

## Index

Figure, table, and reaction locations are indicated in bold typeface

- acetone  
 as amphiphilic binary mixture, 252  
 molecular structure, **244**
- acidosis, 75
- Adam–Gibbs relation, 157–158, **158**, 293–294, **295**
- adenylate kinase (ADK) (enzyme), 101, **101**
- Alzheimer’s disease, 109–110, 123
- amphiphilic effects, 207–209, 243–258, **244**, **247**, **249**, **251**, **255**, **257**, 342. *See also* surficants, hydrophobic effects, hydrophilic effects
- Angel, C. A., 308
- anomalies. *See also* Widom line  
 amphiphilic binary mixtures, 245–253, **247**, **249**, **251**  
 bulk water, 13–21, **14**, **16**, **17**, **19**, **20**, **21**, **22**  
 explained by computer simulation for hydration layer, 144  
 glass transition, 88–90, **89**  
 ice formation, 306, 308  
 large number of in water, 323–326  
 structural. *See* local order  
 of supercooled water, 310  
 of supercooling, 324  
 thermodynamic. *See* specific heat. *See* temperature of maximum density (TMD), isothermal compressibility (Kt), coefficient of thermal expansion ( $f_{1ar}/f_0$ )  
 and two-stage water model, 22–23
- aqueous salt solutions. *See* electrolytes
- Arrhenius equation, 17–18
- association  
 hydrophobic, 227  
 residence time of water molecules in proteins, 109
- Bagchi, B., 86, 130
- Barron, L. D., 196
- Bell, L., 342
- Ben-Amotz, D., 227
- bending mode (hydrogen bond), 39, 69
- Bernal, J. D., 324
- Berne, B., 56, 57
- Bhattacharyya, S. M., 88, 130, 265
- bifurcated hydrogen bond, 67–68
- billiard ball model (of liquids), 324–325
- biological water. *See also* bulk water  
 DNA, 83  
 functions in, 97–113, **99**, **100**, **101**, **103**, **104**, **105**, **106**, **108**, **113**  
 inside a carbon nanotube, 277–283, **278**, **279**, **281**, **282**  
 molecular characteristics of, 83–84  
 molecular differences with bulk water, 81–83, **82**  
 natural selection in biomolecules, 187–192, **189**  
 protein hydration layer, **82**, 83, 88–90, **89**  
 and protein synthesis, 192–197, **195**  
 theoretical studies of, 84–88, 91–95, **91**
- blood  
 lipid bilayers in, 178, **178**  
 pH, 75–76
- Boltzmann law, 288, 291, 298, 303
- Bondi, A., 227
- bound water molecule (biological water). *See also* free water molecules (biological water)  
 definition, 84  
 in dynamic exchange model, 86–88  
 in lipid surface, 180  
 in micelles, 266–268, **267**
- bovine serum albumin (BSA), 128–129
- Brown, Robert, 27
- Brownian motion, 27–28, **29**, **37**, 51, **52**
- bulk water. *See also* heavy water, biological water  
 anomalies, 13–21, **14**, **16**, **19**, **20**, **21**, **22**  
 characteristics of, 3, 7–9, **8**  
 computer simulations of, 6–7  
 freezing of, 305–315, **310**, **312**, **313**  
 inherent structures in, 61–70, **63**, **64**, **65**, **66**  
 modeling, 9–10  
 molecular differences with biological water, 81–83, **82**  
 molecular structure of, 4–7, **4**, **5**, 324  
 pH, 71–75, **73**

