

## INDEX

- $E_{xc}$ , 54
- activated process, 12
- activation energy, 370
- Allen-Cahn equation, 230–232  
 derivation, 245–247  
 in one dimension, 231  
 in three dimensions, 232
- Arrhenius equation, 371
- atomic units, 46
- band gap  
 issues with LDA and GGA, 60
- basis functions, 54
- basis set, 55  
 comparison of Slater and Gaussian functions, 56  
 Gaussian function, 56  
 plane waves, 56  
 real space grid, 57  
 Slater function, 56  
 superposition error, 57
- binning methods, 386  
 averages in molecular dynamics, 111–112  
 dependence on bin size, 387
- Bloch's theorem, 55, 349
- bond-order potential  
 REBO, 87
- bond-order potentials, 86–88  
 reactive empirical bond-order (REBO) potential, 87  
 Tersoff potential, 86
- Born-Mayer potential, 74
- Box-Muller method, 386
- bulk modulus, 380
- Cahn-Hilliard equation, 232–233  
 derivation, 247–248  
 in one dimension, 232  
 in three dimensions, 233
- canonical (NVT) ensemble, 357–359  
 average kinetic energy, 359  
 average quantities, 357
- comparison with microcanonical ensemble, 360–361
- configurational integral, 358
- distribution of the total energy, 363
- partition function, 357
- partition function for continuous systems, 358
- relation to Helmholtz free energy, 358
- relative probability between two states, 357
- weighting function, 357
- Cauchy relations, 75, 380
- cellular automata  
 von Neumann original formulation, 211
- basic description, 212
- Game of Life, 216  
 glider, 216  
 rules, 216
- lattice Boltzmann method, 219
- lattice-gas model, 218–219  
 rules, 218
- Moore environment, 215
- one-dimensional rules, 212–215
- recrystallization, 220–222
- relation to Monte Carlo, 227
- Rule 62, 214
- Rule 90, 213
- simple “solidification” model, 216
- spinodal decomposition, 222–225  
 rules, 223–224
- two-dimensional, 215–218
- two-dimensional environments, 215
- von Neuman environment, 215
- central-force potential, 75, 328–329  
 Cauchy relations, 75  
 equation of motion, 97  
 force, 97
- chemical reaction rates, 370–371  
 Arrhenius equation, 371
- classical mechanics  
 conservation of total energy, 326  
 harmonic oscillator, 327–328
- kinetic energy, 325
- potential energy, 325
- cohesive energy, 62–63  
 definition, 62  
 expansion in hierarchy of interactions, 63
- metals  
 Universal Binding Curve (UBC), 80
- types of bonding, 63
- complementary error function, 319
- complex number, 315, 316  
 cosine, 317  
 Euler's formula, 316  
 magnitude, 316  
 sine, 317
- compressibility, 380
- computer code  
 verification, 6
- correlation function, 364  
 time, 365
- Coulomb energy, 331  
 charged particles, 331  
 continuous charge distribution, 331  
 Thomas-Fermi model, 48
- Coulomb force, 330
- Coulomb potential, 46, 330  
 continuous charge distribution, 331  
 multipole expansion, 333  
 spherically truncated, 42
- cross product, 312
- crystal structures, 284–291  
 basis, 284  
 body-centered cubic, 286  
 direct lattice, 288–289  
 face-centered cubic, 286  
 hexagonal closest packed, 286  
 lattice directions, 287  
 lattice planes, 287  
 lattice vector, 284  
 non-cubic lattices, 290–291  
 packing sequence, 286, 287  
 primitive unit cell, 288  
 reciprocal lattice, 289

410 | **Index**

- crystal structures (*cont.*)  
 simple hexagonal, 286  
 table of basic crystal systems, 285
- cutoff  
 see potential cutoff, 31
- damped dynamics, 249–251
- de Broglie wavelength, 358
- defects  
 dislocations, 292–302  
 vacancy concentration, 292
- density-functional theory, 47
- determinant  
 of a matrix, 313
- diffusion, 306–308  
 activated process, 12  
 bulk  
