
INTRODUCTION TO
**MOLECULAR
STRUCTURE
&
THERMO-
DYNAMICS**

FRANK PAUL INCROPERA

INTRODUCTION TO
**MOLECULAR STRUCTURE
AND THERMODYNAMICS**

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to
Andrea,
Ann,
and
Jim

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P R E F A C E

Although not entirely evident from the title, this text is intended for use by engineers in a course on statistical thermodynamics. It does not carry the title *Statistical Thermodynamics* because it adopts an approach to the subject which is not traditional.

The usual course in statistical thermodynamics will have a single, over-riding objective: to provide an alternative view of thermodynamics which enables an independent prediction and interpretation of thermodynamic properties. In the course for which this text is intended, this objective remains important. However, an additional objective, *which assumes the same level of importance*, is to provide the student with a sound understanding of the molecular structure of matter. Although it may seem excessive to the thermodynamicist, fully one-half of the text is devoted to this objective.

Extensive treatment of molecular structure may be justified on several grounds. It provides the student a sound basis for developing a true appreciation of the methods of statistical mechanics and is also essential to any serious application of the subject. Moreover, it provides the engineering student with valuable background for subsequent study of such topics as radiation transfer, chemical kinetics, combustion and air pollution, energy conversion, gas dynamics, and optical physics, each a vital area of concern to the thermal scientist.

One might argue that, although a background in molecular structure is essential to serious consideration of the above topics, a course in statistical thermodynamics is not the proper vehicle for obtaining this background. I disagree. Molecular structure and statistical thermodynamics are, in the pedagogical sense, highly complementary subjects. Consideration of molecular structure provides the student with conceptual underpinnings which allow for more than just a shallow appreciation of statistical mechanics. It has been my experience that, without a firm appreciation for the molecular

properties of matter, the student is likely to perceive statistical mechanics in somewhat of a mystical light. An understanding of molecular structure also provides the student with the confidence and the facility to attempt more than just the simplest applications. Conversely, the process of using one's understanding of molecular structure in statistical thermodynamics enhances this understanding and, in fact, provides a certain credibility to the subject. The fact that this understanding is applicable to numerous disciplines which transcend statistical mechanics is then an added dividend.

I have attempted to write a text which systematically describes the important notions of modern physics (with emphasis on molecular structure), develops statistical methods based on these notions, and considers a variety of thermodynamic applications. It is intended for use by mechanical, aeronautical, chemical, and nuclear engineers, and the only prerequisite is prior completion of a first course in thermodynamics.

The material on atomic and molecular physics is divided into three categories: a discussion of the old quantum theory, a discussion of the Schrödinger theory of quantum mechanics, and detailed consideration of atomic and molecular structure. Although the old quantum theory (Chapter 2) is of limited applicability, it does introduce the student to many important notions in a painless fashion. The Schrödinger theory (Chapters 3-5) is then used to reinforce the ideas developed from the old quantum theory and to provide a firmer foundation for quantum mechanics. Simple solutions obtained from this theory provide important insight to the structure of matter, as well as results useful to the prediction of thermodynamic properties. Subsequent chapters on atomic and molecular structure (Chapters 6 and 7) are intended to provide more than just a simplistic view of molecular properties.

It should be noted that attention is restricted to the inherent structure of matter and its relationship to thermodynamic properties. With but two exceptions (relating to the theories of blackbody radiation and real gases), the subject of molecular interactions and its relationship to transport phenomena is ignored. Although it is clearly an important area, it is too far removed from the subject of thermodynamics to merit serious consideration in this text.

With regard to statistical methods, the choice is between the Gibbs, or ensemble, method and a quantum version of the Maxwell-Boltzmann method. The methods differ with respect to the model to which the statistical averaging procedures are applied. For the Gibbs model averaging procedures are applied to a large number of replicas of the assembly of interest; for the Maxwell-Boltzmann method the averaging is applied directly to the large number of particles which comprise the assembly.

On the basis of rigor and general applicability, the choice is simple. The Gibbs method is based upon sound statistical procedures which may be

applied to any physical assembly. The same statement may not be made for the Maxwell-Boltzmann method. However, on pedagogical grounds I have found the Maxwell-Boltzmann approach to be superior. In alternating between the two approaches when teaching the kind of course for which this text is intended, I have found students to be far more receptive to the Maxwell-Boltzmann method. In particular, certain abstractions inherent in the Gibbs model make it difficult for the student to assimilate the details and retain sight of the overall objectives of statistical mechanics. In contrast, because of the direct connection between the statistical procedures and particle behavior in the Maxwell-Boltzmann approach, assimilation by the students is far less difficult.

