THIRD EDITION

Intermolecular and Surface Forces

分子间力和表面力

第3版

Jacob N. Israelachvili

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Intermolecular and Surface Forces

Preface to the Third Edition

Updating the first and second editions of *Intermolecular and Surface Forces* was not easy. The field has exploded in many directions, both at the fundamental and applied levels, and into new areas. New terms have appeared such as complex fluids, soft matter, nanoscience, nanotechnology, nano-structured materials, biomimickry, and bio-inspired systems. Biological systems are being increasingly understood and copied at all length scales, accompanied by an increasing appreciation of dynamic (nonequilibrium, time- and rate-dependent) interactions. Ever more sophisticated experimental techniques and powerful computers now allow for highly complex systems to be studied and analyzed. Computers can now accurately mimic complex systems and even derive new equations without actually understanding what is going on (in the traditional sense).

The third edition contains updated material and also expands into new fields where molecular forces play a role, such as friction, lubrication, and dynamic (non-equilibrium) interactions. The aim has remained to provide basic physical insights and simple theoretical methods for calculating or estimating the magnitudes of various interactions—linking the fundamental science with practical and engineering applications. The focus is on fundamental aspects that may be applied to different phenomena rather than particular systems or the hot topics of the day.[†]

There are now many more worked examples scattered throughout each chapter and more end-of-chapter problems. The Worked Examples are intended to illustrate different ways of solving problems, both numerical and conceptual, that do not simply involve plugging numbers into an equation. The problems and discussion topics at the end of each chapter are similar, but they are often more subtle, and in some cases open-ended—in other words, ripe for discussion. Difficult problems are starred (*), and many problems have the answers provided but not how to solve them.

In preparing the third edition I have been helped by many. I am particularly grateful to Erika Eiser, Suzanne Giasson, Yu Tian, Eric Kaler, Joe Zasadzinski, Dan Schwartz, William Ducker, Marjorie Longo, Hongbo Zeng, Carlos Drummond, Stefan Karpitschka, Tonya Kuhl, Uzi Landman, Mark Robbins, Patricia McGuiggan, Kai Kristiansen, Roger Horn, Hugo Christianson, Yuval Golan, Xavier Banquy, Travers Anderson, Wren Greene, Malte Hammer, Jing Yu, Nataly Belman, Hernan Makse, Swapan Ghosh, Ayao Kitahara, Brian Vincent, Phil Pincus, and Dov Levine. Special thanks to Marina Ruths for her thorough reading and critical comments, Nancy Emerson for helping to organize the manuscript and references, Dottie McLaren for the illustrations, and Trudi Carey for her loving support.

Santa Barbara, California
December, 29 2009

[†]As another example of change, today's "hot" topic should really be described as "cool."

Preface to Second Edition

Since 1985, when the first edition of this book appeared, there has been much experimental and theoretical progress in this multidisciplinary subject. The nature of some "old" forces have been clarified while "new" forces have been discovered. The subject has matured into a rigorous discipline and a unifying area of chemistry, physics, and biology, and many university courses now routinely contain material on molecular and surface interactions. On the more practical side, many industrial and chemical engineering processes are now beginning to be understood and controlled at the fundamental level. It is with these developments in mind, together with the feedback I received from numerous colleagues, that the second edition was prepared.

The second edition is basically an updated version of the first, but it contains more than 100 problems. Most appear at the end of each chapter, but some appear as worked examples in the text. These problems should enhance the suitability of the book as an advanced undergraduate or graduate textbook. The problems have been devised to stimulate the mind; many are based on genuine research problems, others are tricky, some are extensions of the text into more advanced areas, and a few are open-ended to invite further reading, discussion, and even speculation.

The text itself has been expanded to include recent developments in the areas of surface-force measurements, solvation and structural forces, hydration and hydrophobic forces, ion-correlation forces, thermal fluctuation forces, and particle and surface interactions in polymer melts and polymer solutions.