 random walk, 18  
 diffusion coefficient, 13  
 Fick's first law, 307  
 Fick's second law, 307  
 mean square displacement, 308  
 random walk, 11, 12
- diffusion coefficient, 366  
 random walk, 15, 16  
 relation to velocity autocorrelation function, 366
- dimensional analysis, 6
- dipole-dipole energy, 333
- Dirac delta function, 320  
 graphical representation, 320
- direct lattice, 288–289
- dislocation dynamics simulations,  
 256–265  
 limitations, 263–264  
 three-dimensional, 260–263  
 annihilation, 262  
 boundary conditions, 262  
 challenges, 260  
 climb, 261  
 junctions, 262  
 representation of dislocations, 260
- two-dimensional, 256–260  
 boundary conditions, 258  
 equation of motion, 258  
 force, 257
- dislocations, 292–302  
 annihilation, 299  
 climb, 295  
 cross slip, 295  
 damped equation of motion, 301  
 drag, 301  
 edge, 293
- edge dislocation, 293  
 Frank-Read source, 300  
 intersection, 300  
 intersections, 300  
 junctions, 300  
 line tension, 299  
 mixed dislocation, 293  
 movement and plastic strain, 297  
 movement of edge, 294  
 movement of screw, 295  
 overdamped dynamics, 301  
 partials in *fcc* crystals, 302  
 Peach-Koehler force, 297  
 Peierls-Nabarro stress, 295  
 plastic deformation, 292–293  
 screw, 293  
 screw dislocation, 293  
 self energy, 299  
 stress arising from, 298  
 stress from linear, 298
- dispersion energy  
 see van der Waals energy, 65
- dot product, 311
- Drude model, 65–67
- dynamics  
 damped, 249–251  
 Langevin, 251–252  
 overdamped, 250
- elastic constants, 378
- elasticity  
 displacement function, 376  
 elastic constants, 378  
 engineering stress and strain,  
 378–379  
 isotropic solids, 379–381  
 strain  
 plastic, 381  
 total, 381  
 strain energy, 378, 379  
 strain energy density, 378  
 strain tensor, 378  
 stress tensor, 376
- electron density, 46  
 Thomas-Fermi model, 48
- electron spin, 342
- electrostatic energy, 331  
 continuous charge distribution, 331  
 units, 282
- electrostatic force, 330  
 units, 282
- electrostatic potential, 330  
 continuous charge distribution, 331
- multipole expansion, 333
- embedded-atom model, 81–84
- end-to-end probability distribution for a  
 random walk, 17
- energy  
 conversion between units, 282  
 exchange-correlation, 54  
 Kohn-Sham  
 exchange correlation, 53  
 per atom, 30  
 per cell, 29  
 Thomas-Fermi model  
 closed-shell atoms, 50  
 comparison with Hartree-Fock  
 energies, 50  
 Coulomb, 48  
 total, 48  
 Thomas-Fermi-Dirac model  
 exchange, 49  
 total, 49  
 units, 281
- engineering stress/strain, 378
- ensemble, 355–362  
 average quantities, 355, 356  
 canonical (*NVT*), 357–359  
 average kinetic energy, 359  
 average quantities, 357  
 configurational integral, 358  
 partition function, 357  
 relation to Helmholtz free energy,  
 358  
 weighting function, 357
- classical systems with continuous  
 potentials, 356
- comparison of canonical and  
 microcanonical, 360–361
- grand canonical ( $\mu VT$ )  
 partition function, 362  
 relation to pressure, 362
- isobaric-isothermal (*NPT*)  
 partition function, 361  
 relation to Gibbs free energy, 362
- J. W. Gibbs, 355
- microcanonical (*NVE*), 360  
 relation to entropy, 360  
 partition function, 356  
 probability density, 355  
 weighting function, 356
- ensembles  
 equivalence of, 364
- entropy  
 relation to microcanonical (*NVE*)  
 ensemble, 360

- equation of motion  
 central-force potential, 97
- equipartition theorem, 359
- ergodicity, 356
- error function, 319
- Euler angles, 314
- Ewald method, 37–39
- exchange energy, 343–346  
