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Werner Ebeling
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Vladimir Filinov

Quantum Statistics of Dense Gases and Nonideal Plasmas

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Preface

The physics of dense gases and nonideal plasmas, along with the physics of matter with high energy density, form together a growing field. The physics of dense gases is connected with the name of the pioneer Johannes Diderik van der Waals from the Netherlands (Nobel Prize 1910). The foundations for the theory of nonideal plasmas were laid 50 years later by another pioneer from the Netherlands, Peter Debye (Nobel Prize 1936), with the introduction of the screening concept. So it should be no surprise that the quantum statistics of dense gases also began in the Netherlands with the work of Uhlenbeck and Beth in 1936/1937. Important contributions to the physics of real gases are due to subsequent work by Mayer, Fuchs, Kirkwood, Bogolyubov, Yvon, Born, and Green. This development culminated in the van der Waals Centennial Conference in Amsterdam 1973 and international conferences on statistical physics organized by the IUPAP.

The physics of nonideal plasmas, otherwise known as strongly coupled plasmas, began with the work of Debye and Hückel, Onsager, Falkenhagen, Bjerrum, Eggert, and Saha in the 1920s and culminated in the 1960s. The first conference on "Strongly Coupled Plasmas" was held in 1977 in Orleans la Source, France, and was followed by a series of conferences under this name. A parallel series called "Physics of Nonideal Plasmas" started in 1980 in a village near Rostock, and then continued biennially, with the latest in Almaty, Kazakhstan, in 2015. The physics of extreme states of matter is still in *status nascendi*. The increasing interest in dense gases and plasmas is connected with the fact that more than 99% of the visible Universe is evidently in this state, and a large part of this exists at extremely high energy density. We are only just beginning to explore the world outside the narrow window of the little solid state planet on which we live. In order to understand our place in the Universe, we have to extend research to dense gases and plasmas including exotic states.

In this view, we feel like part of a large international collaboration which includes many researchers, universities, and very big research organizations such as CERN in Geneva, DESY in Hamburg, UNILAC and SIS in Darmstadt, ITEP in Moscow, SPS, LHC, and so on. A second group of big international collaborations like COBE and subsequent projects is concentrating on the study of astrophysical objects. This is also at present at the forefront of international research. It is based on new possibilities for observing distant objects from satellites and rockets. Many exciting insights have come recently from this field.

However, this book is definitely not about big colliders, telescopes, and space missions. Our aim is to explore the basic physics and in particular the quantum statistical thermodynamics and kinetics of states of matter, starting from dense gases and nonideal plasmas and ending with matter at high energy densities. We are convinced that thermodynamics and quantum statistics are still the main foundation on which even the most advanced research is being built. In spite of the development of so many modern concepts, the seemingly old concepts of thermodynamics and transport are still the basis for the whole field.

The body of the present book is based on lectures at universities and presentations at seminars and international conferences. Furthermore, the book draws upon many original publications and in particular on a long collaboration between the present authors which started in the 1970s. We mention in particular:

- The courses of lectures on quantum statistics and plasma physics given by Werner Ebeling at the University of Rostock between 1970 and 1979, at the University of Paris VI in 1977, at the Humboldt University in Berlin, between 1980 and 2001, and in guest lectures in Minneapolis 1986, Moscow 2003, and Krakow 2005. The latest full lecture cycle was given at Humboldt University in Berlin by Werner Ebeling in collaboration with Thorsten Pöschel and several former coworkers, including Dieter Beule, Andreas Förster, Lutz Molgedey, Jens Ortner, Waldemar Richert, and Ilya Valuev, and several former students and aspirants, including Jörn Dunkel, Hendrik Hache, Stefan Hilbert, Dirk Holste, Ines Leike, Ulf Leonhardt, Burkhard Militzer, Thomas Pohl, Saltanat Sadykova, Friedemann Schautz, Michael Spahn, Mario Steinberg, and others.
- Lecture courses given by Vladimir Fortov at the Moscow Institute of Physics and Technology on extreme states of matter on earth and in the cosmos (Fortov 2008, 2009, 2011).
- Presentations of the present authors at a series of international conferences, such as the IUPAP conferences under the headings “Statistical Physics” (STATPHYS), “Strongly Coupled Coulomb Systems” (SCCS), and “Physics of Nonideal Plasmas” (PNP).
- The long-standing collaboration between the authors and their colleagues in Berlin, Rostock, Moscow, and other research centers around the world, resulting in many shared articles and several shared books since the 1980s.

