THERMAL PHYSICS

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AN INTRODUCTION TO THERMODYNAMICS,
STATISTICAL MECHANICS AND KINETIC THEORY

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Preface

The number of lectures devoted to traditional subjects such as thermodynamics has decreased recently in many honours degree courses owing to the commendable desire to introduce current research topics to undergraduates. The leisurely discussion of thermodynamics given in the standard undergraduate texts is now rather out of proportion to the time that the student is prepared to devote to the subject. One method of saving time is to teach a course purely from the atomic view of matter and in some way to 'derive' the laws of thermodynamics from the results of statistical mechanics. This approach is also claimed to be more likely to arouse the interest of students already familiar with elementary atomic physics but has the great disadvantage of presenting thermodynamics as a trivial and dependent subject rather than as one of the greatest achievements of physics.

There is of course no doubt that much can be learnt by a judicious mixture of the macroscopic and microscopic approaches and so this book covers both thermodynamics and statistical mechanics. However, they are first introduced separately and then their strengths and weaknesses are further explored by examining a number of selected topics from both points of view. A chapter is also devoted to the kinetic theory of the transport properties of gases, partly because of the importance of the results in such fields as vacuum physics and partly to emphasise the great increase in difficulty associated with the study of systems away from thermal equilibrium.

The main objections to the teaching of thermodynamics without the introduction of statistical mechanics have always seemed to me to centre on the tortuous approach to the second law of thermodynamics given in most elementary textbooks. An engineer may find proofs based on hypothetical engines driving each other backwards and forwards fascinating, but to many physics students these seem rather special phenomena on which to base a general law of science. The physical *need* for a second law of thermodynamics is therefore discussed in some detail in chapters 2 and 3 and then the mathematical theorem of Carathéodory stated. The distinction between this theorem and the statement of the second law of thermodynamics in the form given by Carathéodory is

then carefully explained. Once the concept of an integrating factor for the first law of thermodynamics has been established the whole subject can be developed in a logical fashion and heat engines dealt with *en passant*.

The wide application of the methods of thermodynamics and statistical mechanics in modern research is demonstrated in chapter 10 where such varied subjects as the 3 K stellar background radiation, Pomeranchuk cooling of ^3He to within a few thousandths of a degree of absolute zero, the thermodynamic inequalities at phase transitions and negative temperature are treated, and references given to fuller accounts in accessible journals.

It is hoped that these modern examples will both arouse the interest of the student and impress upon him the continuing importance of a subject whose origins lie in the nineteenth century but which will always occupy a central position in physics.

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To the Student

Thermal physics is the study of the properties of systems containing a large number of atoms. In this sense it therefore covers nearly all physics although it will be seen that most of this book is concerned with the special case of systems in thermal equilibrium. The concepts of thermal physics, perhaps more than any other branch of physics, are most easily grasped in detail once a certain breadth of experience has been obtained. This short book — the essentials of the subject are developed in 154 pages — is therefore designed to provide a broad foundation for the study of the more difficult concepts and applications of thermal physics and does not attempt to provide completely rigorous proofs of every point which is discussed. Consult the reading list at the back of the book when you find a point which does not seem to be dealt with to your satisfaction or when you wish to increase your knowledge of some aspect of the subject. The mathematics required for the book is revised in appendixes I – III.

At the end of each chapter will be found a set of exercises. It is essential that the reader attempt these exercises — some of the results of which are used in the text — and is able to understand the answers given at the end of the book, although a fuller understanding of, say, chapter 3 may well come after reading chapter 7.

The final chapter is designed to show the techniques of thermal physics at work. The selection of topics includes some of the most interesting recent developments in physics and astronomy as well as a number of more traditional topics which were too important to leave out.

To summarise: try to see chapters 2 – 7 *as a whole*, work the exercises and study the solutions, use the book list to extend your knowledge.

List of Symbols

a	given radius; van der Waals constant
b	van der Waals constant
B_V, B_P	virial coefficients
$C_V (C_P)$	heat capacity at constant volume (pressure); virial coefficients
$c_V (c_P)$	specific heat per molecule at constant volume (pressure)
c	speed of light
c_s	speed of sound
d	diameter
E	energy of whole system
$\mathcal{F}$	tension
$G (g)$	Gibbs free energy (per unit mass)
$H (h)$	Enthalpy (per unit mass)
I	nuclear spin
J	rotational quantum number
$k (k)$	wave vector (magnitude)
k	Boltzmann constant
l	latent heat
m	mass of one molecule
m_0	mass of system
$\mathcal{M}$	total magnetic moment
M	molar mass, magnetisation
N	number of molecules
n	number of molecules per unit volume
$p(p)$	momentum (magnitude)
P	pressure
Q	quantity of heat
R	gas constant
r	position, integer (subscript)
$S(s)$	entropy (per unit mass); spin of a particle
T	absolute temperature
$U(u)$	internal energy (per unit volume)

V	volume
v	speed
$\mathbf{v}$	velocity
W	work; number of microstates
Z	partition function
$\mathcal{J}$	grand partition function
α	coefficient of expansion, Lagrange undetermined multiplier; critical index
β	$1/kT$ (Lagrange undetermined multiplier); critical index
γ	C_p/C_v ; Lagrange undetermined multiplier; coefficient of electronic specific heat, critical index
$\Gamma(n)$	gamma function (appendix II)
ϵ	individual particle energy
$\xi(z)$	Riemann zeta function (appendix II)
η	coefficient of viscosity
θ	temperature; angle
κ	thermal conductivity
κ_T	isothermal compressibility
λ	mean free path; wavelength
μ	magnetic moment; Lagrange undetermined multiplier
ν	frequency
ρ	density
σ	scattering cross-section; Stefan – Boltzmann constant
τ	relaxation time
ϕ	angle; integrating factor
χ	susceptibility
Ψ, ψ	wavefunction

Approximate Values for Fundamental Constants

Charge on proton (e)	$1.6 \times 10^{-19} \text{ C}$
Planck constant (h)	$6.6 \times 10^{-34} \text{ J s}$
Avogadro constant (N_A)	$6.0 \times 10^{23} \text{ mol}^{-1}$
Gas constant (R)	$8.3 \text{ J K}^{-1} \text{ mol}^{-1}$
Boltzmann constant (k)	$1.4 \times 10^{-23} \text{ J K}^{-1}$
	$8.6 \times 10^{-5} \text{ eV K}^{-1}$
Stefan - Boltzmann constant (σ)	$5.7 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
Rest mass of electron	$9.1 \times 10^{-31} \text{ kg}$
Rest mass of proton	$1.7 \times 10^{-27} \text{ kg}$
Rydberg constant (R_∞)	$1.1 \times 10^7 \text{ m}^{-1}$
Bohr magneton	$9.3 \times 10^{-24} \text{ J T}^{-1}$
Nuclear magneton	$5.0 \times 10^{-27} \text{ J T}^{-1}$

A pressure of 1 atmosphere $\equiv$ 760 mm mercury $= 1.0 \times 10^5 \text{ N m}^{-2} = 1.0 \times 10^5 \text{ Pa}$
 (1 mm mercury = 1 torr = 133 Pa)

An energy of 1 eV $\equiv 1.6 \times 10^{-19} \text{ J}$

At room temperature a thermal energy $kT \approx 300 \text{ K} \approx 0.026 \text{ eV}$

Normal temperature and pressure (N.T.P.) $T = 273 \text{ K}$, $P = 1 \text{ atmosphere}$

One mole of a perfect gas occupies 22.4 l (0.0224 m^3) at N.T.P.