diagonal, 300, 302; and quantum fluctuations, 201
 observables, thermodynamic, 4, 302
 ensemble average, 11, 299; in phase space, 144
 fluctuations of, Chap. 16
 using density matrix, 299; invariant expression for, 302
 observer, entropy of, 308
 occupation number, n , 123
 and scattering rates, 218
 equilibrium, f , fermions, 125; fluctuations, Prob. 16.1; bosons, 124; uncondensed gas, 132
 macroscopic, in Bose condensation, 131
 non-equilibrium, in transport, 230, 233
 occupation density, 129
 off-diagonal operators, 201, 300, 302
 Ohm's law, 196, 228, 233; failure at high frequencies, Prob. 17.3
 one-to-one and one-to-many jump rates, 19, 304
 Onsager
 non-equilibrium thermodynamics, 238, 241; coefficients, 239, Prob. 17.7; reciprocal relations, 241
 solution of 2-D Ising model, 282
 operators, quantum, 201, 299

330 *Index*

- Oppenheimer, Born–Oppenheimer approximation, 89
- orbits of planets, ergodic assumption, 290
- order–disorder transformation in alloys, Prob. 18.6
- ordering process, order parameter, 250, 251, 252; near critical point, 276, 281
- ortho-H₂, Prob. 12.9
- oscillator, harmonic, energy levels, 15; statistics and Planck's formula, 87, Prob. 9.1; *S*, 88
- P*, pressure or polarisation or product number, 115
- p*, probability, 11, or momentum or electric dipole moment or free path
- pair binding energy, ϵ , 155
- pair function, radial distribution, g , 157, 165; of virial expansion, f_{ij} , 163
- para-H₂, Prob. 12.9
- paramagnetism, 94, 185
 and ferromagnetism, 251
 cooling by adiabatic demagnetisation, 96, 186, Prob. 15.5; nuclear, 190
 energy of ion in magnetic field, 185, Prob. 15.3
 fluctuations of, 202
 heat capacity, Schottky anomaly, 96, Prob. 9.2
 of conduction electrons, Prob. 12.3
 quantum numbers, 185
 sites as identifiable systems, 121
- partial derivatives, 78; mathematical relations between 79, 80; Maxwell relations, 80, 116
- partial pressure, Prob. 11.1
- particle
 flow, 114; particle heat, 115
 indistinguishable, Chap. 12; bosons, 122, 124, 129; fermions, 122, 125, 129; uncondensed, 132, 162; Gibbs' paradox, Prob. 13.5; *see also* electrons
 partition function, ζ , 134; molecular internal, 135
 reservoir, 113; for fermions, 128; for bosons, 131
 state, 123; as identifiable system, 132
- partition function, Z , 32
 and density matrix, 302
 and F , 93
 as route to functions of state, 93
 classical form, Z_{cl} , 149, 162
 grand partition function, Ξ , and Φ , 118; of gas, 133
 of paramagnetic salt, 94; of fluid, 162; of hard sphere fluid, Prob. 14.7
 one particle, ζ , 134; molecular internal, 135, Prob. 9.4
- past and future, 294; and ensemble microstructure, 295
- Pauli, exclusion principle, 123; paramagnetism of conduction electrons, Prob. 12.3
- Peltier heat, Π , 237, 241; at $T=0$, Prob. 15.7
- Percus–Yevick theory of equation of state, 166
- permittivity, $\epsilon(\omega)$, for polar dielectrics, Prob. 17.4; *see also* polarisability
- persistence, in transport theory, 227
- perturbation, and scattering between approximate energy states, 15
 non-randomising, 21, 306
- Petit, Dulong–Petit law of lattice heat capacity, 109
- phase, phase change, 246, Chap. 18
 and equation of state, Chap. 14
 diagram, 247; ferromagnetic, 249; binary, 268, 272; of H₂O, Prob. 18.1; of ⁴He, Prob. 18.2; of ³He/⁴He, Prob. 18.5
 equilibrium, and G , 74; and μ , 115; phase rule, 272
 first order, 250, 254–68; higher order, *see* critical point
 latent heat and H , 74
 mixed phase region, 258, 278
 nucleation, barrier, 263; rate of, 265; limit of supersaturation, 268
 of vapour–liquid, 257, 278; of ferromagnetic, 249, 255; of superconductor, 191, Prob. 15.6; of binary mixture, 268
 theories of, *see* critical point
- phase coherence and the density matrix, 300, 304; principle of random equilibrium phases, 301
- phase space, 140, 145, 288–298
 accessibility in, 144, 148; ergodic problem, 288; disconnected parts, 289
 approach to equilibrium, 144; H -theorem, 297
 canonical variables, 146
 dimensionless volume, $d\Omega$, 144, 145
 Hamilton's equations, 146
 Liouville's theorem, 145
 trajectories in, 140, 144–9, 288–98
 volume per quantum state, 143
- phonon, 108
 drag, 234
 heat capacity, 109
 non-ergodic behaviour, 289
 scattering, 220, 232
 thermal expansion, Prob. 10.6
- photon, *see also* radiation
 as non-identifiable particle, 120
 momentum and pressure, 83, 91
 scattering rate, 219
- Planck, energy in oscillator, 87; theory of radiation, 105; photon scattering rates, 218
- planetary orbits and ergodic problem, 290
- polarisability, α_p , of polar gas, Langevin theory, Prob. 15.1; high frequency, Prob. 17.4
 fluctuation in, 208, Prob. 16.2
- polarisation charges and field, 181
- polarisation of photons, 105; of phonons, 107

