AN INTRODUCTION TO

equations of state

THEORY AND APPLICATIONS

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with a Foreword by

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FOREWORD BY EDWARD TELLER

Is physics completed? At the time when the behavior of atoms was finally understood this seemed to be a very real question.

A few problems remained. These included the relations between elementary particles and the unification of gravitation, electromagnetism and nuclear physics. About the latter not much was known and its importance was underestimated.

Today particles appear less elementary and unification looks more ambitious than ever.

This book on the equation of state gives impressive evidence that a great chapter of science including most of physics, chemistry and a great portion of astronomy is, indeed, completed and unified. Just one idea had to be added to the systematic knowledge of the elementary building blocks. That idea developed into the theory of probability and statistical physics.

The structure of statistical mechanics is deceptively simple. The main point appears to be to separate a bigger system into components whose energies can be added while their probabilities can be multiplied. From this statement it follows that probability depends on energy in an exponential manner. Classical equation of state theories in all of their approaches depend on this one circumstance. The quantities and ideas used in the comprehensive description of the development of two centuries are remarkably homogeneous, even uniform.

Yet, the theory of the equation of state spans an enormous range. Obviously, huge numbers are involved. More importantly, the methods of thinking are quite diverse. On the one end we have reversible processes. On the other irreversibility is the main rule. The distinction between causality and probabilistic arguments is even more basic. Einstein never was reconciled to 'laws' of probability from which there was no appeal to the supreme court of causality.

A discussion of the equation of state gives an impressive demonstration of how great a fraction of the inorganic world is explained by the revolution called quantum mechanics. At the same time the equation of state presents the tools by which our experimental knowledge can be extended into regions of extreme concentrations of energy and matter.

All this leads up to a part of physics which may move faster and farther than any other branch: astrophysics. Neutron stars and black holes are realistic examples of the two frontiers of physics: nuclear forces and general relativity. The authors use the same mathematics, the same concepts to introduce problems of astrophysics as they have used to explain the common properties of matter.

The first man whose ideas about atoms are still remembered is a philosopher from Thessaly: Democritos. Almost two and a half millennia ago he suggested that matter may not be divisible without limitations. A serious revival of his idea started around 1800. Since that time science has been accelerating. It still produces unexpected facts and the completion of physics is not in sight. My preconceived idea is that science is open-ended. In this book the reader will find an exciting review of the rich past and he also will get a glimpse into a future which may be unlimited.

PREFACE

The equation of state is the relation between the pressure, the temperature and the density (specific volume) of a physical system and is related both to fundamental physics and to applications in astrophysics, gases and condensed matter, and nuclear and elementary particle theory.

In the same way that Newtonian mechanics can be regarded as the foundation of physics, so the equation of state of ideal gases can be considered to be the foundation of thermodynamics, hydrodynamics and chemistry. Furthermore, as mechanics was extended to take account of relativity and quantization, so the equation of state had to be developed to describe states of matter in extreme density and temperature domains.

The main aim of this book is to provide the reader with a basic understanding of the development of the equation of state. It should be of value to undergraduate and graduate students with an interest in astrophysics, solid state matter under extreme conditions, plasma physics and shock waves, as well as special aspects of nuclear and elementary particle physics.

The systematic derivation of essential physical theory includes several original expressions. The elements of classical statistics and the Bose–Einstein and Fermi–Dirac equations of state (EOS) are based on partition functions and the Thomas–Fermi model derivation includes the exchange interactions which lead to the Thomas–Fermi–Dirac equation. Special attention is given to the virial theorem. A new treatment of the Grüneisen EOS, based on Einstein's and Debye's models of solids, is given which highlights Einstein's ingenious contributions. Fluid mechanics and the kinetic theory are derived with particular emphasis on shock waves and a special meaning is given to the relation between the equation of state, Grüneisen coefficients, cold pressure and high pressure shock waves in solids.

The book also describes several important applications of the equation of state together with accounts of the most recent research results including original new presentations. The study of inertial confinement fusion, especially laser fusion or particle beam fusion, is one of the fields in which pressures of nearly 10 gigaatmospheres and temperatures of about 100 million degrees are being achieved. These extreme conditions are described in a detailed and novel manner. The application of the equation of state to the extreme conditions of astrophysics is dealt with, special attention being given to the stability of normal stars based on radiation pressure and particle pressure. The equation of state in nuclear matter is described using the Hagedorn theory; this subject can either be related to the theory of strong interaction or to the model of the early universe.

This book is only a stroll through the equations of state in science and many more applications can be considered. In particular the physics of phase transitions could be the basis for a complementary volume on the equations of state. We believe that the book emphasizes the importance of equations of state in science and that further academic study and research is required to bring this subject to the attention of science students.

