

}
AN INTRODUCTION TO

equations of state


THEORY AND APPLICATIONS

SHALOM ELIEZER

AJOY GHATAK

HEINRICH HORA

EDWARD TELLER



AN INTRODUCTION TO

equations of state

THEORY AND APPLICATIONS

SHALOM ELIEZER

Department of Plasma Physics, SOREQ Nuclear Research Centre, Israel

AJOY GHATAK

Department of Electrical Engineering, National University of Singapore

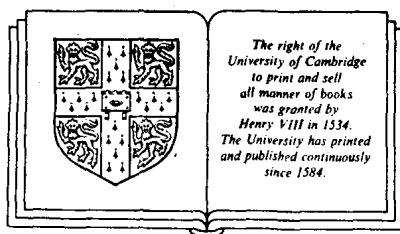
HEINRICH HORA

Department of Theoretical Physics, University of New South Wales, Australia

with a Foreword by

EDWARD TELLER

Lawrence Livermore National Laboratory, USA



CAMBRIDGE UNIVERSITY PRESS

Cambridge

London New York New Rochelle

Melbourne Sydney

Published by the Press Syndicate of the University of Cambridge
The Pitt Building, Trumpington Street, Cambridge CB2 1RP
32 East 57th Street, New York, NY 10022, USA
10 Stamford Road, Oakleigh, Melbourne 3166, Australia

© Cambridge University Press 1986

First published 1986

Printed in Great Britain at the University Press, Cambridge

British Library cataloguing in publication data

Eliezer, Shalom

An introduction to equations of state: theory
and applications.

1. Mathematical physics 2. Equations of state

I. Title II. Ghatak, A.K. III. Hora, Heinrich
530.1'5 QC20.7.E6/

Library of Congress cataloging in publication data

Eliezer, Shalom.

An introduction to equations of state.

Bibliography: p.

Includes index.

1. Equations of state. I. Ghatak, Ajoy K

II. Hora, Heinrich, 1931-. III. Title.

QC173.4.E65E45, 1986 530.4 85-29094

ISBN 0 521 271

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 gigatmospheres 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

Shalom Eliezer
Ajay Ghatak
Heinrich Hora

CONTENTS

<i>Foreword</i>	ix
<i>Preface</i>	xi
1 Introduction	1
1.1 General remarks	1
1.2 Phenomena at various densities and temperatures	2
1.3 Quantum pressure and compressibility	6
1.4 Pressure-temperature diagram	8
1.5 Radiation effects	11
2 A summary of thermodynamics	15
2.1 Phenomenology	15
2.2 Statistical picture	21
2.3 Maxwell-Boltzmann distribution	23
3 Equation of state for an ideal gas	28
3.1 The partition function	28
3.2 Thermodynamic functions	30
3.3 The Gibb's paradox	31
4 Law of equipartition of energy and effects of vibrational and rotational motions	34
4.1 Classical considerations	34
4.2 The partition function	40
4.3 The vibrational partition function	42
4.4 The rotational partition function	44
4.5 The electronic partition function	47
4.6 Summary	47
5 Bose-Einstein equation of state	49
5.1 Introduction	49
5.2 Classical statistics	50
5.3 Bose-Einstein statistics without restriction on the total number of particles: photons	51