- carbamide. *See* urea
- cell theory, 298–299, **299**
- chaotropes. *See* ionization
- chromatography, 202
- clathrate hydration molecular structure, 124, 132–133
- clusters. *See also* percolating network
- amphiphilic effects and, 253–254, **255**
  - DMSO, 246–249, **249**
  - hydrogen bond, 67, 330
- coefficient of thermal expansion (ar), 16–17, **17**
- collapse, **229**
- computer simulation. *See also* spectroscopy, nuclear
- magnetic resonance experiments (NMR), inherent structures (IS), experiments
  - and protein hydration layer thickness, 121, 124
  - dielectric relaxation, 143
  - DMSO, 245–249, **247, 249**
  - DNA hydration, 158, **171**
  - to explain water anomalies, 144
  - hydration layer, 140–142, **141, 142, 146, 146**
  - of ice formation, 308, 310–314, **312, 313**
  - lipid bilayer, 180–181, **181**
  - of molecular motion, 31, 136–138
  - molecular motion in hydration layer, **139**
  - of polarizable water molecules, 41
  - of protein glass transition phase, 144–145, **145**
  - solvation dynamics (SD), 142–143
  - in surficants, 266, 269
  - of water confined between silica surfaces, 204–205, **204, 205, 206**
  - of water density, 15
  - water glass transition, **89, 144–145, 145**
- concentration
- dependence in DMSO, 245–249, **247**
  - dependence of conductivity in electrolytes, 211
  - dependence of ions solutions and water dynamics, 203–204
- conductivity. *See* polarization
- continuum model (of collective orientational relaxation), 54
- core–shell model, 270–273, **270, 271, 272**
- covalent bonds. *See also* hydrogen bonds
- rarity of breaking in bulk water, 97–98
  - transfer of electron density in, 8, **8**
  - of water creating V shape, 4, **4**
- Crick, F. H. C., 152
- crystallographic experiments, 167–169
- da Vinci, Leonardo, 97
- D’Angelo, M., 268
- Darwin, Charles, 187
- Dawkins, Richard, 187
- Debye–Hückel–Onsager law, 45, **46, 210–211**
- Debye–Waller coefficient, 203
- density fluctuations. *See also* temperature of maximum density (TMD)
- of protein hydration layer, 137
  - in supercritical water, 318–319, **319**
  - of water on silica surface, 204–205, **205, 206**
- density maximum. *See* temperature of maximum density (TMD)
- dielectric constant
- being useful in chemical processes, 8
  - and light scattering, 55–57
  - in lipid bilayer, 184
  - polarization increases, 9
- dielectric relaxation (DR). *See also* relaxation time, electrolytes
- computer simulation, 143
  - DNA, 83
  - hydrogen bond breaking kinetics, 40–41
  - and protein hydration layer, 83, 120, 124–125, **125**
  - in reverse micelles, 268–269
- diffusion. *See also* viscosity, relaxation time
- Adam–Gibbs relation, 157–158, **158, 293–294, 295**
  - along DNA 174, **175**
  - and inherent structure not containing information on, 70
  - of ions in bulk water, 45–46, **46**
  - of ions in methanol, 250
  - in lipid surface, 182–184
  - Rosenfeld relation, 291–293, **295**
  - single file, 277, 280, **281**
- Dill, K. A., 342
- dioxane
- as amphiphilic binary mixture, 252–253
  - molecular structure, **244**
- DMSO
- as amphiphilic binary mixture, 245–249, **247, 249**
  - biological applications of, 256–258, **257**
  - clustering in, 253–254, **255**
  - molecular structure, **244**
- DNA. *See also* protein synthesis
- and drug recognition, 107–109, **108**
  - effects of nanoconfinement in, 161
  - entropy and diffusion in, 156–159, **158**
  - groove structure in, 153–155, **154**
  - hydration of constituents in, 152–153, 163–164, **164**
  - intercalation of drugs into, 101–105, **101, 103, 104, 105**
  - and protein hydration layer dynamics, 167–175, **171, 175**
  - replication sequencing, 188, 196
  - solvation dynamics in, 155–156, **156**
  - spine of hydration in, 159–160
  - stabilizing effect of water in, 151–152
- drinking water. *See* bulk water
- dynamic equilibrium
- of bound and free biological water molecules, 86, 136
  - in dynamic exchange model, 91–95, **91**
- dynamic exchange model, 85, **85, 86–88, 91–95, 91**
- Einstein, Albert, 28
- Einstein relation law, 45
- electrolytes. *See also* polarization, ionization, dielectric relaxation (DR)
- conductivity in, 209–211
  - electron transfer in, **46, 47–49, 48**
  - ionic conductivity in, 45–46, **46**
  - in lipid surface, 184