I am grateful to many colleagues who commented on the first edition, and I have used their suggestions in writing the second. In particular, my thanks go to Hans Lyklema, Håkan Wennerström and Jacob Klein, to Helen Vydra and Josefin Isrealachvili for typing the manuscript, to Dottie McLaren for drawing many of the figures, to my wife Karina who supported me throughout, and finally to my students who have sat through my lectures and by their questions have unwittingly contributed the most.

Santa Barbara, California
October 24, 1989

Preface to the First Edition

Intermolecular forces embrace all forms of matter, and yet one finds very few university courses devoted to all aspects of this important subject. I wrote this book with the aim of presenting a comprehensive and unified introduction to intermolecular and surface forces, describing their role in determining the properties of simple systems such as gases, liquids, and solids, but especially of more complex, and more interesting, systems. These are neither simple liquids nor solids, but rather a myriad of dissolved solute molecules, small molecular aggregates, or macroscopic particles interacting in liquid or vapor. It is the forces in such systems that ultimately determine the behavior and properties of everyday things: soils, milk and cheese, paints and ink, adhesives and lubricants, many technological processes, detergents, micelles, biological molecules and membranes, and we ourselves—for each of us is one big biocolloidal system composed of about 75% water, as are most living organisms.

This subject therefore touches on a very broad area of phenomena in physics, chemistry, chemical engineering, and biology, in which there have been tremendous advances in the past 15 years. These advances can be viewed in isolation within each discipline or within a broader multidisciplinary framework. The latter approach is adopted in this book, where I have tried to present a general view of intermolecular and surface forces with examples of the various and often seemingly disparate phenomena in which they play a role.

Because of the wide range of topics covered and the different disciplines to which the book is addressed, I have presumed only a basic knowledge of the "molecular sciences": physics (elementary concepts of energy and force, electrostatics), chemistry (basic thermodynamics and quantum mechanics), and mathematics (algebra and elementary calculus). The mathematical and theoretical developments, in particular, have been kept at a simple, unsophisticated level throughout. Vectors are omitted altogether. Most equations are derived from first principles followed by examples of how they apply to specific situations. More complicated equations are stated but are again carefully explained and demonstrated.

In a book such as this, of modest size yet covering such a wide spectrum, it has not been possible to treat each topic exhaustively or rigorously, and specialists may find their particular subject discussed somewhat superficially.

The text is divided into three parts, the first dealing with the interactions between atoms and molecules, the second with the interactions between "hard" particles and surfaces, and the third with "soft" molecular aggregates in solution such as micelles (aggregates of surfactant molecules) and biological membranes (aggregates of lipids and proteins). While the fundamental forces are, of course, the same in each of these categories, they manifest themselves in sufficiently different ways that, I believe, they are best treated in three parts.

The primary aim of the book is to provide a thorough grounding in the theories and concepts of intermolecular forces so that the reader will be able to appreciate which forces are important in whatever system he or she is dealing with and to apply these theories correctly to specific problems (research or otherwise). The book is intended for final-year undergraduate students, graduate students, and nonspecialist research workers.

I am deeply grateful to the following people who have read the text and made valuable comments for improving its presentation: Derek Chan, David Gruen, Bertil Halle, Roger Horn, Stjepan Marcelja, John Mitchell, Håkan Wennerström, and Lee White. My thanks also extend to Diana Wallace for typing the manuscript and to Tim Sawkins for his careful drawing of most of the figures. But above all, I am indebted to my wife, Karina, without whose constant support this book would not have been written.