Following the personal interests of these authors, which go along the same lines in the tradition of quantum statistical thermodynamics in Berlin, Rostock, and Moscow, we concentrate on the development of fundamentals and applications to gases and plasmas, including dense nonideal and exotic gases and plasmas. Most of the existing textbooks and monographs on quantum statistics have some bias toward condensed matter and solid states.

This book is written at an intermediate level and addressed to students and young scientists at an advanced level. We include a few results obtained only recently. In general, the book should be accessible to students of the higher semesters, doctorands, and young researchers in the field. We have tried to be self-contained, repeating, and explaining the most relevant tools.

During their careers, the present authors, or at least some of them, have actually met several of the pioneers of the quantum statistics of dense gases and plasmas, such as Alexander A. Abrikosov, Nikolay N. Bogolyubov, Alexander S. Davydov, Hans Falkenhagen, Michael Fisher, Vitali L. Ginzburg, Günter Kelbg, Yuri L. Klimontovich, Rolf Landauer, Joel Lebowitz, Joseph E. Mayer, Ruslan L. Stratonovich, Alexander A. Vedenov, Yakov B. Zeldovich, and others. These people influenced our views through their advice and personal discussions, and so we must express our gratitude to them. In particular, we are grateful to Günter Kelbg, Yuri L. Klimontovich, and Yakov B. Zeldovich. Furthermore, we are very grateful for a long and very fruitful collaboration with many colleagues in the field, including David Blaschke (Wroclaw), Michael Bonitz (Kiel), Alexander Chetverikov (Saratov), Dietmar Ebert (Berlin), Viktor A. Gryaznov (Chernogolovka), Holger Fehske (Greifswald), Yuri B. Ivanov (Moscow), Wolf D. Kraeft (Greifswald), Dietrich Kremp (Rostock), Pavel Levashov (Moscow), Genri Norman (Moscow), Gerd Röpke (Rostock), Ronald Redmer (Rostock), Heidi Reinholz (Rostock), Manfred Schlanges (Greifswald), Boris Sharkov (Moscow), Werner Stolzmann (Kiel), Sergey Trigger (Berlin), and Manuel G. Velarde (Madrid). We should also mention that the last two chapters were written in close collaboration with A.S. Larkin, who provided the main contributions to the results. Particularly sincere thanks go to Thorsten Pöschel, who actively participated in the lectures at Humboldt University in Berlin and wrote lecture notes describing the basic tools of quantum statistics, which will appear separately.

In conclusion, let us express the wish that the present book might contribute to the general education of the present generation of physicists in the field of dense fluids. Two of the authors are theoreticians, while the other (V.E.F.) took part in many pioneering experiments in the field, including experiments with extreme pressures generated by shocks or laser beams which helped, e.g., in experimentally confirming plasma phase transitions. V.E.F. has also been in charge of major international research projects and experiments. When running these and other big research projects in our field, we have reached the conclusion that physicists of the younger generation need more knowledge and ability to solve problems involving dense gases, nonideal plasmas, and extreme states of matter. We hope the book will help them to understand the problems and methods of a rather new and fascinating field.

Berlin, Germany — Werner Ebeling
Moscow, Russia — Vladimir E. Fortov
Moscow, Russia — Vladimir Filinov
May 2017

Contents

Chapter 1
Physics of Dense Gases, Nonideal Plasmas, and High Energy Density Matter

Here we summarize the most important results in this field of physics, which is growing due to the dominant role of these forms of matter in the cosmos. We describe the progress made in physical studies and the statistical theory of dense gases and nonideal plasmas, including their historical roots in the work of van der Waals, Debye, Saha, Planck, Einstein, and others. We present the basic tools required for the quantum statistical description of nonideal fluid systems, including analytical methods and computer simulations, and we discuss studies of plasma-like matter with high energy density.

