

Molecular Engineering Thermodynamics

Building up gradually from first principles, this unique introduction to modern thermodynamics integrates classical, statistical, and molecular approaches, and is especially designed to support students studying chemical, biochemical, and materials engineering. In addition to covering traditional problems in engineering thermodynamics in the context of biology and materials chemistry, students are introduced to the thermodynamics of DNA, proteins, polymers, and surfaces.

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- All the necessary mathematical background, plus resources summarizing commonly used symbols, useful equations of state, microscopic balances for open systems, and links to useful online tools and datasets.

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“This is a book to use many times. First as a textbook that explains the principles of thermodynamics and statistical mechanics with rigour and clarity. The importance and the contemporary relevance of the subject matter is illustrated in many examples from physics, chemical engineering and biology – and it is to these examples that future readers are likely to return time and again. They illustrate how thermodynamics can be used as a framework to organize and quantify our understanding of an amazing variety of physical phenomena. A textbook to hold on to.”

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“The book by Professors J. J. de Pablo and J. D. Schieber, titled *Molecular Engineering Thermodynamics*, is both sensible and innovative. They use a postulational approach to present the basic ideas of the subject, which, I believe, is the best way to teach equilibrium thermodynamics, since it is clear and concise. Their book is also important because they show how thermodynamics can be used to attack problems involving chemical reaction equilibria, properties of polymer solutions and blends, and surfaces and interfaces. They also make it clear how thermodynamics may be applied to engineering flow systems (which are not at equilibrium). A chapter on statistical mechanics shows how molecular ideas fit into the subject of thermodynamics.”

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Molecular Engineering Thermodynamics

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To Marina, Clara, and Luis, and to Jennifer and Nathaniel

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PREFACE

Students of engineering and the physical sciences are often introduced to thermodynamics in a way that has evolved little over the last several decades.

This book is an outgrowth of the sense that thermodynamics courses should reflect changes in the problems that engineers and scientists encounter in practice. Important industrial sectors, including the oil, chemical, semiconductor, and pharmaceutical, continue to recruit large numbers of scientists and engineers, but new demands require them to be more versatile, and able to apply fundamental thermodynamic concepts in a wider range of situations. At the same time, start-ups in emerging fields must be nimble and rely on a work force that is equally comfortable applying thermodynamic principles to rationalize observations in biology or advanced materials design. Traditional boundaries between science and engineering are becoming blurred, and versatility in engineering is necessarily built on a broader understanding of far-reaching scientific principles. Engineering students must place greater emphasis on broadly applicable scientific concepts and learn how to use these in different contexts, and students in the sciences must gain a better appreciation for how such concepts are applied in engineering practice.

One clear and common trend in most engineering and scientific disciplines is that of control over smaller length scales. Experimental methods are able to probe and manipulate the behavior of individual molecules, and large-scale processes can be used to mass produce ultra-small electronic devices. We have entered the age of “molecular engineering,” and it is important to emphasize molecular-level concepts in thermodynamics texts.

This manuscript grew out of a set of lecture notes that, with the help of our students and colleagues, we assembled over the last decade. It was originally inspired by the texts and papers that we learned from and, over the course of time, the original content was re-organized in a manner that became easier to deliver in a classroom setting. As we taught and re-taught our thermodynamics courses, we had an opportunity to collect a wide variety of examples of applications of thermodynamics from different disciplines. While we have tried to acknowledge all of the original sources from which ideas and content were taken, we have been influenced by more researchers than we could know. We offer our deepest apologies to any authors who may have inadvertently been omitted from our list of references, and welcome any suggested corrections. Thermodynamics is a mature subject, and we do not make any claims to present in this text a new or original interpretation.