5.4	Bose–Einstein statistics for a constant number of particles	55
5.4.1	Bose–Einstein condensation	62
6	Fermi–Dirac equation of state	66
6.1	Overview	66
6.2	The grand partition function and other thermodynamic functions	66
6.2.1	The Fermi–Dirac distribution function	69
6.3	Relativistic considerations	76
6.4	Adiabatic processes	83
6.4.1	Non-relativistic case	83
6.4.2	Extreme relativistic case	84
7	Ionization equilibrium and the Saha equation	86
7.1	Introduction	86
7.2	The thermodynamic formulation	86
7.3	The Saha ionisation formula	89
8	Debye–Hückel equation of state	96
8.1	Introduction	96
8.2	Charged particle description	97
8.3	Electrostatic energy	99
8.4	Total free energy and equation of state	101
9	The Thomas–Fermi and related models	104
9.1	Overview	104
9.2	The Thomas–Fermi model at $T = 0$	105
9.2.1	Consideration of a gas of atoms	108
9.2.2	Solution of the Thomas–Fermi equation	109
9.2.3	Derivation of the Thomas–Fermi equation using variational principle	120
9.2.4	The kinetic and potential energies of an atom	121
9.2.5	Calculation of pressure	128
9.3	Inclusion of exchange interaction: the Thomas–Fermi–Dirac equation	132
9.3.1	Calculation of pressure	136
9.4	Derivation of equation (9.103) using the virial theorem	139
9.5	The Thomas–Fermi model at finite temperatures	141
9.5.1	Calculation of thermodynamic functions	144
9.6	Exchange and quantum corrections to the Thomas–Fermi model	149
10	Grüneisen equation of state	153
10.1	Introduction	153
10.2	The Einstein model of solids	155
10.3	The Debye model of solids	157
10.4	The Grüneisen relation	160
10.5	Slater–Landau calculation of γ	161
10.6	Results and discussion	164

11	An introduction to fluid mechanics in relation to shock waves	165
11.1	Fluid equations of motion	165
11.1.1	Mass conservation equation	165
11.1.2	Momentum conservation equation	166
11.1.3	Energy conservation equation	167
11.2	Sound waves and Riemann invariants	169
11.3	Rarefaction waves	173
11.4	Shock waves and the Hugoniot relation	176
12	Derivation of hydrodynamics from kinetic theory	184
12.1	Foundations of hydrodynamics	184
12.2	Distribution functions and the Boltzmann equation	185
12.3	Loss of information	189
12.4	Derivation of macroscopic equations	190
12.4.1	The equation of continuity (mass conservation)	191
12.4.2	The equation of motion (momentum conservation)	191
13	Studies of the equations of state from high pressure shock waves in solids	197
13.1	Introduction	197
13.2	The Grüneisen coefficient $\gamma(V)$ and an equation for the cold pressure P_c	200
13.3	The specific volume V_{0c} of the 'zero point' and the initial conditions for the P_c equation	204
13.4	Isentropic processes near the Hugoniot curve and the free surface velocity	208
13.5	Equations of state for aluminum, copper and lead	210
13.6	Semi-empirical interpolation equation of state	217
14	Equation of state and inertial confinement fusion	221
14.1	Pellet fusion	221
14.2	The limiting case of isentropic (shock-free) volume ignition (self-similarity model)	223
14.3	Central core ignition with minimized entropy production	232
14.4	Alternative driving schemes: nonlinear force, cannon ball	242
14.4.1	The nonlinear-force pushing	242
14.4.2	The cannon ball scheme	244
14.5	The two-temperature equation of state	246
14.5.1	Electronic contributions to the EOS	247
14.5.2	The ion contributions to the EOS	248
14.5.3	Results and discussion	255
15	Applications of equations of state in astrophysics	257
15.1	Overview	257
15.1.1	The equation of state for an ideal gas	259
15.1.2	The equation of state for a degenerate electron gas	262
15.1.3	The radiation pressure	267

15.2	The equation of hydrostatic equilibrium	267
15.3	Expressions for pressure and temperature inside a star	269
15.4	Numerical estimates of P_c , \bar{P} and \bar{T} by assuming uniform density inside the star	272
15.5	Some useful theorems	273
15.6	The gravitational potential energy and the virial theorem	274
15.6.1	The gravitational potential energy	274
15.6.2	The virial theorem	275
15.7	Qualitative understanding of the evolution of a star	279
15.8	The contribution due to radiation pressure	283
15.9	The polytropic model	286
15.10	The standard model	294
15.11	The white dwarf stars	299
15.11.1	Solution of the equation of hydrostatic equilibrium for a completely degenerate gas in the extreme relativistic limit	300
15.11.2	The general solution corresponding to a completely degenerate gas	301
16	Equations of state in elementary particle physics	305
16.1	Overview	305
16.2	Hagedorn model of strong interactions	306
16.2.1	Introduction	306
16.2.2	The partition function	308
16.2.3	The bootstrap condition	310
16.2.4	The thermodynamic functions: pressure and energy	315
16.2.5	Transverse momentum distribution	317
	Appendixes	321
1	A free particle inside a box and the density of states	321
2	The Stirling formula	325
3	Table of Fermi–Dirac functions	326
4	Derivation of the virial theorem result	333
5	Tables of Thomas–Fermi corrected equation of state	337
6	Some mathematical relations for Chapter 13	351
7	A note on the Lawson criterion	353
8	Derivation of the equation describing hydrostatic equilibrium for a completely degenerate gas	354
	References	355
	Index	362