1.1 Strongly Coupled Fluid Matter: A New Field of Physics

In 1873, in his dissertation presented at the University of Leiden, the Dutch physicist Johannes Diderik van der Waals developed a new model of dense gases and fluids. This work opened the way to understanding matter in nonideal states (van der Waals 1873) (see Fig. 1.1). By *nonideal states* we mean here states of matter that are not described by the classical ideal gas law, i.e., the relation between pressure, density, and temperature $p = nk_B T$. Fifty years later, Peter Debye (1884–1966), another eminent Dutch scientist, founded the science of nonideal Coulomb systems with a lecture given in 1923 to the Nederlandsch Natuuren Congres (see Fig. 1.2). The enormous progress made in the science of nonideal gases and nonideal plasmas in the 100 years after the initiation by van der Waals and his school and 50 years after the work of Debye and his school was summarized in 1973 at the van der Waals Centennial Physics Conference in Amsterdam.

Many physicists believe that this field is of less importance than the physics of condensed matter, since solid state electronics has such a big impact on our everyday life. But this is certainly a form of ignorance on their part, since less than one percent of matter in the Universe is in a condensed state. More than 99 percent of our world

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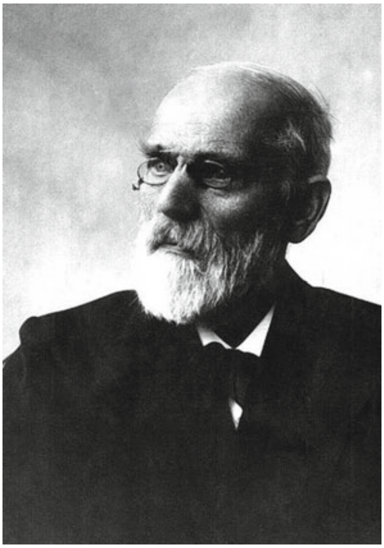

Fig. 1.1 J. D. van der Waals (1837–1923), Nobel Prize 1910. Photo from Nobelprize.org

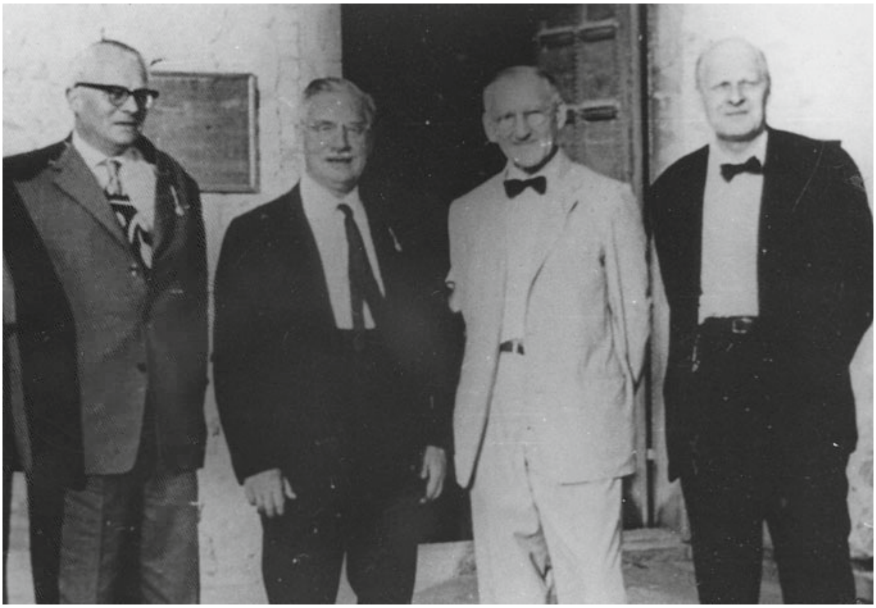

Fig. 1.2 Peter Debye (1884–1966), Nobel Prize 1936, and his coworkers (Hans Falkenhagen, left, Kasimir Fajans, second from the right, and Lars Onsager, right). Photo from Falkenhagen's archive

is in a gaseous, plasma, or extreme fluid state. Our planet is surrounded by a gas atmosphere and we use gases in many technological devices. Space around the Earth and interstellar matter is mostly in a gaseous or plasma state. Furthermore, we should not forget the matter in the Sun and the many stars, from the giants to the white dwarfs and exotic stars such as neutron stars and others, as well as many less known objects like 'dark matter'.