Canberra, Australia
October 24, 1984

Units, Symbols, Useful Quantities and Relations

Much of the published literature and equations on intermolecular and surface forces are based on the CGS system of units. In this book the *Système International* (SI) is used. In this system the basic units are the **kilogram** (kg) for mass, the **meter** (m) for length, the **second** (s) for time, the **kelvin** (K) for temperature, the **ampére** (A) for electrical quantities, and the **mole** (mol) for quantity of mass. Some old units such as gramme (1 gm = 1 g = 10^{-3} kg) , centimeter (1 cm = 10^{-2} m), ångstrom (1 Å = 10^{-10} m) and degree centigrade (°C) are still commonly used, although they are not part of the SI system. The SI system has many advantages over the CGS, not least when it comes to forces. For example, force is expressed in newtons (N) without reference to the acceleration due to the earth's gravitation, which is implicit in some formulae based on the CGS system. Note that units, prefixes, words, and abbreviations are usually unitalicized—that is, in text format (e.g., J, K, m, N, volts V), whereas variables are italicized (e.g., stiffness *K*, mass *m*, number *N*, maximum number N_{max}, velocity or volume *V*).

Derived SI Units

Quantity	SI Unit	Symbol	Definition of Unit
Energy	Joule	J	kg m^2 s^{-2} (also Nm and CV)
Force	Newton	N	J m^{-1} = kg m s^{-2}
Power	Watt	W	J s^{-1} = kg m^2 s^{-3}
Pressure	Pascal	Pa	N m^{-2}
Electric charge	Coulomb	C	A s
Electric potential	Volt	V	J A^{-1} s^{-1} = J C^{-1}
Electric field	Volt/meter		V m^{-1}
Frequency	Hertz	Hz	s^{-1}

Fraction	10^{12}	10^9	10^6	10^3	10^{-1}	10^{-2}	10^{-3}	10^{-6}	10^{-9}	10^{-12}	10^{-15}	10^{-21}
Prefix symbol	T	G	M	k	d	c	m	μ	n	p	f	z

Definitions of Terms and Symbols Used in the Text

a	Atomic or molecular radius (m), surfactant headgroup area (m^2)
a, b	Constants in equations of state
a_0	Bohr radius, atomic unit (a.u.) of length 0.053 nm, optimum headgroup area (m^2)
A, A_{ijk}	Hamaker constant for media i and k interacting across medium j (J), area (m^2), Helmholtz free energy

c	Interaction constant (J m^6), aqueous solute concentration in mole fraction units (mol dm^{-3}/55.5 or M/55.5), concentration number density (m^{-3}), volume fraction
d	Distance, diameter (m)
D	Distance between two surfaces (m)
Da	Dalton unit of molecular weight (same as MW)
E	Electric field strength (V m^{-1}), energy (J, eV, erg)
F	Force (N) or, when between two planar surfaces, force per unit area (N m^{-2})
G	Gibbs free energy
h, H	Height (m), enthalpy, hardness (Pa), hour (also *hr*)
I	Ionization potential (J)
i	$\sqrt{-1}$
k_a	Area compressibility modulus (J m^{-2} or N m^{-1})
k_b	Bending or curvature modulus (J)
k, K	Elastic modulus (N m^{-2}), spring constant or stiffness (N m^{-1})
K_a	Reaction constant, association constant (M^{-1})
K_d	Dissociation constant ($K_d = 1/K_a$)
l, ℓ	Length (m), unit segment length in polymer chain (m)
l_P	Persistence length of worm-like chain polymer (m)
l_c	Critical hydrocarbon chain length (m)
L	Latent heat (J mol^{-1}), thickness of polymer brush layer (m)
m, M	Mass (kg), molarity, molar mass, molecular weight (also *MW*), mean aggregation number
M	Concentration (mol dm^{-3}, 10^3 mol m^{-3}, moles/liter)
M_W, M	Molecular weight, molar mass (g mol^{-1}), atomic mass (g), mass of atom or molecule $\times$ N_o, mass of atom or molecule/mass of $\frac{1}{12}$ of ^{12}C atom, Da (if not specified, e.g., PEO 1,000, assume Da)
n, N	Refractive index; number of atoms, molecules, moles, bonds, segments in a polymer chain, micelle aggregation number
p, P	Pressure (N m^{-2})
P_L, P_y	Laplace pressure, yield stress (Pa)
pK	$-\log_{10}$[concentration or activity of H^+ ions in M]
Q, q	Charge (C)
r, R	Radius (m), interatomic distance (m), atomic or molecular radius (m)
r_k	Kelvin radius (m)
R_g, R_F	Radius of gyration of polymer (m), Flory radius of polymer (m)
s	Mean distance between polymer anchoring sites (m)
S	Entropy, solubility
t	Time (s)
T	Temperature (K)
T_M, T_B	Melting or boiling points (K or °C)
T_c, T_m	Lipid chain melting temperature
u	Dipole moment (C m)
U	Molar cohesive energy (J mol^{-1}), internal energy (J mol^{-1})
v, V	Volume (m^3), velocity or speed (m s^{-1}), molar volume (m^3)
w, W, W_0	Interaction free energy, pair potential (J). Between two planar surfaces: Work of adhesion, cohesion or interaction free energy per unit area (J m^{-2})
x, y, z	Position along the x-, y- or z- axis, arbitrary variables