- polarization, 30  
viscosity in, 211–212
- electrons. *See* molecular structure
- ellipsoid in a sea of spheres model (EISS), 51–52
- Elsaesser, T., 40
- energy  
entropy balance, 290  
microscopic states of, 15  
similarities between water density at different temperatures, 18  
water molecules can form many structures, 9
- enthalpy (*H*). *See also* thermodynamics, entropy  
in bulk water, 23–24  
of DNA protein hydration, 168  
in hydrophobic effects, 215, 217, **221**  
stability of bound water molecule, 84  
of water molecules near ions, 203
- entropy. *See also* thermodynamics, enthalpy (*H*)  
calculation of, 295–300, **299**  
definition of, 287–290  
and diffusion, 291–294, **295**  
of DNA hydration interaction, 156–157  
of DNA protein hydration, 168  
during incalation, 104–105, **105**  
in hydrophobic effects, 215, 217, **221**  
in ice formation, 305  
in inherent structures, 61  
in lipid surface, 180  
in micelles, 267, 268, **268**  
and molecular configurations, 15, 23–24  
and vibrational molecular motion, 289–290, 296, 302  
of water molecules near ions, 203
- enzyme catalysis  
in aqueous urea solution, 208–209  
covalent bond in, 97–98  
role of water in, 99–101, **99**, **100**, **101**
- enzyme kinetics. *See* enzyme catalysis
- ethanol  
as amphiphilic binary mixtures, 250, **251**  
clustering in, 253–254, **255**  
molecular structure, **244**
- Evans, D. J., 217, 219
- experiments. *See also* spectroscopy, nuclear magnetic resonance experiments (NMR), computer simulation  
crystallographic, 167–169  
light scattering, 55–57  
NALMA, 128  
NMR, 57–58, 126–127, 170  
QENS, 127–128
- extended network. *See* percolating network
- Fayer, M. D., 33, 274
- Fersht, A. R., 188, 192–194
- fibril growth, 111–112
- Fleming, G. R., 129, 325
- Flory, Paul, 227, 228, 330
- Flory–Huggins theory, 228–230, **229**
- fluctuation. *See* nucleation
- fluorescence up-conversion technique, 170
- food, 76
- force constant matrix, 69
- force law (hydrophobic), 234
- Frank, H. S., 217, 219
- free energy  
barriers, 146, **146**, 180, 182–184, 185  
change in DNA hydration, 157  
surfactants and, 266–268, **267**, **268**
- free water molecules (biological water). *See also* bound water molecule (biological water)  
definition, 84  
in dynamic exchange model, 86–88, 91–95  
in lipid surface, 180  
in micelles, 266–268, **268**
- freezing 307  
biological water, 310, 314–315  
bulk water, 305–309, 310, **310**, **312**, **313**
- Fuoss, R. M., 212
- Geissler, L., 74
- Gibbs, J., 325, 327
- glass transition phase (water), 144–145, **145**
- grooves (DNA)  
entropy in, 299–300  
molecular motion in, 154–155  
structure, 153–155, **154**, 159
- Grote, R. E., 48
- Grote–Hynes theory, 48–49
- Grüneisen, E., 211
- guanidinium hydrochloride, 209
- Guoy–Chapman layer 262, **263**
- Halle, B., 127
- Hamming matrix, 332–333
- Hang-Jun, L., 279
- Hansen, E., 51
- heavy water. *See also* bulk water. *See also* biological water  
effect of temperature on, 33–35, **34**, **35**  
freezing of, 309  
supercooling, 33–35  
and vibrational spectroscopy, 128–129
- Henchman, R. H., 298
- Herschbach, D. R., 227
- heterogeneous surface topology  
in DNA protein 170, **171**  
of protein hydration layer, 135  
in proteins, 122  
in RNA, 161–162
- Hopfield, J. J., 188
- Hopfield–Ninio scheme, 190–192
- hydration layer. *See also* Stern layer, protein hydration layer  
computer simulations of, 136–138, **139**  
surface topology, 124
- hydrodynamic friction, 121
- hydrogen bond breaking  
breaking in hydration layer, **139**  
in hydration layer, 137–138  
kinetics, 36–49, **38**, **39**, **40**, **44**, **46**, **48**
- hydrogen bond defects. *See* orientational order  
molecular structure