In teaching a two-semester undergraduate sequence, as well as our own graduate courses, we also had ample occasion to realize which concepts students could fully appreciate and remember and which ones they could not. At times, we experienced a fear of reprisal at the mere mention of entropy. Our lecture notes gradually evolved into a postulatory presentation of thermodynamics that allowed us to transition between different aspects and applications

of thermodynamics without having to re-introduce some of the underlying principles. Outlining the geometrical framework of thermodynamics from the beginning made it easier to later exploit its consequences in a wide range of applications. Thermodynamic stability, colligative properties, phase equilibria, or adsorption at surfaces and interfaces could all be introduced in a seamless manner, always starting from a common approach. Also examples ranging from the entropy loss associated with polymer stretching to the extraction of heavy molecules using super-critical fluids could be more easily discussed within the same sequence of lectures.

At our own institutions, we have used the text in a two-semester sequence for undergraduate students, or for a one-semester course for graduate students. In the past, the text has been used by chemical and biological engineers, biomedical engineers, materials scientists, and chemists. Particular attention has been devoted to illustrating new concepts with examples from various disciplines, ranging from chemistry to physics and biology.

Our presentation of thermodynamics has been heavily influenced by Callen's classic text. Our manuscript begins with the statement of three postulates in Chapter 2. These postulates are then used to introduce the concept of thermodynamic surfaces, and the minimization (or maximization) of thermodynamic potentials in Chapter 3. Examples of our non-traditional approach to engineering thermodynamics are illustrated with the manipulation of individual DNA molecules using optical tweezers and the adsorption of protein molecules onto surfaces. Chapter 4 is devoted to thermodynamic stability and its consequences. These ideas are subsequently built upon to analyze thermodynamic processes, such as cycles, turbines, and fuel cells. Our discussion of such processes is necessarily more concise than that encountered in traditional engineering texts. If needed, that material can be supplemented with examples already available in the literature. This five-chapter introduction to classical thermodynamics is followed by a chapter on statistical mechanics, in which a connection is made between the thermodynamic potentials introduced earlier and the behavior of collections of molecules. The presentation of statistical mechanics can be facilitated considerably by relying on software for molecular simulations that is widely available online. This is also the chapter in which the idea of fluctuations is introduced, a subject of importance in small, especially biological, systems.

The introduction to statistical mechanics is followed by a chapter on the nature and origin of intermolecular forces that serves to establish a link between chemistry, structure, and the ensuing thermodynamic behaviour. The subsequent two chapters are devoted to a discussion of phase equilibria in a wide variety of contexts, including systems comprising gas, liquid, and solid phases. Our presentation is based on the texts by Prausnitz et al. and by Sandler. Concepts from phase equilibria are illustrated with examples ranging from super-critical extraction to the modeling of the blood–brain barrier through water–octanol partitioning. Chapter 10 is devoted to chemical equilibria and the study of reacting systems. The examples that are discussed range from reactions encountered in semiconductor manufacturing to biotechnology processes (e.g., polymerase chain reaction). Simple stochastic concepts are introduced for the study of fluctuations in small reaction volumes. Although polymers are introduced throughout the text in earlier examples, Chapter 11 is devoted to polymer solubility, including copolymers and the compressibility that arises with super-critical solvents, as used in foaming. Chapter 12 is devoted to the thermodynamics of surfaces, and builds on the original introduction by

Guggenheim with examples related to the characteristics of super-hydrophobic surfaces and the collapse of nanoscopic structures encountered in nano-lithographic processes.

There are four appendices. The first appendix reviews all the mathematical background necessary for the manipulations in the text above algebra. The text makes extensive use of partial differentiation, Taylor-series expansion, the chain rule, Jacobian transformations, and Leibniz's rule; all students are expected to have proficiency in these tools. For completeness, the Gauss divergence theorem is included, but it is essential only for a later appendix. The cubic-equation solutions are useful for numerical work in single-component vapour–liquid stability predictions, whereas combinatorics is an essential tool in statistical-mechanical calculations. Appendix B summarizes all key information about several equation-of-state models for pure systems. Appendix C derives the microscopic balances from first principles. These derivations make a strong connection with the subject of transport phenomena and provide the basis for all flowing-system analyses considered in Chapter 5. The final appendix provides a small amount of physical data necessary for performing calculations using the sorts of models presented in Appendix B. Much more complete physical data are obtainable online, or from software.