Index

331

- potential, advanced, 296
 potential, contact, 197, Prob. 15.7
 potential, interatomic, 154
 potentials, thermodynamic, Chap. 7; table 70;
 involving μ , 116
 chemical or electrochemical, μ , *see*
 chemical potential
 F, 68; *H*, 67, 72; *G*, 67, 74; *A*, 75; Φ , 116
 potential energy, in thermodynamics, 68,
 117
 potential energy of imperfect gas, Prob. 14.3
 power spectrum of fluctuations, 209
 practical representations, quantum, 15, 304;
 classical, 291, 294, 298
 pressure, *P*
 and *S*, 64
 fluctuations, 200, 207, 208
 negative, Prob. 18.4
 of gas, 51, 133; of fluid or solid, Chap. 14;
 of photons, 83, 91; of vapour, 80
 partial, Prob. 11.1
 statistical formulae for, 52, 87, 93, 133
 principle, *see also* law, quantum theory
 adiabatic invariance, 43
 Carnot's, 60
 detailed balance, 24
 equal equilibrium probability, 23, 301;
 classical form, 145, 148
 ergodic, 21, 148
 jump rate symmetry, 19, 219, 305
 random equilibrium phases, 301
 uniform local probability, 294; and *H*-
 theorem, 297, 306
 probability, 11–14; statistical convergence,
 11
 and mean values, 13
 canonical Boltzmann, p_i , 32;
 microcanonical, 23; grand canonical,
 118
 conditional and absolute, 14; statistical
 independence, 14
 description of thermodynamic state, 3, 18,
 307
 distribution function, 4, 13
 ensemble, 11, 18; classical, 144
 fluctuation, Chap. 16
 initial, 3, 12; uniformity of, 294; off-
 diagonal, 304
 joint, 14
 state, \tilde{p}_i , 18; classical density, \tilde{p} , 144;
 density matrix, $\tilde{\rho}_{ij}$, 299
 process energy, and *H*, 72
 product number, P_p , 115
 propellers and cavitation, Prob. 18.4
 pure heat flow, and *S*, 59

Q, electric charge (alternative to *Z*)
q, heat, 7, *or* canonical position variable, 146
 quantised flux lines in superconductors, 193
 quantum effects, in heat capacities, 87, 91; in
 equation of state, 169, Prob. 14.6; in
 fluctuations, 201
 quantum state, *see* state
 quantum theory
 Bohr–Sommerfeld condition, 143
 exchange energy, 252
 exchange principle, 121, 122; bosons and
 fermions, 122; exclusion principle, 123
 field theory, Nambu, 86; Dirac, 218
 in electric and magnetic fields, 182, 184
 matrix element, 19; matrix mechanics,
 298; density matrix, ρ_{ij} , 299, 301, 304
 operator, expectation value of, 201, 299;
 off-diagonal, 201, 300, 302; macroscopic,
 304
 principle of adiabatic invariance, 43
 time reversibility of, 303
 transition rates, 18, 23; master equation,
 20, 305; dependence on occupation
 number, 218; for non-randomising
 perturbations, 21, 306
 uncertainty principle, 18, 140
 quasi-Boltzmann distribution of fluctuations,
 207, Prob. 16.6
 quasi-ergodic trajectories, 291
 quenching of alloys, 270
 quenching of heat capacities, oscillator, 87;
 rotator, 91; photons, 105; phonons, 109