hydrogen bond lifetime  
 and anharmonic coupling, 39–40  
 geometric definition, 36, **38**  
 in micelles, 266  
 quantification, 50, 58–59, 324  
 and time correlation functions, 36–39, **38, 39**

hydrogen bond network  
 being percolating, 6–7  
 fluctuations in, 324, 330–334  
 impossibility near large hydrophobic object, 234–235, **235**  
 low energy excitations in liquid water, 69  
 on mica surface, 207  
 micelle disruption, 263  
 not sustained in biological water in three dimensions, 84  
 protein, 124  
 in supercritical water, 318, 321

hydrogen bond types  
 in biology, 67–68, 81–83  
 in DNA, 163–164, **164**  
 in micelles, 266–268, **267, 268**  
 RNA interactions, 105–107, **106**  
 of silica surfaces, **204, 205**  
 strength difference in protein backbone and side chain atoms, 121–123, **122**  
 in urea water, 209

hydrogen bonds. *See also* inherent structures (IS), covalent bonds  
 bifurcated, 5, **6**  
 and difficulty in ice creation, 310  
 diversity of in water, 8  
 fluctuating molecular networks in water, 9  
 lifetime of, 7, 140–142, **141, 142**  
 long-lasting, 311–314, **312, 313**  
 orientational order in, 50  
 potential energy, 324, 331–333  
 tetrahedral structure, 5, 50, 71–72

hydrolases (enzyme), 99–101, **99, 100**

hydrolysis, 187–196, **189, 195**

hydropathy scale, 220–221, **222**

hydrophilic effects. *See also* hydrophobic effects, amphiphilic effects  
 on electrolytes, 209–212  
 in ion solvation, **203**  
 on mica surface, **207**  
 on parallel silica surfaces, 204–205, **205**  
 on protein surface, 122, 123, 124, 132–133, **133**

hydrophobic effects. *See also* hydrophilic effects, amphiphilic effects  
 collapse, 227–230, **229**  
 at different length scales, 234–235, **235**  
 environment in lipid bilayer, 184  
 force law, 234  
 history of, 215–217  
 and hydrophobic hydration, 217–220, **220, 221, 222**  
 in iceberg model, 217, 219  
 ice-like water structures on silica, 205, **206**  
 of ions due to enthalpy and solvation energy, 203  
 molecular interactions in, 230–233, 236–241

in nanotubes, 280  
 and pair hydrophobicity, 221–227, **223, 224, 225, 226**  
 on protein surface, 122, 123, 132–133, **133**

Hynes, J. T., 31–32, 40, 48

ice. *See also* supercooling, nucleation  
 density of, 14  
 formation, 305–306, 308, 309, 310, **312, 313**  
 formation in carbon nanotubes, 310, 314–315  
 from micro-droplets, 308  
 phase diagram of water into, 306–307, **307**  
 polymorphs in, 9  
 tetrahedral molecular of, 6

iceberg model  
 hydrophobic effects, 217, 219  
 of protein hydration layer, 118, **119, 124**

inherent structures (IS). *See also* hydrogen bonds, computer simulation  
 bond transition in, 67–68  
 temperature and, 62–66, **63, 64, 65, 66**

intercalation, 101–105, **101, 103, 104, 105**

interfacial water. *See* protein hydration layer

inverted hydration molecular structure, 124, 132–133

ionization. *See also* electrolytes  
 auto, 71–72, 74  
 conductivity, 45–46, **46**  
 and water, 47–49, **48, 202–204, 203**

Ising model, 273–274, **275, 294**

isobaric specific heat (Cp). *See* specific heat (Cp)

isoenergetic structural arrangements. *See* polymorphs

isothermal compressibility (Kt), 15–16, **16, 23–24**

Jimenez, R., 43

Jones–Dole coefficient, 203–204

Jones–Dole equation, 212

jump motion. *See* rotational molecular motion

Kauzmann, Walter, 215

kinetic proofreading (KPR), 187–196, **189, 195**

Kohlrausch’s law, 210

kosmotropes. *See* ionization

Kubo, R. J., 203

Kubo-Oxtoby theory of frequency modulation, 40

Laage, Damien, 31–32

Laage–Hynes mechanism, 339

Landau theory, 325–326

Lang, M. J., 45

Laria, D., 321

Levitt, M., 105

light scattering experiments, 55–57

linear molecular motion. *See* translational molecular motion

lipid bilayer. *See also* protein hydration layer  
 hydration of constituents in, 179  
 molecular structure of, 177–179, **178**  
 molecular transport in, 182–184  
 potential energy in, 180, 184  
 solvation dynamics (SD), 181, **182**  
 water dynamics in, 180–181, **181**