In the last few decades, condensed states of matter have dominated physicists' education, but we should bear in mind that, on the scale of the Universe, the solid state is a relatively rare form of matter. This rather special state is based on bound states of electrons and nuclei, forming atoms and molecules. Bound states exist only in a small region of density and temperature. Such conditions came into existence a few billion years ago on our planet and made the evolution of life and technology possible (see, e.g., Feistel et al. 1989, 2011). Life is based on the existence of atoms and molecules as bound states of electrons and nuclei. However, in most parts of our Universe, e.g., in stars, atoms do not exist, since the densities and temperatures are too high. Most matter is in extreme plasma states under very high pressure, like the matter in white dwarfs and neutron stars. The physics of gases and plasmas at high pressures and temperatures plays an important role in our understanding of the structure and evolution of astrophysical objects: neutron and 'strange' quark stars, black holes, pulsars, supernovas, magnetars, giant planets, and exoplanets. In the future, this new physics may also be relevant for technological development (Fortov 2011, 2013).

In the last few decades there has been extensive work on dense plasmas, with applications ranging from inertial confinement fusion, Z-pinch experiments, X-ray Thompson scattering, and exploding wire experiments to describing the astrophysics of white dwarfs and the interiors of giant planets (Fortov 2011, 2013).

In the present book we consider mostly dense forms of hydrogen, helium, and other noble gases and plasmas, as well as alkali plasmas. A topic of special interest to us is chemical and phase equilibria. Central issues are the influence of strong coupling on the equation of state and transport properties. Experimental methods are not discussed in detail in the present book. A minimum of information is given about important experiments and references (for more detail, see Fortov 2009, 2011, 2013).

1.2 Physics of Dense Classical Fluids

1.2.1 Van der Waals Equation of State and Interactions

The theory of gases developed in the dissertation presented by van der Waals in 1873, and this may be considered as the starting point for the modern theory of nonideal fluids and phase transitions. Van der Waals' approach was based on a simple physical model of interactions between particles which takes into account short range repulsive and long range attractive forces.

The model equation for the pressure is

$$p = \frac{k_{\mathrm{B}}T}{v-b} - \frac{a}{v^2}\,, \qquad v = \frac{V}{N} = \frac{1}{n}\,, \tag{1.1}$$

where V is the volume, N the particle number, n the density, and T the temperature. The van der Waals model predicts that, below a critical temperature T_{c}, there will coexistence two phases which differ from each other by the density of molecules. In connection with the development of more rigorous theories, it became clear that van der Waals' approach is restricted to relatively weak attractive forces which either decay with the distance faster than $1/r^3$ or satisfy the so-called Kac conditions. Therefore the conditions for applicability to Coulomb forces are not given.

Prototype Models of Interaction

There are hundreds of models describing the interactions between molecules, atoms, or elementary particles (Hirschfelder et al. 1954). There are forces of attraction like van der Waals forces, chemical forces, etc., and repulsive forces due to Coulomb repulsion between charges and the Pauli principle. The typical shape is a decaying function with a minimum. Such systems are called prototype models when they play a special role, either because they possess some universality for classes of real substances or because they allow exact solutions. We restrict our study mainly to three-dimensional problems.