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 century, there is again

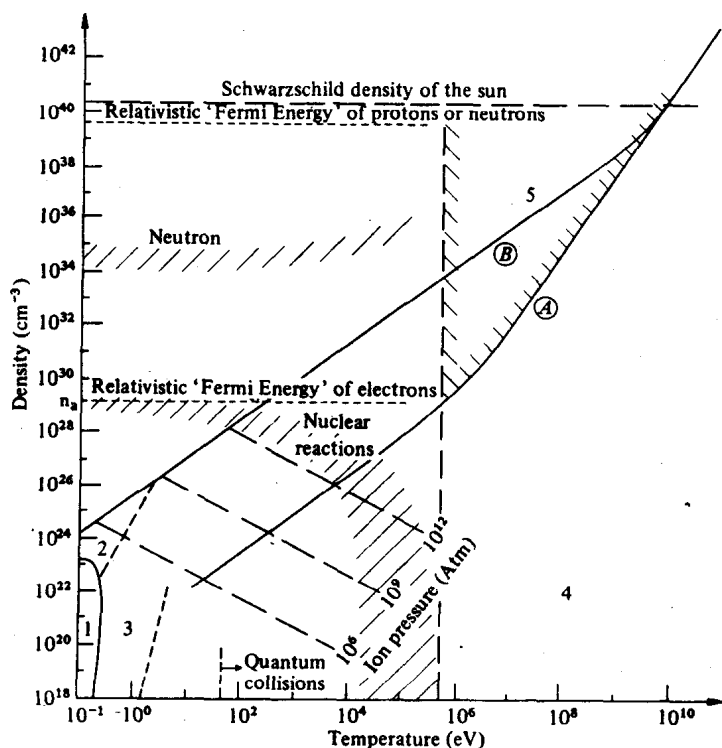
now a high priority in modern physics to solve the numerous deficiencies in our knowledge of equations of state. The development of equations of state is again sought to meet the needs of the rapidly advancing modern physics of extreme states of matter.

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

$$PV = RT \quad (1.1)$$

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

$$P = nkT \quad (1.2)$$

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 Nozières 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^*

$$kT^* = \frac{4}{3} Z^2 m_0 c^2 \alpha^2 \quad (1.3)$$

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

$$xp = h \quad (1.4)$$

resulting in

$$E_q = \frac{h^2}{2m} n^{2/3} \quad (1.5)$$

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}

$$\begin{aligned} \varepsilon_F &= \frac{h^2}{2m_0} n^{2/3} \frac{(3/\pi)^{2/3}}{4} \\ &= 5.82 \times 10^{-27} n^{2/3} \text{erg} = 3.652 \times 10^{-15} n^{2/3} \text{eV} \end{aligned} \quad (1.6)$$

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 $E = m_0 c^2 [(p^2/m_0^2 c^2) + 1]^{1/2}$ where $p = m_0 v / (1 - v^2/c^2)^{1/2}$, one arrives at the relativistically generalized Fermi energy

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

where the Compton wave length of the electron $\lambda_c = h/m_0 c$ was used. Above the density $n_c = \lambda_c^{-3}$, the Fermi energy of the electrons is relativistic

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

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 $m_0 c^2$ 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 $m_0 c^2$ 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} cm^{-3} , the reaction between protons p and electrons e to produce neutrons n and neutrinos ν



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} 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

$$R = 2M_0\gamma_0/c^2 \quad (1.10)$$

($\gamma_0 \approx$ 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

$$\kappa = -\frac{1}{V} \frac{\partial V}{\partial P} = \frac{1}{P} \quad (1.11)$$

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