R, gas constant, 62, *or* resistance *or* reagent
 number, 115, *or* transition rate, 218
r, number of reactions *or* distance between
 atomic centres, 154; r_0 , hard core
 distance; r^* , equilibrium distance
 radial distribution function, 157; formal
 expression for, 158; for solids and fluids,
 174
 radiation
 black body, *or* equilibrium, 103, 106;
 density of, 82, 106; frequency
 distribution of, 105; Stefan–Boltzmann
 constant, σ , 106; visible, Prob. 10.1;
 adiabatic expansion of, Prob. 10.2
 by accelerating charge, 296
 cosmic background, Prob. 10.2
 emissivity, e , 107, Prob. 10.3
 momentum and pressure of, 83, 91
 random close packing, in fluids, 173
 random equilibrium phases, principle of, 301
 randomisation in thermodynamics, 5, 20, 39,
 145; and time reversal symmetry, 21,
 293, 303; non-randomising
 perturbations, 21, 306
 rate of activated process, 216; chemical
 reaction, 216; dependence on *T*, 216;
 nucleation, 265
 rates of quantum jumps, 18, 24, 304; and
 occupation number, 218
 ratio, Lorenz, $\kappa/\sigma T$, 236
 Rayleigh–Jeans classical theory of radiation,
 105
 reaction, chemical, *see* chemical
 thermodynamics
 reagent number, R_r , 115

332 *Index*

- reciprocal relations, in non-equilibrium thermodynamics, 241
- reduced variables, in law of corresponding states, 167, 175; near critical point, 280
- reflection coefficient and emissivity, 107, Prob. 10.3
- refrigerator, 61; dilution, Prob. 18.5
- relaxation time, 228
and transport, 228
difference from scattering time, 228, 232, Prob. 17.5
- renormalisation near critical point, 284
- representative point, in velocity space, 51; in phase space, 140, 145
- representation, quantum, 3, 15, 18; classical, 144
abnormal, 292, 303
matrix, 298
practical, 291, 304
representation-independent formulae, 302
- reservoir, thermal, 30
and Boltzmann distribution, behaviour of $g_R(E_R)$, 31
for heat engine, 59
in availability calculations, 75
- reservoir, particle, 113
and Gibbs distribution, 117
for bosons, 131; for fermions, 128
- resistivity, *see* conductivity
- response functions and fluctuations, 203
- reversed jump rates, equality of, 19, 23; proof, 304
and occupation number, 218
- reversible and irreversible changes, 7
and S , 40, 58
hysteresis, 256, 262
problem of time reversal symmetry, 293, 303, *see also* time reversibility
reversible heat and work, 7, 43
- rotator, energy of, 91; partition function, Prob. 9.4
- rubber elasticity, Prob. 9.6
- S , entropy, Chap. 4, *or* spin quantum number
- s , entropy per particle *or* order parameter *or* interparticle spacing
- Sackur-Tetrode expression for S in non-condensed gas, 133
- satellites, temperature control of, 107
- saturation, magnetic, 94
- scaling hypothesis, near critical point, 279, 285, Prob. 18.7
- scattering
centres, as randomising perturbation, 306
in metals, 231
rates, one-to-many and one-to-one, 18, 24, 304; reverse, 19, 23; and occupation number, 218; and l , 224; and relaxation time, 228
small angle, 228, 232, Prob. 17.5
term in Boltzmann equation, 231
- Schottky anomaly in heat capacity, 96, Prob. 9.2
- Schrödinger's equation, and particle symmetry, 122; in electric and magnetic fields, 182, 184; matrix form, 301
- second law of thermodynamics, statements, 9, 57, 59, 60; statistical character, 29, 149; in fluctuations, 307; *see also*, entropy, general, increase of
- Seebeck thermoelectric emf, η_S , 235, 237
- self-consistent ordered state, 252
- self-consistent treatment of dense systems, 165
- self and mutual electric and magnetic energies, 181, 184
- semiconductor, occupation of donor state, Prob. 11.4; electron-hole equilibrium, 135; μ when heavily doped, Prob. 12.5
- semipermeable membrane, 113, Prob. 11.1; and entropy of mixing, 136, Prob. 12.7
- separation of gases, Prob. 12.7
- shear wave, in solid, 107
- shot noise, 212
- singularity of functions of state at critical point, 279, Prob. 18.7
- skin effect, anomalous, Prob. 17.3
- small angle scattering, 228, 232, Prob. 17.5
- small current limit of transport theory, 230
- small systems, T , 32; S , 40
- soft ferromagnetic, 257, 262
- solid, lattice waves and lattice heat capacity, 107; expansion, Prob. 10.6; binding energy, heat of sublimation, Prob. 14.1; vacancies, 98
- solidification of alloys, 270
- solubility, mutual, 270, 272
- Sommerfeld, Bohr-Sommerfeld quantum condition, 143
- specific heat, *see* heat capacity
- spectrum, spectral density
absorption and emission, 107; emissivity, e , 107, Prob. 10.3
of black body radiation, 105
of fluctuations, 209; Johnson noise, 212, Probs. 16.7, 16.8
of lattice modes, 109; Einstein and Debye spectra, 110; neutron spectroscopy of, 109
- spin
energy, in a magnetic field, 184, Prob. 15.3; exchange, in ferromagnetics, 252
ferromagnetic systems, 249, 251, 254, 276; spin waves, 257
illustration of meaning of density matrix, 299
nuclear, and negative T , 36; and third law, 44; cooling of, 185; nuclear magnetic resonance, 36; in $o\text{-H}_2$ and $p\text{-H}_2$, Prob. 12.9
paramagnetic systems, quantum numbers, 185; magnetisation, 94, 185; cooling by adiabatic demagnetisation, 96, 186, Prob. 15.5