$\dot{x}$	Time derivative of variable x, for example, velocity = dx/dt ($m\ s^{-1}$)
$\ddot{x}$	Acceleration, $d(dx/dt)/dt = d^2x/dt^2$ ($m\ s^{-2}$)
X	Dimensionless concentration (e.g., mole fraction)
Y	Young's modulus ($N\ m^{-2}$)
z	Valency
α	Polarizability ($C^2\ m^2\ J^{-1}$), interaction energy parameter (J or $J\ m^{-1}$)
γ	Surface tension ($N\ m^{-1}$), surface energy ($J\ m^{-2}$), $\tanh(e\psi_o/4kT) \rightarrow \tanh[\psi_o(mV)/103]$ at 298 K
γ_i, γ_{AB}	Interfacial energy ($J\ m^{-2}$)
Γ	Surface coverage, surface density, 2D density (number per m^2)
δ	Stern layer thickness (m), elastically or plastically deformed distance (m)
$\varepsilon(\nu)$	Dielectric permittivity at frequency ν
ε	Relative permittivity, static dielectric constant at zero frequency $\varepsilon(0)$, strain
$\in$	Energy (J or $J\ m^{-1}$)
θ, ϕ, ψ, α	Angle (deg or rad), contact angle (deg)
θ	Theta temperature of solvent (°C, K)
κ	Inverse Debye length (m^{-1})
λ, λ_o	Characteristic exponential decay length, wavelength (m), line tension (N)
ξ	Correlation length (m)
μ	Chemical potential, coefficient of friction (COF)
μ^i, μ^o	Standard part of chemical potential due to molecular interactions
ν, ν_I	Frequency (s^{-1} or Hz), ionization frequency (s^{-1})
ρ	Number density (m^{-3}) or mass density ($kg\ m^{-3}$)
σ	Atomic or molecular diameter (m), surface charge density ($C\ m^{-2}$), standard deviation
τ	Characteristic relaxation time (s), lifetime (s), stress ($N\ m^{-2}$, Pa)
η	Viscosity (Pa s)
Ω	Solid angle
ψ, ψ_0	Electrostatic potential (V), surface potential (V)
Π	Two-dimensional surface pressure ($N\ m^{-1}$)
$\approx$, $\sim$	Approximately equal to, roughly equal to
$>$, $<$	Greater than, less than
$\lesssim$ $\gtrsim$	Slightly greater than/less than
$\leq$,	Less than or equal to
$\geq$,	Greater than or equal to
$\gg$, $\ll$	Much greater than, much less than
$\equiv$	Equivalent to
$\propto$	Proportional to
$\parallel$, $\perp$	Parallel to, perpendicular or normal to
Δ	Change or difference in
$\lvert X \rvert$	"Modulus" (positive or absolute value) of X
$\langle X \rangle$, $\overline{X}$	Average or mean of X
[X]	Concentration of X
$\rightarrow$, $\rightarrow$, $\Rightarrow$	Approaches, implies, leads to
$1\vert 2$, $\alpha\vert\beta$	Interface between media 1 and 2 or phases α and β
■ ■ ■	Start or end of **Worked Example**