Thermodynamics is a mature, large discipline, yet its application is found in an ever-growing number of problems. A single textbook cannot be expected to cover all that important ground. This book is intended to give students a broader flavor of the subject than they might otherwise experience. We expect that this text will require continuous adaptation to our changing discipline. However, we believe that the approach taken here is sufficiently robust to facilitate incorporation of new challenges and inclusion of new topics, and is appropriate for introductory or intermediate-level courses in the sciences and engineering disciplines.

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We are indebted to the many students at Wisconsin and Illinois who suffered through our courses in thermodynamics and who worked with us on this text. We have benefited considerably from the advice of many of our colleagues, who have patiently worked through earlier versions of this text and used it in their lectures. We are grateful to the Department of Chemical and Biological Engineering at the University of Wisconsin for the award of a Hougen Fellowship; that fellowship allowed Jay Schieber to spend a semester in Madison, during which some of the material in this text was developed. Juan de Pablo is grateful for the Howard Curler Distinguished Professorship; without that professorship it would have been difficult to complete this text. Juan de Pablo would like to thank the Department of Chemical and Biological Engineering at the University of Wisconsin for providing a collegial and scholarly environment in which to launch an academic career. We are also grateful to our new colleagues at the University of Chicago for creating a stimulating atmosphere that will undoubtedly nurture the development of the nascent field of molecular engineering.

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DEFINITIONS

Symbol	Name	Where introduced or defined
A	Area	Fundamental
A_{chain}	Cross-sectional area per chain	Eqn. (11.53)
a	Parameter in several models	
a_i	Activity of species i	Eqn. (9.6), p. 283
A_s	Cross-sectional area	p. 151
A_0, A_1, \dots	Constants	
a_0	Parameter in various models	
a_K	Kuhn step length	Eqn. (2.84), p. 49
b	Parameter in various models	
$C(T)$	Heat capacity	Eqns. (3.16)
c	Parameter in various models	
C_L, c_L	Constant-length heat capacity	Eqn. (3.97), p. 83
C_P, c_P	Constant-pressure heat capacity	Eqn. (3.62), p. 70
C_V, c_V	Constant-volume heat capacity	Eqn. (3.84), p. 80
c_i	Molar concentration of species i	Section C.1 of Appendix C
E	Electric field	
E_{tot}	Total energy of system	Eqn. (5.5), p. 151
\vec{F}	Force	Fundamental, p. 4
F	Helmholtz potential	Eqn. (3.10), p. 55
f	Specific Helmholtz potential	$:= F/N$
f_i	Fugacity	Eqn. (8.41), p. 258
f_i^{pure}	Fugacity of pure component	Eqn. (8.41), p. 258
F_0	Helmholtz potential at reference state	
F^R	Residual Helmholtz potential	Eqn. (4.66), p. 136
\vec{g}	Gravitational vector	Fundamental, Table D.5, p. 468
g	Specific Gibbs free energy	$:= G/N$
G	Gibbs free energy	Eqn. (3.11), p. 55
G_0	Gibbs free energy at reference state	
G^R	Residual Gibbs free energy	Eqn. (4.66), p. 136
H	Enthalpy	Eqn. (3.9), p. 55
\hbar	Reduced Planck constant	Fundamental, Table D.5, p. 468
h	Specific enthalpy	$:= H/N$
H_0	Enthalpy at reference state	
\vec{J}_i	Molar flux of species i	Section C.1 of Appendix C
H^R	Residual enthalpy	Eqn. (4.66), p. 136