The simplest model of interactions is the hard-sphere model. The interaction between two hard spheres with diameter d is described by the hard core potential:

$$U_{\mathrm{HC}}(r) = \begin{cases} \infty & \text{if} r < d, \\ 0 & \text{if} r \geq d. \end{cases} \tag{1.2}$$

Including a range of attractions yields the piecewise constant square-well potential. Many results exist also for a prototype model with softer repulsion (Hansen et al. 1976):

$$U_{\mathrm{SR}}(r) = \varepsilon \frac{a^n}{r^n}\,, \qquad n = 6, 9, 12, \dots\,. \tag{1.3}$$

These potential models are more or less empirical. The Coulomb potential is the special case with $n = 1$. Calculations based on quantum-mechanical first order perturbation theory yield an exponential repulsion based on the forces due to the Pauli exclusion for overlapping atomic core wave functions. In the simplest approximation, this leads to an exponential repulsive law:

$$U_{\mathrm{E}}(r) = U_0 \exp\big[-b(r-\sigma)\big]\,. \tag{1.4}$$

This potential contains the hard-core potential in the limit $b \to \infty$. Another interaction potential based on quantum mechanical calculations is the Morse potential:

$$U_{\rm M}(r) = D\Big\{\exp\big[-2b(r-\sigma)\big] - 2\exp\big[-b(r-\sigma)\big]\Big\}\,. \tag{1.5}$$

Here the positive term describes the repulsive forces due to the Pauli exclusion for overlapping atomic core wave functions. The negative term models qualitatively the attraction due to induced quantum-mechanical dipole–dipole forces.

The Toda model is an exponential potential with an additional (nonphysical) linear attraction, leading to a minimum of the potential at $r = \sigma$. Beside the depth of the potential $-D$, further important physical information is contained in the frequency of oscillations around the minimum $m\omega_0^2 = 2Db^2$ and in the stiffness of the potential which is proportional to the parameter b. The Toda potential is very useful since it allows fully analytical calculations. Figure 1.3 shows that the Toda potential and the Morse potential agree nicely at smaller distances, up to the minimum and a bit beyond. Note that a good fit of the Toda and Morse potentials is obtained near the minimum if the Toda parameters are related to the Morse parameters by the relations $a_{\rm T} = (2/3)bD$, $b_{\rm T} = 3b$ (Chetverikov et al. 2011).

A prototype model closely related to the exponential and the Morse model of interactions is the Yukawa model:

$$V_{ab}^{\rm Y}(r) = g_{ab}\frac{\exp(-\eta r)}{r}\,. \tag{1.6}$$

This potential was developed by Hideki Yukawa in 1935 in order to describe strong forces in elementary particle physics, mediated by the exchange of massive particles. The Yukawa potential now plays a paradigmatic role in statistical physics, since it has found applications in many fields (Fortov 2013). We will use this potential as a standard model for a gas with weak interactions and in particular for a quantum gas with weak interactions. A specially important property of the Yukawa potential is the existence of a Fourier transform, which is defined by

$$\tilde{V}_{ab}^{\rm Y}(\mathbf{t}) = \int_V \mathrm{d}\mathbf{r}\, V_{ab}^{\rm Y}(r)\exp(\mathrm{i}\mathbf{t}\cdot\mathbf{r}) = \frac{4\pi g_{ab}}{t^2+\eta^2}\,. \tag{1.7}$$

The Yukawa potential contains the Coulomb potential in the limit $\eta \to 0$. The interaction between two charges e_a and e_b is described (in rational units) by the potential

$$V_{ab}(r) = \frac{e_a e_b}{\varepsilon_{\rm r} r}\,. \tag{1.8}$$

In most cases we will assume without comment that the charges are in a vacuum $\varepsilon_{\rm r} = 1$.

The Coulomb potential is long-range. It was Joseph E. Mayer (1904–1983) who first noticed that the Fourier transform of the Coulomb potential is of primary importance for solving problems of screening and cluster theory (Mayer 1950). Strictly speaking, the integral over the volume is divergent for Coulomb interactions when the volume is infinite. This is an important problem and the Coulomb potential in its