 Thomas-Fermi-Dirac model, 49
- exchange-correlation energy, 54–55  
 comparison of LDA and GGA results for Cu, 59  
 comparison of LDA and GGA results for Si, 59  
 GGA, 55  
 hybrid methods, 55  
 LDA, 54
- exp-6 potential, 74
- extensive quantities, 351
- fast multipole method, 39–41
- fluctuations in  $E$   
 size dependence, 363
- force  
 central-force potential, 97  
 Coulomb (electrostatic), 330  
 gradient of potential, 96, 325  
 units, 281
- function  
 complementary error function, 319  
 Dirac delta function, 320  
 Dirac delta function representation, 320  
 error function, 319  
 Gaussian distribution, 318  
 Kronecker delta, 319
- functionals, 321–322  
 derivatives, 321–322
- fundamental constants  
 definition of symbols, 281  
 values, 281
- Game of Life, 216  
 glider, 216  
 rules, 216
- Gaussian distribution, 318
- Gay-Berne model, 173
- generalized gradient approximations (GGA), 55
- Gibbs free energy  
 relation to isobaric-isothermal ( $NPT$ ) ensemble, 362
- Gibbs, J. W., 355
- gradient, 312
- grain boundary, 303  
 energy, 304  
 tilt boundary, 303  
 twist boundary, 303
- grain growth, 305–306  
 boundary model, 253–254  
 curvature driven, 306  
 effects of anisotropy in mobility, 208  
 studies with Potts model, 208  
 Potts model, 196–198  
 vertex model, 254–256  
 von Neumann relation, 306
- grand canonical ( $\mu VT$ ) ensemble  
 Monte Carlo simulations, 153  
 partition function, 362  
 relation to pressure, 362
- Hamiltonian  
 classical mechanics, 326  
 conservation of in classical mechanics, 326  
 quantum mechanics, 46
- harmonic oscillator  
 classical mechanics, 327–328
- harmonic transition state theory, 373–374  
 rate constant, 373
- Hartree method, 47
- Hartree-Fock method, 47
- heat capacity, 362  
 relation to fluctuations in  $E$ , 362–363
- Helmholtz free energy  
 relation to canonical ( $NVT$ ) ensemble, 358
- Hohenberg-Kohn theorem, 51
- hydrogen atom  
 quantum mechanics, 341
- intensive quantities, 351
- interaction potential  
 cutoff, 31  
 cutoff for molecular dynamics, 107
- interaction sum  
 pair potential, 28–29
- interatomic potential, 63–91  
 bond-order potentials, 86  
 Born-Mayer potential, 74  
 central-force, 75  
 comparison of potentials, 73
- covalent solids, 84–88  
 angular-dependent potentials, 85  
 bond-order potentials, 86–88  
 determining the parameters, 91  
 exp-6 potential, 74  
 ionic interaction, 76  
 shell model, 77–78
- Lennard-Jones potential  
 see Lennard-Jones potential, 67
- metals, 78–84  
 embedded-atom model, 81–84  
 pair potential, 78  
 volume-dependent potential, 79
- Mie ( $m, n$ ) potential, 72
- Morse potential, 74
- origins, 64
- pair potential, 67
- reactive force potential, 88  
 COMB potential, 88
- short-range interaction, 65
- Stillinger-Weber potential for silicon, 85
- Tersoff potential, 87
- units, 67
- van der Waals energy, 65–67
- intermolecular potential, 163–168  
 atom-atom, 164  
 bond angle bending potential, 166  
 bond stretching potential, 166  
 dihedral angle torsion potential, 167  
 electrostatic interactions, 165  
 water-water interaction, 178–180
- Ising model, 139–145  
 energy, 139  
 energy change with spin flip, 142  
 magnetization, 140  
 Monte Carlo calculations of, 141–144  
 reduced units, 140  
 spin-spin correlation function, 140
- isobaric-isothermal ( $NPT$ ) ensemble  
 partition function, 361  
 relation to Gibbs free energy, 362
- isotropic elasticity, 380
- Johnson-Mehl-Avrami-Kolmogorov (JMAK) growth equation, 221
- kinetic energy, 324  
 average, 359  
 classical mechanics, 325  
 Thomas-Fermi model, 48  