The approach adopted for this text involves initially exposing the student to the fact that alternative statistical procedures exist. In addition to providing a cursory description of the procedures, statistical concepts important to each are introduced (Chapter 8). The Maxwell-Boltzmann method is then developed (Chapter 9) and applied to several physical assemblies (Chapters 10–13). At the point beyond which further application of the method is impossible, the Gibbs approach is developed (Chapter 14). The similarities and differences between the Gibbs and Maxwell-Boltzmann methods are discussed, and the student, having been through one statistical development and being cognizant of the overall objectives of statistical mechanics, has little difficulty appreciating the nature and merit of the Gibbs approach.

At Purdue the contents of this text are covered in a one-semester course. Two periods are devoted weekly to lectures, and one period is devoted to *preceptorials*, for which the class is divided into smaller groups of no more than ten students. The preceptorials emphasize informal discussions which focus on conceptual difficulties experienced by the students and on the questions provided at the end of each chapter. These sessions have provided an outstanding vehicle for stimulating student interest and insuring a thorough understanding of important concepts.

It is a pleasure to acknowledge the people who have made meaningful contributions to this work: to Professor Arthur "Mac" Mellor, for providing strong support for the approach adopted in the text and for introducing the use of preceptorials; to Professor Robert W. Fox, for many stimulating discussions on the educational process and for helping to develop my awareness of student needs; to Professor Richard E. Sonntag of the University of Michigan, for many useful suggestions on the manuscript; and to Mrs. Bonnie Brown, for her meticulous efforts in typing the notes on which this manuscript is based.

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S Y M B O L S

| | |
|----------|---|
| A | Helmholtz free energy |
| A_{nm} | Einstein coefficient for spontaneous emission |
| a | acceleration Helmholtz free energy per mass |
| a_0 | Bohr radius |
| B | dynamical variable second virial coefficient |
| B_e | rotational constant |
| B_{mn} | Einstein coefficient for absorption |
| B_{nm} | Einstein coefficient for stimulated emission |
| b_2 | cluster integral |
| C | normalization constant |
| C_j | group degeneracy |
| C_p | constant pressure heat capacity |
| C_V | constant volume heat capacity |
| c | speed of light |
| c_p | specific heat at constant pressure |
| c_v | specific heat at constant volume |
| D_e | rotational <u>stretching</u> constant |

| | |
|----------------|---|
| D_0 | dissociation energy |
| D_1, D_2 | Debye crystalline property functions |
| d_c | distance of closest approach |
| d | <u>inexact differential</u> |
| E | internal energy voltage |
| E'' | radiation flux |
| $E_{b\lambda}$ | monochromatic blackbody emissive power |
| e | electronic charge internal energy per mass |
| F | <u>rotational term value</u> |
| F | interparticle force |
| f | distribution function |
| $f(c)$ | Maxwellian speed distribution |
| $f(e^{tr})$ | Maxwellian energy distribution |
| $f(\nu)$ | frequency distribution function for normal vibrations in a Debye crystal |
| G | Gibbs free energy <u>vibrational term value</u> |
| g | degeneracy Gibbs free energy per mass Lande factor |
| H | enthalpy Hamiltonian |
| H | magnetic field intensity |
| h | enthalpy per mass Planck's constant |
| \hbar | $h/2\pi$ |
| I | ionization potential moment of inertia nuclear spin quantum number |
| J | rotational quantum number total angular momentum quantum number |

| | |
|----------|---|
| J | total angular momentum vector |
| <i>j</i> | total angular momentum quantum number for one electron |
| j | total angular momentum vector for one electron |
| <i>k</i> | Boltzmann's constant vibrational force constant wave number ($1/\lambda$) |
| \hbar | $2\pi/\lambda$ |
| <i>L</i> | length of a cubical cavity orbital angular momentum quantum number |
| L | orbital angular momentum vector |
| <i>l</i> | orbital angular momentum quantum number for one electron |
| l | orbital angular momentum vector for one electron |
| <i>M</i> | number of microstates in a macrostate |
| M_{mp} | number of microstates in the most probable macrostate |
| <i>m</i> | particle mass |
| m_l | magnetic quantum number |
| m_j | total momentum orientational quantum number |
| m_0 | rest mass |
| m_s | spin orientational quantum number |
| <i>N</i> | number of particles |
| N_0 | Avogadro's number |
| <i>n</i> | general quantum number designation particle number density principal quantum number |
| <i>P</i> | general thermodynamic property |
| P_a | power absorbed by an oscillating electron in a blackbody radiation field |
| P_e | power radiated by an oscillating electron |
| P_m | probability of a macrostate |
| P_q | power radiated by an oscillating charge |