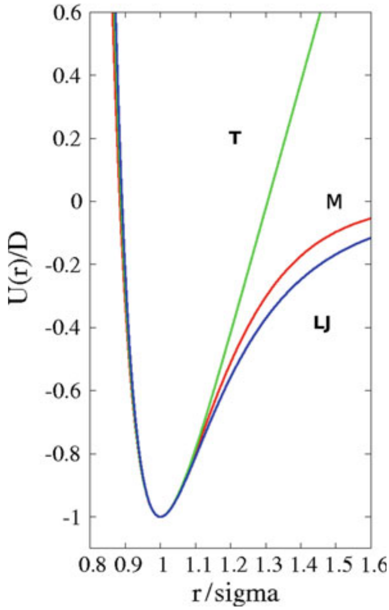

Fig. 1.3 Interaction between the atoms: The depth, frequency, stiffness, and other details about the interaction of atoms may be fitted by different potentials. Here we represent the Toda potential (*upper curve*), the Morse potential (*middle curve*), and the (r^{-12}, r^{-6}) Lennard-Jones potential (*lower curve*), suitably scaled around the minimum to have identical values at the minimum and identical values of the second derivative (frequency) and the third derivative (stiffness)

original form, needs some regularization. The great pioneer of the statistical theory of Coulomb systems, Joseph Mayer, proposed to introduce the Coulomb potential as the limit of a Yukawa potential for small $\eta \to 0$. This leads to a well defined limit for the Fourier transform.

One of the most popular models in the theory of gases and liquids is the Lennard-Jones (6–12)-potential which is semi-empirical with respect to the repulsive part, but well founded by quantum calculations for the attractive part. We scale here in such a way that the minimum $(-D)$ is at $r = \sigma$:

$$U_L(r) = D\left(\frac{\sigma^{12}}{r^{12}} - 2\frac{\sigma^6}{r^6}\right) . \tag{1.9}$$

A more general form is the Lennard-Jones (n-m)-potential. Characteristics of the potential are the energy at the minimum D, the distance r_0 where the potential energy goes from positive to negative values (crosses zero), and the location of the minimum at $r = \sigma$. Some typical data are given in Table 1.1. Note that there are many other potential models on the market, each adapted to certain practical applications (Hirschfelder et al. 1954).

We consider in this book two classes of these prototype models with quite different methods:

1. Potentials with a hard core like the hard sphere, Morse, and Lennard-Jones potentials. Here the classical limit is well defined and normally quantum effects including degeneracy give only small corrections. A special case are gases at

Table 1.1 Lennard-Jones potential. Energy at the minimum D and location of the minimum σ for various molecules

Substance	D [eV]	σ [Å]
H_2	4.5	0.75
O_2	5.1	1.20
C_2	5.6	1.31
Cl_2	2.5	1.98

extremely small temperatures, where quantum effects are strong. However, these special systems are not the main focus of the book.

2. Potentials with no singularity at $r = 0$ or a weak singularity like r^{-1} and a relatively long tail at $r \to \infty$.

The main assumption is, however, that the Fourier transform is well defined. Examples are the Coulomb potential and the Yukawa potential. For this class of systems, quantum effects are strong as a rule. In particular, for the Coulomb system, the ground state is determined completely by quantum effects. Therefore perturbation theories around the classical limit make no sense in this case and quantum-statistical tools are essential from the very beginning. On the other hand, expansions with respect to interactions including weak correlations, but without any restriction due to degeneracy, are sometimes appropriate.

1.2.2 Statistical Theory of Dense Classical Gases

The van der Waals theory has a long prehistory which began in the seventeenth century (Simonyi 1990). Robert Boyle (1627–1691) experimented with gases and found the first gas law (Boyle's law), which says that at a constant temperature T, the volume V of a given mass of gas is inversely proportional to the pressure ($p = C/V$, where here and in the following C denotes an appropriate constant). The second perfect gas law says that, at constant volume, the absolute pressure is proportional to the absolute temperature ($p = CT$). One application is the hydrogen thermometer. Standard temperature and pressure are defined as 273.15 K (0 degrees Celsius) and 101.325 kPa (760 mm Hg).