 uniform electron gas, 340

412 **Index**

- kinetic Monte Carlo method  
 activity, 185  
 chemical vapor deposition example, 191–194  
 choosing an event, 185–186  
 events, 184  
 probability of an event, 185  
 relation of probability and rate, 187  
 steps, 186  
 surface diffusion example, 189–191  
 time, 187–189  
 time per event, 189
- kinetics  
 activation energy, 370  
 harmonic transition state theory, 373–374  
 reaction coordinate, 369  
 saddle point, 369  
 transition state theory, 372–373
- Kohn-Sham method, 51–54
- Kratky-Porod model, 161
- Kronecker delta, 319
- Lamé constant, 379
- Langevin  
 dynamics, 251–252  
 equation, 252
- Laplacian, 312  
 spherical polar coordinates, 313
- lattice-gas model, 218–219  
 rules, 218
- lattice sums  
 direct lattice, 30  
 Ewald method, 37–39  
 fast multipole method, 39–41  
 implementation, 34  
 long-ranged potentials, 35–42  
 minimum image convention, 35  
 neighbor lists, 34  
 neighbor shells, 30  
 pair potential, 29  
 spherically truncated Coulomb potential, 42
- lattice vector, 284
- Lennard-Jones potential, 67–72  
 energetics of simple solids, 70–72, 92–95  
 equivalence of simulations in reduced units, 112  
 molecular dynamics simulation of, 107–116  
 rare gas atoms, 69  
 reduced units, 69  
 table, 107  
 scaled to remove discontinuities, 108
- Levi-Civita tensor, 319
- macrostate, 352
- matrices  
 determinant, 313  
 transpose, 313
- Maxwell-Boltzmann distribution, 106, 359
- Metropolis algorithm, 134–139  
 averages, 136  
 connection to canonical (*NVT*) ensemble, 156–157  
 energy updating, 139  
 implementation, 135  
 sampling, 137–139
- microcanonical (*NVE*) ensemble, 360  
 comparison with canonical ensemble, 360–361  
 partition function, 360  
 relation to entropy, 360
- microstate, 353
- Mie ( $m, n$ ) potential, 72–73  
 energetics of simple solids, 92–95
- minimum image convention, 35
- model  
 definition, 1  
 development, 5–6  
 validation, 6
- molecular dynamics  
 accelerated dynamics, 120–122  
 binned averages, 111–112  
 conservation of energy, 101  
 conservation of total linear momentum, 101  
 constant stress, 119–120  
 guideline for energy conservation, 102  
 initial conditions, 104–106  
 positions, 125–127  
 velocities, 127  
 limitations, 122–123  
 molecular systems, 168–171  
 constrained dynamics, 169–171  
 SHAKE algorithm, 171  
 Nosé-Hoover thermostat, 117–119  
 pair distribution function, 113–115  
 calculation of, 127–128  
 Parrinello-Rahman method, 119–120  
 potential cutoffs, 107  
 simulation with a Lennard-Jones potential, 107–116  
 steps in a calculation, 106–107  
 time step, 100  
 velocity autocorrelation function, 115–116  
 calculation of, 129–130  
 velocity rescaling, 116–117  
 velocity Verlet algorithm, 100  
 Verlet algorithm, 99
- Monte Carlo  
 assessment, 155  
 atomic systems, 145–149  
 analysis, 149  
 canonical (*NVT*) ensemble, 146–149  
 grand canonical ( $\mu VT$ ) ensemble, 152–154  
 Ising model, 141–145  
 isobaric-isothermal (*NPT*) ensemble, 150–152  
 Metropolis algorithm, 134–139  
 averages, 136  
 energy updating, 139  
 implementation, 135  
 sampling, 137–139  
 molecular systems, 171–172  
 macromolecules, 172  
 small molecules, 171–172  
 numerical integration, 131  
 time, 154
- Moore environment  
 cellular automata, 215
- Morse potential, 74
- multipole expansion, 331–333  
 moments, 332  
 multipole moments, 332
- N-fold way, 202–204  
 time, 204
- neighbor lists, 34
- Newton's equation, 96, 324  
 integration, 97–101  
 time step, 100  
 velocity Verlet algorithm, 100  
 Verlet algorithm, 99  