- lipid bilayer diffusion series (LPD), 182–184  
 local density. *See* density fluctuations  
 local order, 19–21, **19**, **20**, **21**  
 low temperature. *See* supercooling  
 lubricant  
   flickering phenomena, 196–197  
   water as, 179, 185  
 Lynden-Bell, R. M., 46  
 lysozyme (enzyme), 100–101, **101**, 128, 129, **130**, 137, 256–258, **257**
- magnetic relaxation dispersion (NMRD), 127  
 Maniwa, Y., 283  
 Marcus theory (of electron transfer), 47–49, **48**  
 Marcus, R. A., 130, 342  
 Matsumoto, M., 310  
 mean square displacement (lipid bilayer), 180, **181**  
 Mendeleev, D., 250  
 Mercedes Benz model, 342  
 metastable state, 310–311, **310**, 341  
 methanol  
   as amphiphilic binary mixture, 250  
   molecular structure, **244**  
 mica, **207**  
 micelles, 261–263, **263**, 342 *See also* reverse micelles  
 microemulsion. *See* reverse micelles  
 model  
   billiard ball, 324–325  
   continuum, 54  
   core–shell, 270–273, **270**, **271**, **272**  
   dynamic exchange, 85, 86–88, 91–95, **91**  
   EISS, 51–52  
   iceberg, **119**, 217, 219  
   Ising, 273–274, **275**, 294  
   reaction–diffusion model, 86  
   two-stage water, 22–23, 310, 325, 335–341, **335**, **338**  
   Weeks–Chandler–Andersen, 236, **338**
- molecular motion  
   Brownian, 27–28, **29**, **37**, 51, **52**  
   of bulk water, 27–35, **29**, **31**, **33**, **34**, **35**, **36**, 49–50  
   rotational, 27, 28–32, **31**, **32**, 51–53, 54, 85, 86–88, 93–95, 154–155, 180–181, **181**, 265, 280–282, **282**, 303  
   surfactants, 265  
   translational, 27, 28, 35, **36**, 85, **85**, 88, 137, 154, 180–181, **181**, 265, 279–280, **281**  
   vibrational, 39–40, **40**, 128–129, 289–290, 296, 302, 320–321
- molecular structure. *See also* polymorphs  
 amphiphilic binary mixtures, 243–245, **244**  
 of DNA, 151–152, 153–155, **154**, 159  
 and entropy of liquid water, 296–297  
 in hydrophobic effects, 230–233  
 lipid bilayer, 177–179, **178**, 182–184  
 and local order, 19–21, **19**, **20**, **21**  
 and potential energy, 62–66, **63**, **65**, **66**  
 of protein hydration layer, 121–124, **122**, 132–133, **133**  
 of RNA, 152  
 surfactants, 261–263, **263**, **264**  
 of water around ions, **203**
- Moras, D., 106  
 myoglobin, 124–125, **125**, 136
- N-acetyl-leucine-methylamide experiments (NALMA), 128  
 Naim, Ben, 342  
 Nandi, N., 45, 86  
 nanotubes (carbon), 18  
   entropy in, 299–300  
   freezing of water in, 310, 314–315  
   molecular structure of, 278  
   molecular structure of water in, 278–279, **278**, **279**  
   relaxation time, 17–18  
   rotational molecular motion of water in, 280–282, **282**  
   translational molecular motion of water in, 279–280, **281**  
   types of, 277, 278, 282  
 natural selection (in biomolecules), 187–192, **189**  
 Nee, T., 54  
 Nernst's law of electrochemistry, 45  
 Nibbering, T. J., 40  
 nuclear magnetic resonance experiments (NMR). *See also* spectroscopy, experiments, computer simulation  
   of DNA hydration interaction, 170  
   and protein hydration layer dynamics, 126–127  
   and relaxation time, 57–58  
 nuclear overhauser effect (NOE), 126–127  
 nucleation, 16–17, 309, **310**, 311–314, **312**, **313**, 342  
   *See also* ice
- Ohmine, I., 67, 310, 325  
 oligomerization, 110–111  
 Onsager, L., 43, 212  
 Onuchic, J. N., 209  
 orientational order molecular structure 6  
   causing five-sided shape, 5, **6**  
   dependence in hydrophobic effects, 224–227, **225**, **226**  
   hydrogen bonds, 50  
   on mica surface, 206–207, **207**  
   promoting diffusion, 67–68  
   relaxation in, 53–54  
   reverse micelles, 269–273, **270**, **271**, **272**  
 Ostwald's dilution law, 211
- pair correlation function  $g(r)$ , 19–21, **19**, **20**, **21**  
 pair hydrophobicity, 221–227, **223**, **224**, **225**, **226**, 233  
 Patey, G. N., 340  
 Pauling, Linus, 4  
 Pecora, R., 56, 57  
 percolating network. *See also* clusters  
   allowing many dynamic processes, 9  
   development of, 325  
   history of, 327–330  
   as reason for many anomalies, 6–7  
 Percus–Yevick equation, 288  
 pH  
   blood pH, 75–76  
   of bulk water, 71–75, **73**