Abbreviations

e.g., eg	For example (from the Latin *exempli gratia*)
cf.	Compare with (from the Latin *confer*), contrast with
i.e., ie	That is, that is to say (from the Latin *id est*)
viz.	Namely (from the Latin, *videlicet*)
etc.	More of the same type (from the Latin *etcetera*)
et al.	And others (from the Latin *et alii*)
Ch.	Chapter
Log	ln or $\log_e$ (logarithm to base e)
Ibid	From same place as the previous reference/citation (from the Latin *ibidem*)
*	Difficult problem
Sect.	Section
FCC	Face Centered Cubic (see also HCP)
HCP	Hexagonal Close Packed (see also FCC)
1D, 2D, 3D	One-dimensional, two-dimensional, three-dimensional
RH	Relative humidity, p/p_{sat} for water vapor
STP	Standard temperature and pressure: T = 25°C = 298.15 K, P = 1 atm = 1.013 × 10^5 Pa. Some authorities have adopted T = 20°C = 293.15 K and P = 100 kPa.
CMC (CAC)	Critical micelle (aggregation) concentration

Conversion from CGS to SI

1 Å (ångstrom) = 10^{-10} m = 10^{-8} cm = 10^{-4} μm = 0.1 nm
1 liter = 10^{-3} m^3 = 1 dm^3
Density, ρ(kg m^{-3}) = $10^3\rho$(g/cm^3)
Molecular weight, M (kg mol^{-1}) = 10^{-3} M (gm/mole)
1 erg = 10^{-7} J
1 cal = 4.184 J
1 kcal mole^{-1} = 4.184 kJ mol^{-1}
1 kT = 4.114 × 10^{-14} erg = 4.114 × 10^{-21} J at 298 K (~25°C)
= 4.045 × 10^{-14} erg = 4.045 × 10^{-21} J at 293 K (~20°C)
= 4.281 × 10^{-14} erg = 4.281 × 10^{-21} J at 310 K (body temperature, ~37°C)
1 kT per molecule = 0.592 kcal mole^{-1} = 2.478 kJ mol^{-1} at 298 K
1 eV = 1.602 × 10^{-12} erg = 1.602 × 10^{-19} J
1 eV per molecule = 23.06 kcal mol^{-1}= 96.48 kJ mol^{-1}
1 cm^{-1} (wave number unit of energy) = 1.986 × 10^{-23} J
1 dyne = 1 g cm s^{-2} = 10^{-3} kg 10^{-2} m s^{-2} = 10^{-5} N
1 dyne cm^{-1} = 1 erg cm^{-2} = 1 mN m^{-1} = 1 mJ m^{-2} (unit of surface tension or energy)
1 dyne cm^{-2} = 10^{-1} Pa or N m^{-2} (unit of pressure).
1 atm = 1.013 × 10^6 dyne cm^{-2} = 1.013 bar = 1.013 × 10^5 Pa (N m^{-2})
1 Torr = 1 mm Hg = 1.316 × 10^{-3} atm = 133.3 Pa (N m^{-2})
0°C = 273.15 K (triple point of water)
1 esu = 3.336 × 10^{-10} C
1 poise (P) = 1 dyne s cm^{-2} = 0.1 N s m^{-2} = 0.1 Pa s (unit of viscosity)
1 Stokes (St) = cm^2 s^{-1} = 10^{-4} m^2 s^{-1} (unit of kinematic viscosity: viscosity/density)
Debye (D) = 10^{-18} esu = 3.336 × 10^{-30} C m (unit of electric dipole moment)