| | |
|--------------------|--|
| p | pressure magnitude of particle momentum |
| \mathbf{p} | particle momentum vector |
| Q | heat transfer molecular partition function |
| Q_N | canonical partition function |
| q | general position coordinate magnitude of the charge per particle |
| R | gas constant radial amplitude function |
| R_∞ | Rydberg constant |
| r | radial coordinate |
| \mathbf{r} | vector position |
| r_e | equilibrium internuclear spacing |
| S | angular amplitude function entropy spin angular momentum quantum number |
| \mathbf{S} | spin angular momentum vector |
| s | entropy per mass spin angular momentum quantum number for one electron |
| T | kinetic energy temperature time-dependent solution to the Schrödinger equation vibration period |
| T_E | Einstein temperature |
| t | time |
| U_λ, U_ν | monochromatic energy density |
| $U_{b\nu}$ | blackbody spectral energy density |
| V | energy potential energy volume |

| | |
|-------------|--|
| v | particle speed specific volume vibrational quantum number |
| W | work |
| W_i | number of possible particle arrangements in the energy states of a group |
| $W(\eta_i)$ | number of <u>ensemble</u> states |
| x, y, z | Cartesian coordinates |
| Z | atomic number compressibility factor configurational integral |

Greek Letters

| | |
|-----------------|--|
| α | fine structure constant separation constant undetermined multiplier |
| α_D | degree of dissociation |
| α_e | rotation-vibration coupling constant |
| α_I | degree of ionization |
| β | separation constant undetermined multiplier |
| β_e | rotation-vibration coupling constant |
| Δh_f^0 | enthalpy of formation |
| ε | particle energy |
| ε_m | Fermi energy |
| ε_0 | permittivity of free space |
| η | number of moles |
| Θ | angular amplitude function |
| θ | angle |
| Λ | quantum number for quantization of the resultant electron orbital angular momentum along the internuclear axis |

| | |
|--------------------|--|
| λ | extent of reaction separation constant wavelength |
| μ | reduced mass |
| $\boldsymbol{\mu}$ | magnetic dipole moment |
| ν | chemical potential frequency <u>stoichiometric</u> coefficient |
| ν_D | Debye frequency |
| ν_{nm} | line radiation frequency |
| ρ | transformation variable defined by equation (5-75) |
| $\sqrt{\Sigma}$ | quantum number for quantization of the resultant electron spin angular momentum along the internuclear axis |
| σ | rotational symmetry factor spin eigenfunction Stefan-Boltzmann constant |
| Φ | angular amplitude function total intermolecular potential of a real gas (the configurational energy) |
| ϕ | angle mass fraction potential function for binary particle interactions |
| Ψ | wave function |
| ψ | amplitude function |
| Ω | number of assembly microstates |
| ω | angular frequency |
| ω_e | vibrational wave number |
| $\omega_e x_e$ | anharmonic correction factor |
| $\omega_e y_e$ | anharmonic correction factor |

Script Letters

| | |
|---------------|------------------------|
| \mathcal{E} | ensemble energy |
| \mathcal{M} | molecular weight |
| \mathcal{R} | universal gas constant |

xx SYMBOLS

Subscripts

| | | | |
|-------|----------------------------------|-----------|----------------------|
| B-E | Bose-Einstein | tot | total |
| C-M-B | corrected Maxwell-Boltzmann | tr | translational |
| e | electron(ic) | v | vibrational |
| | equilibrium internuclear spacing | vib | vibrational |
| | external system motion | Z | Zeeman effect |
| elec | electronic | z | coordinate direction |
| F-D | Fermi-Dirac | λ | wavelength |
| | | ν | frequency |
| i | energy state | | |
| | general species designation | | |
| | internal system motion | | |

Superscripts

| | | | |
|-----|-----------------------------|------|------------------------|
| int | internal | el | molecular electronic |
| j | energy group | elec | electronic |
| l | energy level | nuc | nuclear |
| m | lower energy level or state | rot | rotational |
| | macrostate | | |
| M-B | Maxwell-Boltzmann | tr | translational |
| mp | most probable | vib | vibrational |
| n | normalization condition | + | positive charge |
| | quantized | - | negative charge |
| | upper energy level or state | * | dimensionless variable |
| nuc | nuclear | | |
| o | ground state or level | | |
| | reference state | | |

Marks over Symbols

| | | | |
|------|----------------------|----------|------------------|
| op | operator | \wedge | unit mole |
| pw | pilot wave | $-$ | average |
| R | relativistic effects | $=$ | ensemble average |
| r | rotational | \sim | per particle |
| rev | reversible | | |
| rot | rotational | | |
| SL | spin-orbit effect | | |

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