

Index

- ab initio methods 444
- absolute activity 393
- absolute zero
 - attainability 312, 317
 - crystals 294, 299
 - entropies 305
 - equation of state 315
 - gases 316
 - heat capacities 309, 316
 - metastable phases 310
 - molecular motion 315
 - phase boundaries 311
- acceptance criterion 460–461
- activated complex 429
- activation energy 425, 427
- activity coefficient
 - convention 230, 233
 - definition 230
 - electrolyte 273, 275
 - measurement 235, 239
 - relations 240
 - vapor–liquid equilibrium 255
- addition-of-variable rule 154
- adsorption 17, 342, 379, 401, 419
- amorphous materials 52, 280, 310
- angle potential 465
- Antoine equation 183, 198, 249
- Arrhenius relation 427
- averages
 - ensemble 54, 56, 343
 - simulation 454, 457, 460
 - statistical errors in 464
 - time 54–55
- azeotrope 241, 258, 279

- balance equation 462
- baths 101, 123, 321
- binodal 207
- binomial theorem 16
- blood flow 121
- boiling 145
- boiling point 90–91, 182, 246
- boiling-point elevation 221, 244
- Boltzmann’s constant 12, 58
- Boltzmann’s equation 12, 306, 319

- Boltzmann factor
 - electrolytes 268
 - ensembles 324, 354, 388
- bonded interactions, *see interactions*
- boundaries, *see interfaces and surfaces*
- Bragg–Williams approach 339
- bubble point
 - calculation 250
 - definition 246
- bubbles 147

- calculus manipulations 155
- canonical ensemble
 - classical systems 357
 - definition 324
 - partition function 324, 346
 - probabilities 323, 345, 354–355
 - independent molecules 333, 364
 - simulation 460
- capacitors 277, 384
- Carnot cycle 120
- catalysts 419, 442–443
- cells 47, 78–79, 242
- chemical potential
 - convention 219, 233
 - electrolytes 275
 - excess quantities 173
 - gradients 158
 - interpretation 143
 - mixture 235
 - reaction equilibrium 406
 - simulation 385
 - solids 280
 - standard quantities 166
- chemical reaction equilibrium, *see reaction equilibrium*
- chi parameter, *see exchange parameter*
- cholesterol 304
- Clapeyron equation 182, 258, 311
- classical force field, *see potential energy function*
- classical systems
 - definition 25
 - density of states 55, 305
 - entropy 317
- classical thermodynamics 7

- Clausius-Clapeyron equation 183
 coarse-grained model 444, 448
 colligative property 223
 combinatorial counting 15, 41
 common-tangent line 203, 265
 compressibility, isentropic 153
 compressibility, isothermal
 thermodynamics 151, 158
 mixtures 158
 sign 211
 statistical mechanics 399
 compressibility factor 171
 conjugate variables 87, 143
 conservative force 114
 constant temperature
 statistical mechanics 348, 370
 states 123
 continuity equation 73
 cooperative reaction 422
 core overlap 453
 critical micelle concentration 423
 critical point 192, 195, 208, 352
 crystals
 classical crystals 301
 Debye model 296, 314
 defects 48
 definition 280
 Einstein model 292, 354
 heat capacity 294, 299, 301
 melting 383
 mixtures 281
 models 88, 290
 orientational degeneracies 307
 vapor pressure 301
 cutoff distance 458, 466
 cyclic process 114

 de Broglie wavelength 166
 Debye-Hückel model 266, 277
 Debye length 268, 279, 465
 Debye model of crystals, *see crystals: Debye model*
 degrees of freedom
 continuous 361
 internal 70
 independent 329, 364
 microscopic 18, 35, 328, 355
 thermodynamic 178
 vapor-liquid 249
 density of states
 classical behavior 375
 interpretation 12-13

 detailed-balance equation 462
 dew point
 calculation 250
 definition 246
 diagram
 Mollier 196
 P - H 174
 P - T 181
 P - V 116
 P - x - y 274
 S - T 313
 T - ρ 181
 T - x - y 247
 x - y 255
 dielectric constant 266
 dimerization 335
 dipole 384-385
 Dirac delta function 364
 distinguishable particles 333
 drops 144, 197, 403
 DNA 47, 119, 356