- spontaneous emission, 218
 spontaneous ordering, 252
 stability of phases, 248, 256, 263, 265, 270
 standing wave modes, 48, 92
 state, classical, 140, 145
 state, thermodynamic, 3; *see also*
 equilibrium, thermal
 canonical, 32; microcanonical, 23; grand
 canonical, 117
 metastable, 213
 states, approximate energy states, 15, 18,
 298, 301, 304
 degenerate, 15
 density of, g , 16, Prob. 4.3
 groups of similar, 18, 305
 joint, of two systems, 25
 of monatomic gas, 48; of oscillator, 15; of
 diatomic molecule, 89; of electron gas,
 126; of semiconductor, 135, Prob. 11.4;
 of paramagnetic ion, 185
 plane wave, de Broglie wavelength, 49;
 thermal, λ_T , 132, 142, Prob. 12.5
 states, other quantum
 exact energy states, difficulties of, 15,
 303
 linearly combined, 298
 product type, 123
 spin, 299
 state vector, 298
 symmetric for bosons, 122; antisymmetric
 for fermions, 122, Probs. 12.2, 12.9
 wave packet, relation to phase space
 description, 140, 143
 statistical
 calculation of functions of state,
 Boltzmann method, 86; from Z , 93;
 from $k \ln g$, 96; from Ξ , 118
 definitions of T , 28; of \bar{S} , 38
 expectation value, 299, 302
 predictions, method, 3, 12
 uncertainty, and \bar{S} , 38, 307; and \bar{p}_{ij} , 299
 see also probability
 Stefan's law, 83, 106; Stefan–Boltzmann
 constant, σ , 106
 stimulated emission, 218
 Stirling's approximation for $n!$, 17
 stratosphere, composition of, Prob. 13.2
 strongly interacting systems, Chaps. 14 and
 18; difficulties of, 86, 97, 153; and third
 law, 45; Nambu formalism for, 86, 302
 sublimation, pressure, 247; latent heat of,
 Prob. 14.1
 sum over states, *see* partition function
 Sun, radiation of, 106
 superconductors, type I, 190, Prob. 15.6;
 type II, 193; high field magnets, 194;
 phase transition in, 191, 250, 280
 supercooling and superheating, 248, 263,
 268
 superfluidity, 131; phase transition, 277
 superinsulation, Prob. 10.3
 superlattice, in order–disorder
 transformation, Prob. 18.6
 superposition approximation, for dense
 systems, 166, 173
 surface
 effects in molecular dynamics and Monte-
 Carlo calculations, 172
 energy, 68, 69, Probs. 8.5, 8.6, 10.5
 enthalpy, Gibbs function, 68
 of solid, 98
 tension, 68; ripples, Prob. 10.5; role in
 nucleation, 263
 surroundings, and second law, 58; and A , 75
 susceptibility, *see* magnetism, polarisability
 symmetry
 jump rate, 19, 219, 305; and detailed
 balance, 23
 particle exchange, symmetric and
 antisymmetric states, 122, Probs. 12.2,
 12.9; of \mathcal{H} , 122
 time reversal, 293, 303; in non-equilibrium
 thermodynamics, 243
 system, thermodynamic
 as identifiable object, 120
 electric and magnetic, Chap. 15
 joint, 25
 large, 28, 31, 41
 small, 32, 40
 variable contents, Chap. 11
 T , temperature, Chap. 3, 59, 63; T_B , Boyle
 temperature, 160; T_J , Joule–Kelvin
 inversion temperature, 161; T^* , Curie
 law temperature, 189
 t , time or reduced temperature or
 temperature difference
 temperature, T , Chap. 3
 Boyle, T_B , 160, 169, Prob. 14.4; Debye, θ_D ,
 111; Joule–Kelvin inversion, T_J , 161,
 Prob. 14.4; triple point, T_{trip} , 247
 critical, T_c , 247; quantum effects on, Prob. 14.6
 empirical, 1, 8
 measurement of low T , 189
 negative and infinite, 35, 36
 radiation, 103, 106
 scales, Celsius, 1; ideal gas, 1; relation to
 statistical definition, 53; relation to
 thermodynamic definition, 59, 62, Prob.
 8.2; Kelvin work scale, 60; Curie law
 temperature, T^* , 189
 statement of second law, 59
 statistical definition for large systems, 28;
 classical form, 149; for small systems, 32
 T^3 heat capacity in solids, 110
 thermodynamic definition, 59
**Temperature, Boltzmann Factors and
 Elementary Kinetic Theory: short course
 Chapters 1, 2, 3, 5, 6, 9.1, 10, 11 and 12
 (omitting 2.7, 3.4, 3.5, 6.7, 6.8, 6.9, and
 12.5 onwards) plus sections 15.3, 16.6,
 16.7, 17.1, 17.2**
 Tetrode, Sackur–Tetrode formula for S in
 uncondensed gas, 133
 thermal activation, 213; rate, 216; activation
 energy, ϕ_A , 217