Definitions

k	Thermal conductivity	
k_B	Boltzmann constant	$:= R/\tilde{N}_A$, Eqn. (2.20), p. 20
K_{tot}	Total kinetic energy of system	Eqn. (5.6), p. 151
l	Distance	
L	Length (of elastic strand)	Fundamental
L_0	Length at reference state	
l_p	Persistence length	Eqn. (2.85), p. 50
\log	Natural logarithm	$:= \int_1^x (1/x)dx$, $\exp(\log x) = x$
\log_{10}	Logarithm base 10	$10^{(\log_{10} x)} = x$
m	mass	
$\bar{m}_i, m = v, s, g, \dots$	Partial molar property	Eqn. (8.8), p. 251
M_s	Moles of adsorption sites	Eqn. (3.109), p. 90
M_{tot}	Total mass of system	Section 5.1
\dot{m}	Mass flow rate	
M_w	Molecular weight	
M_E	Excess property	Eqn. (9.2), p. 283
\vec{n}	Unit normal vector	Eqn. (5.7), p. 152
N_i	Mole number of species i	Fundamental, p. 15
N_K	Number of Kuhn steps	Eqn. (2.84), p. 49
N_p	Number of persistence lengths	Eqn. (2.85), p. 50
P	Pressure	Eqn. (2.24), p. 23
p_j	Probability of being in microstate j	Eqn. (6.14), p. 186
P_0	Pressure at reference state	
P_s	Spinodal pressure	Section 4.2.1
P_c	Critical pressure	Section 4.2.1
P^{sat}	Saturation pressure	Section 4.2.2
Q	Heat	Eqn. (2.1), p. 10
Q	Canonical-ensemble partition function	Eqn. (6.13), p. 186
$q_{\text{site}}(T)$	Single-site partition function	Eqn. (3.109), p. 90
q_i	Charge of species i	Chapter 7
q_{ij}	Molecule-pair partition function	p. 313
R	Ideal-gas constant	Fundamental, Table D.5, p. 468
r	Number of species	p. 17
R_i	Reaction rate of species i	Section C.1 of Appendix C
S	Entropy	p. 17, defined in Eqn. (2.20), p. 20
s	Specific entropy	$:= S/N$
S_0	Entropy at reference state	
S^R	Residual entropy	Eqn. (4.66), p. 136
S_{tot}	Total entropy of system	Eqn. (5.10), p. 152
T	Temperature	Eqn. (2.25), p. 23
T_0	Temperature at reference state	

T_s	Spinodal temperature	Section 4.2.1
T_c	Critical temperature	Section 4.2.1
\mathcal{T}	Tension	Eqn. (2.72), p. 37
U	Internal energy	Fundamental, p. 9
u	Specific internal energy	$:= U/N$
U_j	Energy of microstate j	p. 184
U_0	Internal energy at reference state	
U_{tot}	Total internal energy of system	Eqn. (5.6), p. 151
U^{R}	Residual internal energy	Eqn. (4.66), p. 136
V	Volume	Fundamental, p. 5
v	Specific volume	$:= V/N$
V_0	Volume at reference state	
\vec{v}	Velocity	$:= d\vec{r}/dt$, p. 4
V^{R}	Residual volume	Eqn. (4.66), p. 136
v_c	Critical volume	Section 4.2.1
v_v	Vapor volume	Section 4.2.2
v_l	Liquid volume	Section 4.2.2
\bar{v}_i^∞	Partial molar volume at infinite dilution for species i	Eqn. (8.90)
W	Work	Eqn. (1.1), p. 4
X	Unconstrained variable	Eqn. (3.23), p. 59
z	Compressibility factor	Eqn. (4.28), p. 121
z_c	Critical compressibility factor	Section 4.27
Δg_b	Base-pair denaturation	Eqn. (3.102), p. 87
Δh_b	Base-pair denaturation	Eqn. (3.102), p. 87
Δs_b	Base-pair denaturation	Eqn. (3.102), p. 87
$d \dots$	Imperfect differential	p. 10
λ	Unspecified generic constant	
β	Parameter in various models	
$\delta(i, j)$ or δ_{ij}	Kronecker delta function	$:= \begin{cases} 1, & i = j \\ 0, & i \neq j \end{cases}$
γ	Parameter in various models	
γ_i	Activity coefficient	Eqn. (9.7), p. 283
ϕ	Fugacity coefficient	Eqn. (8.42), p. 258
Ω	Number of microstates	Eqn. (2.20), p. 20
μ^{d}	Dipole moment	Chapter 7
μ_i	Chemical potential of species i	Eqn. (2.26), p. 23
μ°	Chemical potential under ideal conditions	Eqn. (3.112), p. 92
\mathcal{T}	Tension	Eqn. (2.72), p. 37
ψ, ψ_1, ψ_2	Various functions	
Π	Osmotic pressure	p. 302
α	Coefficient of thermal expansion	Eqn. (3.60), p. 70
α^{P}	Polarizability	p. 217
κ_T	Isothermal compressibility	Eqn. (3.61), p. 70
κ_S	Isentropic compressibility	Eqn. (3.123), p. 102
ϵ_0	Permittivity of vacuum	Chapter 7