Conversion from SI to CGS

1 nm = 10^{-9} m = 10 Å = 10^{-7} cm
1 J = 10^7 erg = 0.239 cal = 6.242 × 10^{18} eV = 5.034 × 10^{22} cm^{-1} = 7.243 × 10^{22} K
1 kJ mol^{-1} = 0.239 kcal $mole^{-1}$ = 0.404 kT per molecule at 298 K
1 N = 10^5 dyne ≡ mass or weight of 0.102 kg (102 gm) in a gravitational field of g = 9.81 m s^{-2}
1 Pa = 1 N m^{-2} = 10 dyne cm^{-2} = 9.872 × 10^{-6}atm = 7.50× 10^{-3} torr = 1.45 × 10^{-4} psi (lb/in^2)
1 bar = 10^5 N m^{-2} = 10^{-5} Pa = 0.9868 atm = 750.06 mm Hg

Useful Quantities and Relations, Other Conversions

Mass of any atom or molecule = M/N_0 (also MW/N_0) g
Mean volume occupied per molecule = $M/(N_o \times$ mass density) m^3
Converting mass density ρ_m (kg m^{-3}) to number density ρ_n (molecules m^{-3}): $\rho_n = \rho_m N_0/M$
Molar concentration: 1 M = 1 mol dm^{-3} (mole/litre) = 6.022 × 10^{26} molecules per m^3
Number density (solution concentration): $\rho = M \times 6.022 \times 10^{26}$ molecules per m^3
Standard volume of ideal gas = 22.414 × 10^{-3} m^3 mol^{-1} (22.414 liters/mole)
$4\pi\varepsilon_0 = 1.113\times10^{-10}$ C^2 J^{-1} m^{-1}
kT/e = RT/F = −25.69 mV at 298 K (~25°C) = −26.72 mV at 310 K (~37°C, body temperature)
1 C m^{-2} = 1 unit charge per 0.16 nm^2 (16 Å^2)
κ^{-1} (Debye length) = $0.304/\sqrt{M}$ nm for 1:1 electrolyte at 298 K (25°C)
Mass of the earth = 5.976 × 10^{24} kg
Density of earth (mean) = 5.518 × 10^3 kg m^{-3}
Values of gravitational acceleration, g: Standard gravity (9.80665 m s^{-2}), Equator (9.780 m s^{-2}), North and south poles (9.832 m s^{-2}), New York (9.801 m s^{-2}), London (9.812 m s^{-2}).

Some Geometric Relations for Truncated Sphere and Cap of Height *d* (Shaded)

$d = R(1-\cos\theta)$, $\sin\theta = r/R$
Chord theorem: $r^2 = (2R-d)d \approx 2Rd$ for $R \gg d$
Volume of sphere: $\frac{4}{3}\pi R^3$; surface area of sphere = $4\pi R^2$
Volume of cap: $\frac{1}{3}\pi d^2(3R-d) = \frac{1}{3}\pi R^3(2+\cos\theta)(1-\cos\theta)^2$
Volume of truncated sphere: $4\pi R^2 -$ volume of cap
Area of curved surface of cap: $2\pi Rd = 2\pi R^2(1-\cos\theta)$
Area of curved surface of sphere: $2\pi R(2R-d) = 2\pi R^2(1+\cos\theta)$
Area of flat circular base of cap: $\pi r^2 = \pi(2R-d)d = \pi R^2\sin^2\theta$

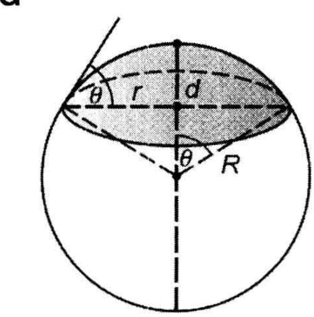

FIGURE I

Table i. Some Properties of Water at 1 atm Pressure

	Values at Different Temperatures						
	0°C (273.15 K)		10°C	20°C	25°C	37°C	50°C
Property	**Ice**	**Liquid**	**(283 K)**	**(293 K)**	**(298 K)**	**(body temp)**	**(323 K)**
Dielectric constant (permittivity) at zero frequency, ε	91.6	87.9	84.0	80.2	78.4	74.2	69.9
Refractive index at 589 nm, n	1.309	1.3343	1.3341	1.3334	1.3329	1.3313	1.3294
Surface tension/energy, γ (mJ m^{-2})	~109	75.6	74.2	72.8	72.0	70.1	67.9
Density, ρ (gm/cm^3 = kg m^{-3}/1000)	0.9167	0.9999†	0.9997	0.9982	0.9970	0.9933	0.9880
Viscosity, η (mPa s)	10^{14} Glacier ice	1.79	1.31	1.00	0.89	0.69	0.55