 Einstein, Albert 1
 Einstein model of crystals, *see crystals: Einstein model*
 Eyring equation 428
 elastic band 119, 400
 elastic modulus 280
 electrolyte solutions 266, 274
 electrostatic interactions, *see interactions: electrostatic*
 electrostatic potential 266
 energy drift 452
 energy-minimum principle 70
 energy landscape 297, 428
 energy of mixing 228
 energy spectrum 24
 ensemble
 canonical 324
 grand canonical 392
 interpretation 36, 320
 isothermal-isobaric 387
 Liouville's theorem 72
 microcanonical 321
 semi-grand 398
 enthalpy
 definition 91, 136
 fundamental form 136
 entropy
 absolute 173, 305, 376
 classical 317

- entropy (cont.)
 concavity 9, 42, 353
 definition 8, 99
 excess 173, 378, 381
 extensivity 9, 41, 58
 Gibbs' formula 336, 396, 400
 interpretation 8
 mixing 45, 75, 169, 217, 260
 partial derivatives 9
 polymer 263, 276
 residual 308, 316–317
- equal a priori probabilities, *see principle of equal a priori probabilities*
- equilibration period 453
- equilibrium
 approach to 68, 76, 418–419
 chemical 67, 82
 definition 6
 mechanical 67, 82
 thermal 58, 63, 82
- equilibrium constant
 definition 404, 408–409
 molecular interpretation 414
 relation to rate coefficients 426
 temperature and pressure dependence 410
- equilibrium states 10, 36, 87
- equipartition theorem 455
- ergodicity 53
- Euler's theorem 84, 138
- eutectic 286, 300–301
- evaporation 237
- excess properties 173, 231, 237, 241, 378, 380–381
- exchange parameter 228, 241, 264
- exponential expansion 16
- extensive properties 84, 91
- extensivity 32, 138
- extent of reaction 405
- external and internal forces 95
- first law of thermodynamics
 closed systems 93, 316
 open systems 107
- flash calculation 252
- Flory-Huggins theory 260, 276
- flow streams 107
- fluctuations
 canonical 343
 stability 399
 correlated 399, 402
 definition 363
 density 398
- energy 64–65, 350, 355, 389, 394
- enthalpy 398
- heat bath 142
- interpretation 36, 343–344
- particle number 394, 399
- reaction equilibrium 414
- volume 389, 398–399
- fluid jets 120–121
- force field, *see potential energy function*
- free charge density 267
- freezing-point depression 224, 281, 302
- fugacity
 coefficient 170
 definition 170
 vapor-liquid equilibrium 255
- fundamental equation
 energy version 83
 entropy version 10, 83
 integrated forms 84
 intensive forms 87
 other work terms 100
 statistical mechanics 343
- Galilean invariance 378
- gas constant 12
- Gibbs adsorption isotherm 146
- Gibbs-Duhem relation 231, 240, 259
- Gibbs free energy
 binary mixture 144, 237
 definition 132
 excess 231, 237, 241
 fundamental form 133
 reaction equilibrium 405, 418
 statistical mechanics 390
- Gibbs' phase rule 180, 232, 417
- grand canonical ensemble
 classical systems 394
 definition 392
 partition function 393
 probabilities 393–394, 399
 simulation 464
- glasses, *see amorphous materials*
- ground state 306, 337
- Hamiltonian
 classical 26, 54
 quantum 23
 virial theorem 382
- hard spheres 380, 401
- harmonic potential 292, 300, 364, 378, 433
- heat 93

- heat capacity
 - behavior at absolute zero 309, 316
 - definition 151
 - measurability 156
 - microscopic interpretation 351, 354, 378, 398
 - relation 152
 - simulation 465
- heat engine 105, 120
- heat of solution 245, 304
- Helmholtz free energy
 - definition 125
 - fundamental form 127
 - solids 146
 - statistical mechanics 326, 355
- Henry's law 239, 242, 386
- Hessian matrix 297
- history independence 6
- H*-theorem 52
- hydrodynamics 369
- hydrogen orbitals 23