Definitions

$\epsilon_a, \epsilon_{\perp}, \epsilon_{\parallel}$	Langmuir adsorption parameters	Eqn. (3.110), p. 91
χ	Flory–Huggins interaction parameter	Eqn. (3.115), p. 92
Ψ	Grand canonical potential	Eqn. (6.47), p. 195
θ	Fraction of filled sites, Langmuir	$:= N/M_s$, Eqn. (3.111), p. 92
θ_i	Angle of orientation between two dipoles	
Δh^{vap}	Heat of vaporization	Eqn. (4.47), p. 128
Φ_{tot}	Total potential energy of system	Eqn. (5.6), p. 151
$\vec{\nabla}$	Vector differential operator	Eqn. (C.6), p. 452
ρ	Mass or molar density	Appendix C
$\tilde{\rho}$	Number density of molecules	
$\vec{\tau}$	Stress tensor	Eqn. (C.9), p. 453
η_s	Newtonian viscosity	Eqn. (C.9), p. 453
D/Dt	Substantial derivative	Eqn. (C.11), p. 453
ϵ	Non-equilibrium energy density	Eqn. (C.15), p. 454
\vec{q}	Heat-flux vector	Section C.3 of Appendix C
Φ_v	Newtonian dissipation function	Eqn. (C.18), p. 455
$\sigma_{\alpha}, \alpha = \text{hf, mf, sw, r}$	Entropy creation rates (densities)	Eqn. (C.29), p. 458
$\sigma_M, M = U, N, V$	Fluctuation variance	Eqn. (6.63), p. 200
$\Sigma_{\alpha}, \alpha = \text{hf, mf, sw, r}$	Entropy-creation rates	Eqn. (5.8), p. 152
Δ	Changes in quantity (equilibrium)	
Δ	Difference in exit (equilibrium) minus inlet (flow)	Eqn. (5.2), p. 150
Δ	Grand canonical partition function	Eqn. (6.46), p. 194
η	Efficiency	Eqn. (5.49), p. 163
ϵ	Coefficient of performance	Eqns. (5.53) and (5.54)
Λ	De Broglie wavelength	Eqn. (6.24)
ω	Acentric factor	Eqn. (B.7)
ω_d	Degeneracy	p. 313

Ξ	Grand canonical partition function	Eqn. (6.47), p. 195
Ψ	Generalized potential	p. 195
ν_0	Electronic frequency of molecule	p. 217
σ, ϵ	Lennard–Jones parameters	p. 220
$\langle \dots \rangle$	Average	Eqns. (6.63) and (8.3), pp. 200, 248
$:=$	“is defined as”	