To change the state of a gas, heat is either added or taken away from it. If the state of a gas is altered without a change in heat, we speak about an adiabatic change. If a compressed gas expands adiabatically, cooling occurs. Since atoms and molecules interact by attractive forces, energy is required as the gas expands to overcome the intermolecular forces. A gas cools as it expands, and if it is rapidly compressed, its temperature rises. Dalton's law of partial pressures says that, in a mixture of gases, the pressure each gas exerts is the same as if it alone occupied the volume. Avogadro's law states that equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. A mole is the amount of a substance containing the number of particles 6.022×10^{23}. Combining the perfect gas laws and Avogadro's law, we get the universal ideal gas law due to Gay-Lussac (1778–1850):

$$p = \nu RT/V \ , \qquad \text{or} \quad p = nk_\mathrm{B}T \ , \qquad n = N/V \ , \tag{1.10}$$

where ν is the number of moles, N is the corresponding number of molecules, R is Avogadro's constant, and k_B is Boltzmann's constant. The energy density of an ideal gas is given by

$$\rho_\mathrm{E}(T) = c_v nT \ . \tag{1.11}$$

Here, c_v is the specific heat, which for normal gases is $c_v = fk_\mathrm{B}/2$, with f the number of degrees of freedom.

An adiabatic process is one without transfer of heat or matter between a system and its surroundings. The equation of state for such processes reads

$$p = Cn^\gamma \ , \qquad \gamma = \frac{2+f}{f} \ , \tag{1.12}$$

with $\gamma = 5/3$ for normal gases and C an appropriate constant.

In a first approach, the definition of temperature scales may be fixed by using the universality of the ideal gas law and fixing the triple point of water by definition to $T_\mathrm{c} = 273.16\,\mathrm{K}$. The triple point of water is that unique temperature at which pure ice, pure water, and pure water vapor can coexist at equilibrium. The triple point is important since there is only one pressure at which all three phases can be in equilibrium with each other.

Soon after van der Waals' work, the method of virial expansions for non-ideal gases was developed. This expansion, which expresses the pressure of a many-particle system in equilibrium as a power series in the density, was introduced in 1901 by Heike Kamerlingh Onnes (1853–1926, Nobel Prize 1913), is a natural generalization of the ideal gas law. Kamerling Onnes represented the pressure of a gas with density n and temperature T as a power series in the density n ($\beta = 1/k_\mathrm{B}T$):

$$\beta p = -\left(\frac{\partial(\beta F)}{\partial V}\right)_{T,N} = n\left[1 - nB_2 - 2n^2B_3(T) - \cdots\right] \ . \tag{1.13}$$

The corresponding expansion for the free energy is

$$F = F_\mathrm{id} - k_\mathrm{B}TV\left[n^2B_2(T) + n^3B_3(T) + \cdots\right] \ . \tag{1.14}$$

An elementary way to get the virial functions including interaction effects starts from the binary correlation functions $g(r)$. By definition, in a fluid of density n, the number of particles in a shell of thickness $\mathrm{d}r$ at distance r from a given center particle is

$$g(r)(4\pi nr^2)\mathrm{d}r \ . \tag{1.15}$$

In a first classical approximation, the binary correlations are given by a Boltzmann factor $g(r) \sim \exp(-\beta U(r)$ and provide the first order mean potential energy

$$g(1,2) = \exp\big[-\beta V(1,2)\big]\,,$$
$$U = \langle U(r)\rangle = \frac{1}{2}\int d\mathbf{r}_1 d\mathbf{r}_2 U(\mathbf{r}_1,\mathbf{r}_2)\exp\big[-\beta U(\mathbf{r}_1,\mathbf{r}_2)\big]\,. \tag{1.16}$$

Since the internal energy U and the free energy F are connected by the thermodynamic relation $U = \partial(\beta F)/\partial\beta$, for the second virial coefficient, we find by integration

$$B_2(T) = \frac{1}{2}\int d\mathbf{r}\Big\{\exp\big[-\beta V(\mathbf{r})\big] - 1\Big\}\,. \tag{1.17}$$

For the higher order virial coefficients we may derive explicit expressions by using the cluster expansion methods of statistical mechanics worked out by Joseph Mayer (1904–1983), Klaus Fuchs (1911–1988), and others (Hirschfelder et al. 1954; Hill 1956; Friedman 1962; Barker and Henderson 1967).