 momentum, 324
- Newton's second law, 96, 324
- non-cubic lattices, 290–291
- normal distribution  
 random distribution, 386
- Nosé-Hoover thermostat, 117–119

- numerical derivatives, 388
  - central difference formula, 388
  - first derivative, 388
  - fourth derivative, 389
  - Laplacian in two dimensions, 390
  - one-dimensional, 388
  - second derivative, compact, 388
  - second derivative, non-compact, 388
  - two-dimensional, 390
- order parameters, 229
  - conserved, 230
  - non-conserved, 230
- pair distribution function, 113–115, 367–368
  - calculation of, 127–128
- pair potential, 27, 67
  - cutoff, 31
- Parrinello-Rahman method, 119–120
- partition function
  - canonical ( $NVT$ ) ensemble, 357
  - canonical ( $NVT$ ) ensemble for continuous systems, 358
  - grand canonical ( $\mu VT$ ) ensemble, 362
  - microcanonical ( $NVE$ ) ensemble, 360
- Pauli exclusion principle, 342
- Peach-Koehler force, 297
- perfect crystal, 29
- periodic boundary conditions, 32–34
  - incommensurate structures, 34
- persistence length, 161
  - relation to stiffness parameter, 161
- phase field
  - Allen-Cahn equation, 230–232
    - derivation, 245–247
  - Cahn-Hilliard equation, 232–233
    - derivation, 247–248
  - diffuse interface approximation, 233
    - plot, 233
- free energy
  - with conserved and non-conserved order parameters, 233
  - with conserved order parameters, 247
  - with non-conserved order parameters, 231, 232, 246
- grain growth, 241–242
- interfacial free energy, 238
- local free energy function
  - multi-phase systems, 240
- one order parameter, 234
- one order parameter with temperature, 239
- solidification of binary alloy, 239
- numerical derivatives in one dimension, 235
- one-dimensional example, 233–237
- solidification, 242–243
- phase space, 353–354
  - simple examples, 353
  - time average, 354
- plastic deformation, 292–293, 381
- plastic strain, 381
  - relation to dislocation motion, 297
- Poisson's ratio, 380
- polymers
  - coarse-grained methods, 172–175
    - bead-spring model, 174
    - Gay-Berne model, 173
    - parameter determination, 174–175
    - pearl-necklace model, 174
    - united atom model, 173
  - introduction to properties, 160–161
  - Kratky-Porod model, 161
  - lattice models, 175–176
    - interactions, 176
    - moves, 175
  - mean monomer position, 160
  - persistence length, 161
  - radius of gyration, 160
  - random-chain model, 161–162
  - self-avoiding walk model, 162–163
    - scaling exponent, 163
  - stiffness parameter
    - relation to Young's modulus, 161
  - Young's modulus
    - relation to stiffness parameter, 161
- potential cutoff, 31
  - error associated with, 31–32
- potential energy, 324
  - average in terms of pair distribution function, 367
  - classical mechanics, 325
  - Coulomb (electrostatic), 331
- potential energy surface, 369
  - activation energy, 370
  - basin, 369
  - reaction coordinate, 369
  - saddle point, 369
- Potts model, 196–198
  - anisotropy in two-dimensional lattices, 199
  - average grain size, 201
- effect of lattice topology, 199
- general Hamiltonian, 198
- Hamiltonian for isotropic growth, 198
- limitations with normal Monte Carlo, 201–202
- Monte Carlo, 198–202
- N-fold way, 202–204
  - time, 204
- pressure
  - average in terms of pair distribution function, 368
  - central force potential, 104, 359
  - definition, 104, 359
  - pair-functional potential, 104
  - relation to grand canonical ( $\mu VT$ ) ensemble, 362
  - units, 281
- probability, 317
  - average, 318
  - continuous, 318
  - Gaussian distribution, 318
  - intersection, 318
  - normalization, 317, 318