- ice skating 302
- ideal gas
 - chemical potential 166
 - classical diatomic 366, 377
 - confined 402
 - dipolar 384
 - equation of state 11, 29, 165
 - energy spectrum 163
 - entropy 11, 116, 165
 - Gibbs free energy 166
 - heat capacity 165
 - Helmholtz free energy 126, 166
 - mixtures 167
 - molecular properties 161
 - partition functions 337, 361, 392, 395
 - polyatomic 167
 - process calculations 115
 - properties 157
 - under gravity 379, 385
- ideal solution
 - chemical potential 218
 - definition 217
 - Gibbs free energy 218
- image particles 457
- implicit solvation model 449
- importance sampling 461
- incompressible liquid 158
- independent molecules 332, 336, 354, 360, 378, 412
- indistinguishability 31, 164, 333, 337, 377
- infinite-state model 77, 337, 355
- integrator 452
- intensive properties 84–85, 91
- interactions
 - bonded 27
 - electrostatic 27, 266, 377, 458, 465
 - long-ranged 458
 - repulsive 28, 32
 - separable 330
 - short-ranged 32
 - van der Waals 27
- internal constraint
 - definition 69
 - use in second law 70
 - use in energy and free energy minimization 70, 134
- interfaces and surfaces
 - confining 402
 - energies of 32
 - interactions with particles 46, 379
 - Gibbs' treatment 145
 - phase equilibrium 192, 303
 - solid phases 303
 - statistical mechanics 403
 - thermodynamics 96, 118, 145, 147, 197, 303
 - thin films 214
- inexact differentials 94
- internal energy 83
- ion atmosphere 267, 271, 277
- ionic strength 269
- Ising model 188, 315, 330, 338–339, 355
- isomerization 80
- isothermal-isobaric ensemble
 - classical systems 390
 - definition 387
 - partition function 388
 - probabilities 388–389, 398
 - simulation 463
- isotopes 307

- Joule experiment 114
- Joule-Thompson process 159

- Kauzmann point 198
- kinetic energy 370, 379

- lattice gas 188
- lattice models 37
- Lagrangian 43
- Langmuir adsorption isotherm 342

- Laplace transform 346
- latent heat
 definition 91, 151, 185
 temperature dependence 196
- Le Chatelier's effect 419
- Legendre transforms
 mathematical definition 128
 physical rationale 133
 statistical mechanics 326, 346, 390, 396
 thermodynamic definition 130
- Lennard-Jones potential 28, 46, 47, 445, 466–469
- Lewis-Randall rule 171, 174, 418
- Lindemann melting criterion 383
- Liouville's theorem 72
- liquid crystals 338–339
- macroscopic properties 6–7
- macrostate
 definition 36, 50
 probabilities 62, 64, 345, 378, 389, 394
- magnetic materials
 fluctuations 400
 spin models 19, 315, 330, 339
 thermodynamics 160
- Margules model 243
- Markov chain 461
- maximum-term method 64, 142, 347, 390
- Maxwell-Boltzmann distribution 368, 377, 379, 437, 453
- Maxwell relations 149
- mean-field approximation 189, 227, 262, 277, 339, 355
- mean-squared displacement 456
- measurable properties 10, 151
- metastable phases, *see stability*
- Metropolis acceptance criterion 460, 463, 465
- microcanonical ensemble
 classical 375, 382
 definition 321
 partition function 321, 375, 382
 probabilities 320
 simulation 450
- microscopic properties 7
- microstate
 definition 12, 35, 328
 probabilities 51, 72, 334, 361, 388, 393
- minimum image distance 457
- molecular simulation 444
- molecular dynamics methods 450, 466–467
- molecular weight 226
- Monte Carlo methods 459, 468–469
- Monte Carlo moves
 acceptance probability 462
 acceptance rate 460
 maximum displacement 460
 overview 459
 particle addition and deletion 464
 proposal probability 462
 single-particle displacement 460, 465
 symmetric 462
 volume scaling 463
- nanoparticles 303
- natural variables 126
- Newton's laws 26, 41, 448, 450
- nonideal gases
 mixtures 171
 pure 170
- nonideal solutions
 definition 230
 vapor-liquid equilibrium 255
- non-natural derivative rule 153
- normal modes 297
- nuclear states 306
- nucleation 198
- oceans 304
- Onsager, Lars 189
- osmotic pressure 224, 237, 240, 421
- Otto cycle 120
- pair potential
 form 41, 445
 truncation 458
 virial 465
- partial molar quantities 233, 238, 259
- partial pressure 168
- particle in a box 23, 162
- partition coefficient 240, 244, 252
- partition function
 degrees of freedom 329
 canonical 319, 346
 classical 357, 375, 382
 configurational 360, 391, 395
 grand canonical 393
 independent molecules 332
 interpretation 321, 396
 isothermal-isobaric 388
 microcanonical 321, 382
 molecular 412