Additional properties: Mass of water molecule: 2.99×10^{-26} kg. Dipole moment: 1.84 D. Rotational correlation time of water molecule in liquid water: $\tau_{rot} \approx 2$ ps.

†Density maximum 1.0000 at 4°C.

Definitions and Glossary

These days, online information is so good and readily accessible that it is no longer necessary to define or introduce basic terms or concepts in a text book. The reader should refer to such sources whenever new or unfamiliar terms are used, such as *simple harmonic motion*, *resonance frequency*, the *Grotthuss Mechanism*, the *Vroman effect*, and *von Schröder's Paradox*. It is for this reason that this glossary is so short.

Amphiphile Molecules such as surfactants and lipids where one part is hydrophilic (the "headgroup") and the other is hydrophobic, usually a long hydrocarbon chain.

Classical An adjective that describes nonquantum mechanical systems whose molecules obey Boltzmann statistics.

Colloid A colloid is a dispersion of particles in solution. The size of colloidal particles is in the microscopic regime, ranging from 0.01 to 100 μm. Only one dimension of a particle needs to be in this range to qualify it as a colloidal particle—for example, a 5 nm thick lipid bilayer of macroscopic area. Particles in the size range from 1 to 100 nm are now referred to as **nanoparticles**, this being the range of sizes where atomic properties make the transition to microscopic or macroscopic properties.

Critical micelle concentration (CMC), critical aggregate concentration (CAC) The concentration at which further addition of solute molecules to a solvent makes them go into finite sized micelles (aggregates) while the monomer concentration remains unchanged at the CMC (CAC).

Directed assembly See **Self-assembly.**

Energy dissipated The energy that one system (molecule, particle or lattice) *transfers* to another system during an interaction. This can be in the form of translational kinetic energy or heat (e.g., internal vibrational and rotational energy).

Engineering conditions Range of time, length, mass, temperature, and so on, encountered in everyday phenomena (see Table 9.1).

Equilibrium Mechanical equilibrium is one where a small deviation from the "equilibrium" state brings the system back to that state; thermodynamic equilibrium is the lowest free-energy state—the state of "true" equilibrium. A system in mechanical equilibrium is not necessarily in the true equilibrium state, from which it may be separated by an energy barrier. A state can also be in thermal equilibrium (the temperature is uniform throughout), but not in mechanical or thermodynamic equilibrium. See Section 22.2 for more on nonequilibrium systems.

Extensive Thermodynamic term for property that depends on the number of molecules N or moles n or the total volume V of the system—for example, the mass or total energy of the system. Cf. **Intensive, Specific**.

Intensive Thermodynamic term for property that does not depend on the size or number of molecules in a thermodynamic system, for example, pressure, temperature, viscosity, surface tension. Cf. **Extensive, Specific**.

Self-assembly The natural (spontaneous, thermodynamically driven) organization of atoms and molecules into multimolecular structures. **Directed** or **engineered assembly** refers to external energy-requiring processes that lead to nonequilibrium, but often long-lived, structures, or to a stable steady-state organization but only so long as there is a constant rate of energy input.

Specific (i) Thermodynamic term for **intensive** property produced by dividing one **extensive** property by another—for example, specific molecular volume (volume occupied per molecule) $v = V/N$, specific molar volume $v = V/n$. Cf. **Intensive, Extensive**. (ii) Biological term for interaction or bond between two specialized groups that uniquely recognize each other. Specific bonds do not have to be strong. Also **complementary, lock-and-key, ligand-receptor (L-R** or **LR)** bonding.

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