We would like to thank our secretaries, Mrs Marie Wesson and Ms Noemi Francisco of the University of New South Wales, for their precise and neat work. Our thanks are also extended to Mrs Catherine Faust (UNSW) for her immaculate preparation of the artwork.

Finally, the authors wish to acknowledge the support of the Gordon-Godfrey bequest, the Australian Research Grant Scheme and the Australian Academy of Sciences which was essential for the preparation of this book. These grants enabled the authors to meet in the australian summer of 1983 at the University of New South Wales in Sydney, where they began their collaboration on the book.

March, 1986

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Introduction

1.1 General remarks

Important branches of physics were developed or originated from the equation of state while (in return) more and more complex formulations of the equations of state were due to the developments of modern physics. The ideal gas law was the first quantitative treatment of chemical kinetics and the beginning of thermodynamics and statistics, resulting in the first complete formulation of the laws of energy conservation and entropy. From the thermodynamics of entropy of radiation, Max Planck discovered the atomistic structure of action (quantization), one of the basic properties of nature. The properties of molecular interaction were described quantitatively for the first time by van der Waal's equation of state.

Nowadays, physics has developed towards research of such extreme conditions of matter, as shock waves in metals at several million atmospheres pressure and strong non-equilibrium states in chemical reactions using laser or plasma technology, while laser produced plasmas now provide matter at pressures of up to a thousand million atmospheres in the laboratory. In astrophysics, we observe objects at much more extreme conditions with pressures and temperatures of many orders of magnitudes beyond the extreme points reached in the laboratory. These astrophysical objects, previously topics of speculation only, are now very serious research fields producing detailed knowledge following the breathtaking development of space technology. The conditions of neutron stars and beyond involve nuclear matter such that the study of the equations of state could become a new route for solving fundamental problems in the physics of elementary particles and nuclei where the combined effort involves the physics of condensed matter and of ordinary high density plasmas.

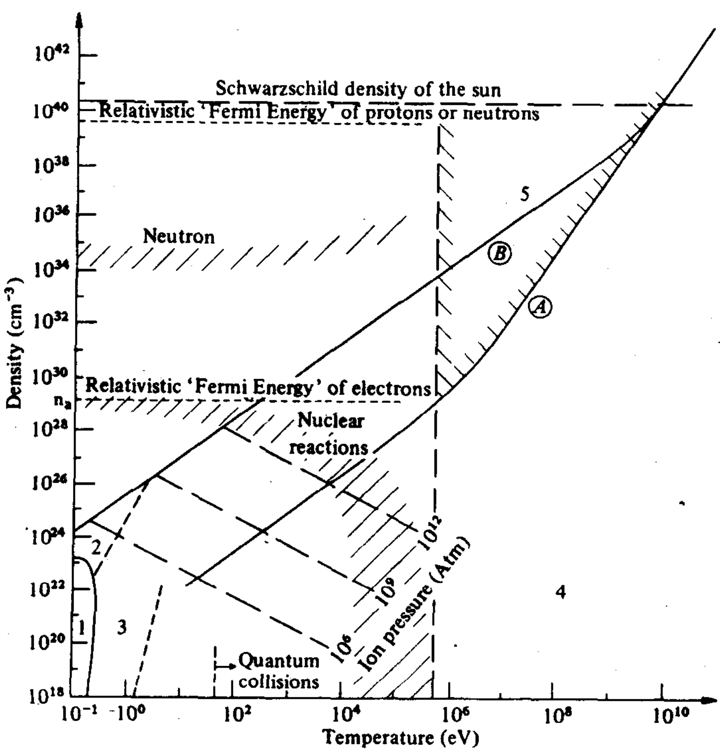
While the study of equations of state was one of the most important problems in physics in the first of the nineteenth centurt, there is again now a high priority in modern physics to solve the numerous deficiencies in our knowledge of equations of state. The development of equations of state is again sought to meet the needs of the rapidly advancing modern physics of extreme states of matter.

Recognizing the lack of knowledge of the equations of state in modern physics, an introductory summary of knowledge of the development of the equations of state will be presented in the following chapters together with a presentation of the derivations and typical results, with the aim of giving an improved, generalized and shorter presentation of this developing field. Together with these basic concepts, numerous important and exciting applications, in the physics of high pressure in solids, metals and plasmas, for dense nuclear fusion, astrophysics and for nuclear and high energy physics, are given.