  - union, 318
- pseudopotential, 57–58
- quantum mechanics
  - antisymmetric wave function, 343
  - Bloch's theorem, 349
  - electron spin, 342
  - exchange energy, 343–346
  - Fermi hole, 345
  - harmonic oscillator, 340–341
  - history, 334–335
  - hydrogen atom, 341–342
  - indistinguishability, 343
  - kinetic energy of uniform electron gas, 340
  - multielectron atoms, 342
  - multielectron systems, 348–349
  - observables, 336–337
  - particle in a box, 337–340
  - Pauli exclusion principle, 342
  - Schrödinger equation, 336
  - variational approaches, 346–347
  - zero-point motion, 341
- radius of gyration, 160
- random number, 383
  - Box-Muller method, 386
  - changing range, 385
  - generator, 383

414 | **Index**

- random number (*cont.*)  
 normal distribution, 386  
 Park-Miller generator, 384  
 seeds, 385
- random walk  
 application to materials, 25  
 bulk diffusion, 18  
 definition, 12  
 diffusion coefficient, 15  
 end-to-end distance probability, 17  
 end-to-end probability distribution, 16–18  
 mean end-to-end distance, 18  
 mean square displacement, 14, 15, 18  
 relation to diffusion coefficient, 13–16  
 simulation, 19–25  
 analysis, 22–25  
 end-to-end probability distribution, 24–25
- rare event, 369
- rate constant, 371  
 harmonic transition-state theory, 373  
 transition-state theory, 372
- reaction coordinate, 369
- reciprocal lattice, 289
- recrystallization, 206  
 cellular automata, 220–222  
 studies with Potts model, 206–208
- rotation matrix, 314
- saddle point, 369
- scale  
 length, 3–4  
 time, 3–4
- Schrödinger equation, 46, 336
- self-avoiding walk model, 162–163  
 scaling exponent, 163
- SHAKE algorithm, 171
- shear modulus, 379
- shell model, 77–78
- simulation  
 definition, 1  
 spherically truncated Coulomb potential, 42  
 spinodal decomposition  
 cellular automata, 222–225  
 rules, 223–224  
 standard deviation, 362  
 stiffness parameter, 161  
 relation to persistence length, 161  
 stochastic process, 11  
 strain  
 energy, 378  
 plastic, 381  
 tensor, 378  
 total, 381  
 stress tensor, 313, 376
- Taylor series, 314  
 one dimension, 314  
 three dimensions, 315
- temperature  
 definition in terms of average kinetic energy, 103
- thermodynamics  
 Maxwell's relations, 351  
 table of basic symbols, 352
- Thomas-Fermi model, 47–51
- Thomas-Fermi-Dirac model, 49
- time correlation function, 365
- total energy  
 conservation of in classical mechanics, 326  
 Kohn-Sham method, 54  
 width of distribution in canonical ensemble, 363
- total strain, 297, 381
- transition-state theory, 372–373  
 harmonic, 373–374  
 rate constant, 372
- translational order parameter, 368
- transpose of a matrix, 313
- Ulam, Stanislaw  
 why Monte Carlo is called Monte Carlo, 131
- united-atom model for polymers, 173
- Universal Binding Curve (UBC), 80
- V&V  
 see validation and verification, 7
- vacancy concentration, 292
- validation, 6
- validation and verification, 7
- van der Waals energy, 65–67  
 Drude model, 65–67
- vectors, 310  
 cross product, 312  
 dot product, 311  
 gradient, 312  
 Laplacian, 312  
 unit vector, 310
- velocity autocorrelation function, 115–116, 365–366  
 calculation of, 129–130  
 relation to diffusion coefficient, 366
- velocity Verlet algorithm, 100
- verification, 6
- Verlet algorithm, 99
- von Neuman environment  
 cellular automata, 215
- von Neumann, John  
 cellular automata, 211  
 grain growth, 306
- wave function, 46, 335  
 antisymmetric, 343  
 basis set, 55, 347
- Young's modulus, 380
- Zener pinning, 205  
 studies with Potts model, 205
- zero-point motion, 341