354

pH (cont.)  
seawater, 77

phase. *See also* supercritical water, supercooling diagram (water–ice), 306–307, **307**  
glass transition, 88–90, **89**, 144–145, **145**, **307**  
metastable state, 310–311, **310**, **341**

phospholipids, 177–179, **178**, 179

photosynthesis, 112–113, **113**

polar perturbations. *See* solvation dynamics (SD)

polarization. *See also* electrolytes  
of DNA, 151–152, 163–164, **164**  
speed of, 44, 45  
and water molecule arrangement, 9, 10

polymorphs, 202, 206, 342. *See also* molecular structure

potential energy 63  
bond transition in inherent structures, 67–68  
in DNA, 161  
of hydrogen bonds, 324, 331  
and molecular structures, 62–66, **63**, **64**, **65**, **66**

potential energy minima. *See* inherent structures (IS)

potential of mean force (PMF), 221–227, **223**, **224**, **225**, **226**

Pratt–Chandler theory (PC), 232, 233, 236–241

protein folding  
flickering phenomena, 196–197  
hydrophobic effects, 220, 224–227, **225**, **226**  
water dynamics in, 109

protein hydration layer. *See also* surface topology, hydration layer  
association in, 90  
binding sites, 107–109, **108**  
and DNA, 167–175, **172**, **175**  
glass transition and, 88–90, **89**  
molecular structure, **119**, **122**, **125**, **130**, **131**, **133**  
and water residence time, 109, 136, 170

protein surface  
inverted molecular structure, 124, 132–133  
topology, 8, 10  
water behavior in, 51

protein synthesis. *See also* DNA  
ADK, 101, **101**  
enzyme catalysis, 97–101, **99**, **100**, **101**, 208–209  
evolution of, 187–192, **189**  
kinetic proofreading, 187–196, **189**, **195**

proteins  
amphiphilic effects on, 245  
data bank, 224–227, **225**, **226**  
denaturization, 208  
effects of DMSO on, 256–258, **257**  
pH of amino acids, 75–76

pump-probe spectroscopy, 269, **270**

quantification of spatial order (to), 20–21, **20**, **21**, 24–25

quantum nature 6  
of hydrogen bonds, **8**, 71–72  
of temperature dependence in water bonds, 74  
of water creating V shape, **6**, 71–72