1.2 Phenomena at various densities and temperatures

The states of all substances are relatively simply described if the density is very low and the temperature is not too close to 0 K. In this case,

Fig. 1.1. Ranges of density and temperature for which equations of state are to be considered.



the ideal equation of state for pressure P in a volume V is determined by the temperature T

$$PV = RT \tag{1.1}$$

where the constant R depends on the number of moles in the volume V and the degree of freedom of the molecules. Expressing V as $1/n$, the density of n atoms of dissociated molecules (or ions) in the gas, eqn. (1.1) reads

$$P = nkT \tag{1.2}$$

where $k = 1.38 \times 10^{-16}$ erg deg^{-1} is Boltzmann's constant.

Fig. 1.1 is a diagram of density and temperature of matter which permits a classification of different states without the pressure – and subsequently the equation of state, being given. The density–temperature diagram of matter in this section is therefore a first classification of the problems discussed in the book. The next step will be to explain the Fermi-pressure in Section 1.3, and Section 1.4 will then provide an overview in terms of a preliminary pressure–temperature diagram for the range of states and their limitations to be treated and extended in the subsequent main sections of the book.

In Fig. 1.1, the range of the ideal equation of state is that of nonionized matter at low densities. At higher densities, range 1 covers condensed matter and range 2 may cover the conditions that ions are fixed in space (crystals), limiting their motion to defined centres of oscillation only (Brush 1967).

Range 3 has no sharp limits of high density and temperature and represents mainly a gaseous state with partial ionization. This state is determined by the Saha equation for describing the degree of dissociation by Boltzmann factors (first studied by Schottky (1920)) and covers strong coupling between electrons and ions (Hansen 1973; Golden 1983; Pines and Noziéres 1966) including the metallic state in the upper part of range 1. Because of the high density and low temperature, the electrostatic plasma effects not only decrease the ionization energy but cause the merging of spectral lines into the vacuum levels or the 'drowning of spectral lines' (Inglis and Teller 1939; Traving 1959) (which as well as the polarization shift (Griem 1981) can be explained in a straightforward way by an electrostatic atom model (Hora 1981, p. 28; Henry and Hora 1983; Henry 1983)). The whole physics of range 3 is not yet extensively developed, neither are the highly complicated equations of state in this range.

At higher temperatures and low densities when there is a high degree of ionization of atoms or the state of fully ionized plasma is reached – range 4 – the resulting plasma is gaseous and kinetically rather simple: a classical ionized gas governed by the ideal equation of state. This state, however, has non-classical properties: the classical Coulomb collisions change into quantum collisions at a temperature T^*

$$kT^* = \tfrac{4}{3} Z^2 m_0 c^2 \alpha^2 \tag{1.3}$$

as detected in plasmas as anomalous resistivity which can be explained quantitatively by this process (Hora 1981, p. 37; Hora 1981a). In (1.3), Z is the number of charges (degree of ionization) of the plasma ions, m_0 is the electron rest mass, c is the speed of light, and the fine structure constant is $\alpha = e^2/\hbar c$ where e is the electron charge and $\hbar = h/2\pi$: h is Planck's constant. Further, in range 4, thermonuclear reactions at temperatures around and above 10^4 eV will begin. Another example of non-classical behaviour is that at thermal equilibrium with equilibrium (opaque) black body radiation in the plasma, a strong coupling between electrons and black body radiation will occur, which we discuss in Section (1.5). Above a temperature $mc^2 = 0.52$ MeV, pair production and other inelastic interactions will occur. Nevertheless, the equation of state may well be the ideal one and of a simple nature.

The range 4 is limited towards higher densities by the curve A in Fig. 1.1 where the quantum effect of degeneracy of electrons will occur. The particles will then have a quantum energy E_q which is higher than the thermal energy. This quantum energy $E_q = p^2/2m$ corresponding to a momentum p is determined by the length $x = 1/n^{1/3}$ of the cube into which the electron with its density n is packed, which has to obey quantization

$$xp = h \tag{1.4}$$

resulting in

$$E_q = \frac{h^2}{2m} n^{2/3} \tag{1.5}$$

Taking into account that each of these volumes can be occupied by two electrons due to the spin and including the correct geometric factors for the spherical atoms, the quantum energy E_q is given by the Fermi energy with the electron density n given in cm^{-3}

$$\varepsilon_F = \frac{h^2}{2m_0} n^{2/3} \frac{(3/\pi)^{2/3}}{4} \tag{1.6}$$

$$= 5.82 \times 10^{-27} n^{2/3} \text{erg} = 3.652 \times 10^{-15} n^{2/3} \text{eV}$$

It is worth noting that this quantum energy is not only related to particles with a spin of $\frac{1}{2}$ (Fermions) following the Fermi–Dirac statistics (Dirac

1926; Fermi, 1928) but it is a basic quantum energy as described before. Only the density of states can be larger than that of the electrons. It is therefore of interest to note curve B for protons in Fig. 1.1, above which density the quantum energy is higher than the temperature.