- multicomponent 398
- reaction coordinate 439
- single-molecule 332, 365, 412
- path-dependence 94
- periodic boundary conditions 457
- perturbation theory 338
- phase
 - definition 176
 - stable 207
 - unstable 207
- phase diagram 181
- phase equilibrium
 - boundaries 182, 258, 275, 311
 - conditions 178
 - discontinuities 184
 - liquid-liquid 229, 238–239, 241, 244
 - liquid-solid 281, 287, 300
 - liquid-vapor 90, 246
 - microscopic view 188
 - order parameters 194
 - polymer-solvent 264
 - with reaction 422
 - solid-solid 302
 - solid-vapor 300
- phase transitions
 - first-order 187
 - second-order 187, 196
- phase space 44, 72
- photon gas 92
- Planck's constant 22, 359
- Poisson-Boltzmann equation 268
- Poisson's equation 267, 277
- polymers 213, 260, 463
- postulatory approach 2
- potential energy function
 - definition 26, 445
 - parameters 446
 - polarizable 448
 - transferability 446
- potential energy landscape, *see energy landscape*
- pressure
 - hydrostatic 304
 - negative 214
 - simulation 456
 - statistical mechanics 372, 394
 - virial 374, 380–381, 456, 465
- principle of equal a priori probabilities 3, 51, 306, 319
- probability
 - density 362
 - joint distribution 368
 - marginal distribution 368
- process paths 93
- production period 454
- proteins and peptides 78–79, 199, 215, 340–341, 443
- pumps 159
- quantum effects 25
- quantum mechanics 21, 306
- quasi-static process 98
- Rachford-Rice method 252, 258, 274
- random-number generation 460
- Raoult's law 220, 242, 249
- reaction coordinates
 - definition 425, 432, 439
 - probability 440
- reaction equilibrium
 - binding 422
 - fluctuations 414
 - gases 407
 - general conditions 404, 407
 - heat effects 419–421
 - independence 417
 - with liquid-vapor equilibrium 422
 - nonideal systems 418
 - partition function 398, 413, 418
 - solutions 409
 - standard enthalpy 411
 - standard free energy 408–409, 418
 - statistical mechanics 412, 418
- reaction rate
 - coefficient 426, 438
 - determinants 438
 - thermodynamics 425
- Redlich-Kwong equation of state 215
- regular-solution model 227, 240, 257, 377, 421
- refrigeration 117, 317
- relative volatility 254, 274
- repulsive interaction, *see interactions*
- response function 151
- reversible process 98, 101
- Sackur-Tetrode equation 45, 85, 92, 165, 375
- sand-piston example 97, 100, 103, 116
- Schrödinger equation 22–23, 293
- second law of thermodynamics
 - closed systems 67
 - open systems 107
 - internal constraints 70

- second virial coefficient 401
- self-diffusivity 456, 466
- semi-grand ensemble 398
- shaft work 110
- soft spheres 381
- solubility
 - gas 241, 244
 - liquid 245
 - statistical mechanics 386
- speed of molecules 370, 377
- speed of sound 158
- spinodal 207
- stability
 - conditions 201, 209, 310, 353
 - connection to fluctuations 399
- state functions 88
- states, *see equilibrium states*
- statistical independence 455–456, 465
- statistical mechanics 12
- Stirling's approximation 16, 19, 40
- sublimation 300
- supercooled liquids 117, 202, 284
- superheated liquids 201
- supersaturated solutions 202
- surfactants 423
- temperature
 - interpretation 34
 - negative 353
 - simulations 455
- thermodynamic beta 324
- thermal expansivity
 - absolute-zero behavior 311
 - definition 151
 - statistical mechanics 402
- thermodynamic potentials
 - definition 125
 - fundamental forms 127
 - integrated and derivative relations 137
 - multicomponent 141
 - per-particle versions 141
- thermodynamic states, *see equilibrium states*
- thermodynamic terminology 15
- thermostat 455
- theta temperature 276
- third law of thermodynamics 305, 358, 417
- throttling 174
- tie line 247, 284, 300
- time step 450
- trajectory 450
- transition probability 461
- transition state
 - definition 426, 431
 - theory 426, 431
- transmission coefficient 438
- triple point 179, 302
- triple-product rule 152
- truncation of interactions, *see pair potential*
- two-state model 38, 53, 56, 60, 315, 326, 335–336, 348, 352
- uncertainty principle 32
- universality 188, 209
- van der Waals equation of state 158, 213, 382
- van der Waals interactions, *see interactions*
- van der Waals loop 192
- van 't Hoff relation 411, 427
- vapor pressure 182
- Verlet algorithms 451, 465
- virial, *see pressure virial*
- virial expansion 173, 400
- virial theorem 382
- water
 - anomalies 159, 302, 401
 - freezing 114, 117, 302, 304
 - hydrophobicity 118, 147, 423
 - residual entropy 317
 - response functions 151, 159, 401
 - supercooling 117, 216
 - triple point 302
 - vaporization 183, 186
- wavefunction 21
- Widom insertion technique 385
- work
 - definition 93, 95
 - electrostatic 97, 273, 278
 - maximum 102, 146
 - pressure-volume 95
 - tension 96