Index

quasi elastic neutron scattering experiments (QENS), 127–128

quenched normal mode, 69

Radhakrishnan, R., 314

radical distribution function. *See* pair correlation function  $g(r)$

Rahman, A., 6, 330

Raoult's law, 245

Rasaiah, J. C., 46, 278, 279

rate of decay, 36–38, **38**, **39**

rate of dissociation, 72

Rayleigh–Brillouin light spectrum, 55

reaction–diffusion model, 86

recognition (DNA), 152, 168–169

relaxation time. *See also* diffusion, dielectric relaxation (DR)  
being collective at low temperatures, 49–50  
in DNA protein, 170  
in inherent structures, 62–63, **64**  
nanopores, 17–18  
non-exponential in biological water, 84, 87  
and nuclear magnetic resonance, 57–58  
surfactants, **264**, 268–269, 273–274, **274**, **275**  
of water between mica surfaces, 206

residence time (in proteins), 109, 136, 170

reverse micelles. *See also* micelles  
dielectric relaxation, 268–269  
entropy in, 299–300  
molecular structure of, 263  
orientational order molecular structure, 269–273, **270**, **271**, **272**  
relaxation time, 273–274, **274**, **275**  
solvation dynamics (SD), 269

Rey, M., 40, 321

ribonuclease-A, 136

RNA  
trapped water molecules in, 105–107, **106**  
water dynamics around, 161–162

Rog, T., 180–181

Rosenfeld relation, 291–293, **295**

rotational molecular motion 27  
in bulk water, 27, 28–32, **31**, **33**  
in DNA grooves, 154–155  
in dynamic exchange model, 85, **85**, 86–88, 93–95  
entropy for, 303  
and jumping, 30–32, **31**, **32**, 51  
in lipid bilayer, 180–181, **181**  
in surfactants, 265  
and time correlation functions, 30, 51–53, **52**, 54  
of water inside a carbon nanotube, 280–282, **282**

rugged landscape, 174, 180

Sackur–Tetrode equation, 288, 299, 300, 301

Saito, S., 310

scaled particle theory (of hydrophobic hydration), 231–232

seawater (pH), 77

single file diffusion, 280, **281**

Skinner, J. L., 40

- solvation dynamics (SD)  
of bulk water, 13, 42–45, **44**  
computer simulation, 142–143  
in DNA, 155–156, **156**  
lipid bilayer, 181, **182**  
and protein hydration layer, 129–131, **130, 131**  
of reverse micelles, 269  
of supercritical water, 321–322
- solvents  
acetone, **244, 252**  
dioxane, **244, 252–253**  
DMSO, **244, 253–254, 255, 256–258, 257**  
ethanol, **244, 250, 251, 253–254, 255**  
methanol, **244, 250**  
tertiary butyl alcohol (TBA), **244, 250–252, 253–254, 255**
- Song, X., 130
- specific heat, 15, **16, 23–24, 289–290, 320, 327**
- spectroscopy. *See also* nuclear magnetic resonance experiments (NMR). *See also* experiments. *See also* computer simulation.  
to detect local collective motion, 333–334, **334**  
fluorescence up-conversion technique, 170  
light scattering, 55–57  
and protein hydration layer dynamics, 128–129  
pump-probe, 269, **270**  
Rayleigh–Brillouin light spectrum, 55  
of supercritical water, 320–321  
terahertz, 121
- speed  
difference between biological and bulk water dynamics, 84  
in DNA groove water, 155  
of electron transfer, 47  
of perturbation, 9  
of polarization response, 44, 45  
of rotational motion, 28–32  
of translational motion, 28  
of water hydration dynamics, 127–128, 131  
of water inside a carbon nanotube, 279–280  
of water molecules with increasing pressure, 35, **36**
- Speedy, J., 308
- spine of hydration (DNA), 157, 159–160
- standard ambient temperature and pressure (SATP), 72, 74
- Stanley, H. E., 325, 328
- statistical mechanics, 288, 290, 301, 308
- Stern layer, 262, **263, 265, 342. See also** hydration layer
- Stillinger, F. H., 6, 62, 231, 233, 236, 325, 330
- Stokes–Einstein relation  
in DNA, 159  
in lipid surface, 185
- subtilisin Carlsberg (protein), 130, **131**
- supercooling. *See also* supercritical water, phase, ice anomalies in, 334–341, **335, 336, 338, 339**  
and coefficient of thermal expansion, 16–18, **17**  
and hydrogen bond of heavy water, 33–35  
and inherent structures, 61, 69  
and local order, 20–21, **20, 21**  
motion becoming collective during, 49–50  
in NALMA experiments, 128  
and protein hydration layer, 88–90, **89**  
and specific heat, 15  
and translational diffusion, 35  
and two-stage model, 325–326
- supercritical water. *See also* supercooling, phase  
definition of, 307  
density fluctuations in, 318–319, **319**  
properties of, 317–318  
spectroscopic studies, 320–321  
vibrational molecular motion, 320–321  
Widom line in, 320
- surface topology. *See also* protein surface, protein hydration layer  
heterogeneous, 122, 135, 161–162, 170, **171**  
and influence on water structure, 206–207, **207**  
lipid, 180, 182–184  
mica, 206–207, **207**  
protein, 122, 123, 124, 132–133, **133**  
in rugged landscape, 90, 174  
silica, 204–205
- surfactants. *See also* amphiphilic effects  
free energy landscape, 266–268, **267, 268**  
molecular motion, 265  
molecular structure of, 261–263, **263, 264, 269–273, 270, 271, 272**  
relaxation time of, 265, 268–269, 273–274, **274, 275**  
solvation dynamics, 265, 269
- Sykes, M. T., 105
- Tanford, Charles, 215, 220
- temperature  
and Brownian motion, 28  
and coefficient of thermal expansion, 16–17, **17**  
dependence in hydrophobic effects, 215, 219–220, **220, 221**  
dependence on amphiphilic effects, 250–252  
and inherent structures, 62–66, **63, 64, 65, 66**  
and isothermal compressibility, 15–16, **16**  
and maximum density, 13–15, **14**  
and pH, 73–74, **73**  
and water motion, **34, 35**
- temperature of maximum density (TMD). *See also*  
density fluctuations  
and coefficient of thermal expansion, 17  
reason for, 327, 329  
temperature, 13–15, **14**
- terahertz spectroscopy, 121
- tertiary butyl alcohol (TBA), 244  
as amphiphilic binary mixture, 250–252  
clustering in, 253–254, **255**  
molecular structure, **244**
- tetrahedral molecular structure  
distorted, 5, **5, 20–21, 21**  
in DNA, 153–160, **158, 159**  
hydrogen bonds 4, 71–72  
ice, 6  
when cooling, 67, 331–332
- theory  
Cell, 298–299, **299**  
Flory–Huggins, 228–230, **229**  
Grote–Hynes, 48–49