The relativistic extension of these limits by using the particle velocity v and the electron rest mass m_0 for the energy $E = m_0c^2[(p^2/m_0{}^2c^2) + 1]^{1/2}$ where $p = m_0v/(1 - v^2/c^2)^{1/2}$, one arrives at the relativistically generalized Fermi energy

$$\varepsilon_F = \frac{(3/\pi)^{2/3}}{4}\frac{h^2}{2m_0}n^{2/3}\frac{1}{(\lambda_c/2)[n + 1/(\lambda_c/2)^3]^{1/3}} \tag{1.7}$$

where the Compton wave length of the electron $\lambda_c = h/m_0c$ was used. Above the density $n_c = \lambda_c{}^{-3}$, the Fermi energy of the electrons is relativistic

$$\varepsilon_F = hcn^{1/3}\frac{(3/\pi)^{2/3}}{4}(n > \lambda_c{}^{-3}) \tag{1.8}$$

and does not depend on the particle mass. For lower densities, (1.7) reduces to (1.6). The quantum (Fermi) energies for protons and electrons merge into the same lines in Fig. 1.1 at high energies, where the relativistic particles cannot be distinguished by their mass. The same phenomenon is known from charges oscillating in a laser field or black body radiation: if the oscillation energy becomes relativistic, the particles have the same energy and cannot be distinguished by their mass (Hora 1981). For temperatures above m_0c^2 and at degenerate densities (Range 5), the electrons cannot follow Fermi–Dirac statistics as will be shown in the Section 1.5 because of strong coupling to the black body radiation.

The remaining part of Fig. 1.1 for temperatures below m_0c^2 and above curve A of degeneracy, is characterized by the limit of relativistic Fermi energy $n_c = (1/\lambda_c)^3$, by the range where nuclear reactions are starting – even for low temperatures – which is for example related to picnonuclear reactions (Harrison 1964) as seen also from an increase of fusion cross-sections at high temperatures (Ichimaru 1984; Niu 1981). We refer also to Brush (1967) concerning these low temperature high density nuclear reactions.

At densities above $10^{34}\,\text{cm}^{-3}$, the reaction between protons p and electrons e to produce neutrons n and neutrinos ν

$$\text{p} + \text{e} = \text{n} + \nu \tag{1.9}$$

will start. The line of relativistic 'Fermi energy' of baryons (protons or neutrons) is therefore heuristic only. The cold fusion of protons to neutrons at these densities of $10^{35}\,\text{cm}^{-3}$ is easily understood from the fact that each electron is then compressed to a diameter of about 2×10^{-12} cm. At these densities electrons have sufficient quantum energy of compression, and can add to the protons which have the same radius. Reaction (1.9) should not be considered as the usual collision process. At lower densities than 10^{35} cm^{-3} the electron simply cannot unite with the proton because it would first need quantum energy, to be compressed to the size of the proton. This is the reason why we – contrary to Brush (1967) – drew the shaded area of the neutron generation for increasing density at higher temperatures, as the thermal motion will reduce the fusion reaction. Huge numbers of neutrinos should be emitted at these densities.

This is the range of densities where nuclear matter can be studied by heavy nuclei collisions. Shock waves are then generated and the density can reach five times the density of nuclear matter. Knowledge of the valid equation of state is then essential (Scheid *et al.* 1974; Stöcker *et al.* 1978; Stöcker 1986) and its details can be studied indirectly from the reactions following the 10^{-13} s duration state of the united nuclei (Stock 1984).

If the mass within the Schwarzschild radius of the Sun

$$R = 2M_0\gamma_0/c^2 \tag{1.10}$$

($\gamma_0 \approx$ gravitation constant, $M_0 \approx$ solar mass) is given the resulting density is the Schwarzschild density as shown in Fig. 1.1. One should note that younger stars of larger mass have a lower Schwarzschild density.

1.3 Quantum pressure and compressibility

In order to demonstrate that the quantum (Fermi) pressure really acts as a pressure even if the temperature of the electrons is very much lower than ε_F, we mention here as an example of its action the compressibility of solids by the quantum pressure.

For the ideal equation of state, (1.2), the compressibility (using $V = 1/n$) is

$$\kappa = -\frac{1}{V}\frac{\partial V}{\partial P} = \frac{1}{P} \tag{1.11}$$

For solids there was the theory of Madelung (1918) (see, e.g., Joos 1976) which was modified slightly later. This was based on the ad hoc assumption of a potential where the best possible fit of the exponent for the radial dependence was found to be of the number nine. Contrary to this highly hypothetical relation, we can explain the compressibilities of solids with a better fit and slope of the plot of the experimental values of the compressibility over three orders of magnitude in dependence on the electron density, if we take the quantum pressure of the valence electrons