334 *Index*

- thermal conductivity, κ , of gas, 224; of metal, 235
- thermal equilibrium, *see* equilibrium
- thermal fluctuations, Chap. 16, *see* fluctuations
- thermal wavelength, λ_T , 132, 142, Prob. 12.5
- thermally activated process, 213; phase nucleation, 265
- thermodynamic
- driving forces, 230, 238
 - observables, functions of state, 4; statistical calculation of, Chap. 9, 118
 - potentials, Chap. 7; involving μ , 116; *see* potential
 - relations, Chap. 8; do not hold in fluctuations, 202; involving μ , 116
 - response functions and fluctuations, 203
 - state, 3, 5; *see* equilibrium
 - system, 2; variable contents, 113; particle not a system, 120
 - temperature, T , 59
- thermodynamics
- classical, Chaps. 5–8; *see* *Classical Thermodynamics, a short course*
 - non-equilibrium, 238, 241
- thermoelectricity, 234, 236, 239
- Peltier heat, σ , and Thomson heat, Π , 237; and S^* , 241
 - Seebeck emf, η_S , 235, 237
 - thermocouple, 235, Prob. 17.6
 - thermopower, $d\eta/dT$, 234, 237; and S^* , 241
 - Thomson relations, 237, 241, Prob. 17.7; justification using Onsager relations, 239, 241
 - upper limit on coefficients, 243
- third law of thermodynamics, 44; use, 65, 82
- Thomson (Lord Kelvin), heat, σ , 237; relations between thermoelectric coefficients, 237, Prob. 17.7; derivation from Onsager relations, 239, 241; *see also* Kelvin
- three-body forces, 155
- time reversibility of laws of mechanics, 21, 293, 303
- internal reversibility, and detailed balance, 24; and Onsager reciprocal relations, 243; failure in external magnetic field, 24; 243
- trace of matrix, invariance of, 300
- trajectory in phase space, 140, 144–9, 288–98; quasi-ergodic, 291; Landau blurring, 295
- transformation of representation, canonical, 298; unitary, 300
- transformation or transition of phase, *see* phase change
- transition rate, quantum, 18, 24; master equation, 20, 304; dependence on occupation number, 218; non-randomising perturbations, 21, 306
- translational energy of molecule, 89; partition function, 135
- transport properties, Chap. 17
- Boltzmann transport equation, 229; small current limit, 230
 - diffusion, in fluid, 175; in gas, Prob. 17.1
 - electrical conductivity, σ , of metals, 228, 233; variation with frequency, Prob. 17.3
 - mean free path approximation, 224
 - relaxation time approximation, 228
 - thermal conductivity, κ , of gas, 224; of metal, 235; Wiedemann–Franz law, 236
 - thermoelectric effects, Seebeck emf, 234; Peltier and Thomson heats, 237; Thomson relations, 237, 241, Prob. 17.7; justified using Onsager relations, 239, 241
 - viscosity, η , of fluid, 175; of gas, Prob. 17.2
- triple point, 247
- absence in He, Prob. 18.2
 - and law of corresponding states, 169
 - of H₂O, Prob. 18.1
- two-body distribution function, 157, 165
- two-port heat engine, 60, 62
- type I and type II superconductors, 191, 193
- U , energy flux density
- u velocity; u_{ij} , pairwise energy contribution, 159
- ultra-violet catastrophe, 105
- uncertainty, statistical, and meaning of \bar{S} , 38, 307; quantum and statistical, in $\hat{\rho}_{ij}$, 299
- uncertainty principle, in scattering between energy states, 18; in phase space, 140
- uniformity of local probability, principle of, 294, 297, 306
- unitary transformation, 300, 303
- universality of critical exponents, 277, 285
- useful work and availability, 75
- V , volume, V_v , volume in velocity space
- v , virial, 155
- v , velocity *or* volume per particle
- vacancies, equilibrium concentration, 98; fluctuations, Prob. 16.6
- van der Waals, attraction, 154
- equation of state, 177; B_2 , values of a , b , 178; as theory of phase transitions, 257; critical point, 258, Prob. 18.3; coexistence curve, 278; equal area rule, 258
 - model, 176; partition function, Prob. 14.7
- vapour pressure, P_{vap} , 80
- and equation of state, 247; equal area rule, 258, 260
 - and latent heat, 80
 - over curved surface, 265
- vapour trail, 268
- variable contents, Chap. 11
- variables
- canonical, in phase space, 146; choice of representation, practical variables, 291, 304