356

theory (cont.)

Kubo-Oxtoby, 40

Landau, 325–326

Marcus, 47–49, **48**

Pratt–Chandler, 232, 233, 236–241

scaled particle, 231–232, 233

thermal motion. *See* Brownian motionthermodynamics. *See also* entropy, enthalpy (H)

bifurcated hydrogen bonds helping, 5

in hydrophobic hydration, 218–219

of protein-hydration interactions, 170–173, **172**

at supercooled temperatures, 13

third law of, 288–289

thickness (protein hydration layer), 118–121, 124

time correlation functions. *See* rotational molecular motiontime trajectory, 31–32, **31**time-dependent fluorescence Stokes shift (TDFSS), 44, **44**

translational molecular motion

in bulk water, 27, 28, 35, **36**

in computer simulations, 137

in DNA grooves, 154

in dynamic exchange model, 85, **85**, 88in lipid bilayer, 180–181, **181**

in surficants, 265

of water inside a carbon nanotube, 279–280, **281**triple point. *See* phase

Trout, B. L., 314

two-stage water model, 22–23, 118, **119**, 310,325–326, 335–341, **335**, **338***Index*

urea, 208–209

vibrational molecular motion

of bulk water, 27, 39–40, **40**

and entropy, 289–290, 296, 302

and protein hydration layer dynamics, 128–129

in supercritical water, 320–321

viscosity. *See also* diffusion

DMSO, 246

in electrolytes, 211–212

volume

expansion upon freezing, 306

fluctuations in, 337–338, **339**and isothermal compressibility, 15–16, **16**

Walter, N. G., 105

water pool, 263, 269

water-fearing. *See* hydrophobic effects

Watson, J. D., 152

Weber, T. A., 62

Weeks–Chandler–Andersen model (WCA), 236

Widom line 317, 320, 336–337, **336**, 342 *See also*

anomalies

Wolynes, P. G., 209

Xiao-Yan, Z., 279

Xia-Wolynes treatment, 294

Zewail, A. H., 88, 107, 130, 170

Zwanzig, R., 54, 62