- variables (*continued*)
 dependent and independent, in thermodynamics, 79
 in equipartition, 151
 natural, for functions of state, 64, 67, 116
 velocity distributions, 50, 51
 velocity of sound in gas, Prob. 5.4
 velocity space, 50; *see also* phase space
 vibrational energy, of oscillator, 87; of molecule, 89; of lattice, 109
 vibration–rotation spectra, 91
 virial, $\overline{v^2}$, 155
 equation of state, 158
 expansion, 162; B_2 , 159, 168; B_2 for van der Waals model, 178; higher coefficients, 164; failure at high density, 165
 theorem, 156, Prob. 14.2
 viscosity, η , in fluids, 175; of gas, Prob. 17.2
 visible radiation, Prob. 10.1
 voltage fluctuations, of resistor emf, 210, Prob. 16.7; across capacitor, Probs. 13.4, 16.8
 volume fluctuations, at fixed P, T , 205; in thermal isolation, Prob. 16.4
 von Kármán, Born–von Kármán theory of lattice heat capacity, 109
 von Neumann, method of macroscopic observables, 304
- W , number of configurations or work function
- w , work
- wave function, *see* states, quantum
- waves, thermally excited, Chap. 10
 electromagnetic, absorption and emission, 107; energy density, 82, 106; pressure of, 83, 91; spectral energy density, 105;
- waves (*continued*)
 Stefan–Boltzmann constant, 106
 in rectangular box, 102; boundary conditions, 102; lattice, in solid, 107; dispersion, 108; mode spectra, 109; heat capacity, 109; T^3 law at low temperature, 110
 velocity, dispersion, 102
- Weiss, ferromagnetic domains, 262; internal field theory of ferromagnetism, 251, 254; defects of, 257; Curie–Weiss susceptibility, 256
- Weyl, general proof of mode density of waves in cavity, 103
- white noise, 212
- Wiedemann–Franz law of ratio of electrical and thermal conductivities of metals, 236
- Widom, scaling laws, 277
- Williams, Bragg–Williams theory of order–disorder transformation, Prob. 18.6
- Wilson, renormalisation, 283
- work, w , 6
 dissipative, 6
 done by heat engine, 60
 in electric and magnetic systems, 182, 184
 reversible and irreversible, 7
 reversible, microscopic expression for, 43
 useful dw_u , and A , 75
- work function of metal, W , 196, Prob. 15.7
- work scale temperature, 60
- Yevick, Percus–Yevick theory of fluid, 166
- Yvon–Born–Green equation of state, 166
- Z , partition function, 32, or charge (alternative to Q)
- zero point energy, 15, Probs. 10.4, 14.1