A survey of the state of the art in the theory of nonideal gases was given in 1973 at the Van der Waals Centennial Conference. The program demonstrated that most prominent scientists in the field like de Boer, Lebowitz, Langer, Widom and Wilson honored van der Waals were working to develop this further (see Fig. 1.4). In particular, we mention reports on the statistical foundations of the van der Waals equation by Klein and Lebowitz and the theory of fluid phase transitions by Langer, Levelt-Sengers, Widom, and Wilson.

1.3 Quantum Physics of Strongly Coupled Gases

1.3.1 Correlations in Bose–Einstein and Fermi–Dirac Gases

The notion of *ideal gas* is not uniquely defined. Often one understands as 'ideal' a gas without interactions, i.e., having an additive Hamiltonian. However, this point of view overlooks the fact that coupling between the particles is more essential than the formal aspect of additivity. At high densities, Fermi–Dirac gases and Bose–Einstein gases are strongly coupled gases due to the Pauli principle and the corresponding exchange effects. So here we shall take an *ideal gas* to be just the usual classical ideal gas consisting of independent particles. Since coupling due to exchange effects plays an important role in dense gases, we first recall the theory of Bose–Einstein and Fermi–Dirac gases. Then we go on to consider the quantum statistics of real gases by including interaction forces, as was first done by Uhlenbeck and Beth in 1936–1937. As we pointed out above, Bose–Einstein and Fermi–Dirac gases are strictly speaking not ideal in the classical sense, since they show rather strong correlations with increasing degeneracy.

Van der Waals Centennial Conference on Statistical Mechanics

PROGRAM

Sunday, 26 August

Registration Desk	: 14.00 - 17.00	Registration
Lounges	: 17.00 - 18.00	Informal get together

Monday, 27 August

Main Hall

10.00	Official Opening	
10.30	J. de Boer	: Opening address
11.30	M. Klein	: Historical origins of the Van der Waals equation
14.00	J. L. Lebowitz	: Exact derivation of the Van der Waals equation
15.30	J. S. Langer	: Metastable states
16.30	J. M. H. Levelt Sengers	: Equation of state and thermodynamic correlations near the critical point

Rijksmuseum

20.30 Official reception

Tuesday, 28 August

Blue Room

9.00	B. Widom	: The critical point and scaling theory
10.30	K. Wilson	: The renormalization group and the critical point
11.30	A. V. Voronel	: High resolution specific heat measurements

14.00 Section meetings

Blue Room	: Critical phenomena
I - II	: Equilibrium properties of liquids
III	: Equation of state, equilibrium properties of gases
IV	: Correlation functions and transport

Fig. 1.4 Johannes D. van der Waals died in 1923, in the year Peter Debye presented the first theory of nonideal charged particle systems. Fifty years later, in 1973, the van der Waals Centennial was held in Amsterdam. Facsimile of the first page of the program

The first quantum statistics of a gas without interactions was in fact already developed in 1900 by Max Planck (1858–1947). Unfortunately, he started with a quite complicated case, the photon gas. This is due to the fact that his colleagues in Berlin had collected a lot of experimental data on radiation which needed theoretical interpretation. The photon gas is a relativistic system of particles with zero mass, i.e., it is a quite special case of a gas. The generalization of Planck's theory was given by Einstein in 1924 for particles with rest mass and integer spins, and for particles with half-integer spins by Fermi in 1926. Einstein's work was based on the happy occasion when the Bengali physicist Satyendra Nath Bose (1894–1974) sent his article *Planck's law and the hypothesis on light quanta* to Einstein. Einstein translated it into German and sent the article to Zeitschrift für Physik (1924), appending several remarks that essentially generalized Bose's approach. He immediately saw the power of Bose's method and the way to apply it to gases (Einstein 1924; Kirsten and Körber 1975; Ginzburg 2001).

Bose had in fact proposed a new method for counting the probabilities of the macrostates. In Bose's interpretation, the radiation field looks like a gas of photons. Einstein applied Bose's new counting method to derive the quantum statistics of monatomic ideal gases. Only eight days after the official date of receipt of Bose's paper, he presented his new results to a session of the Prussian Academy held on 10 July in Berlin. What Einstein appreciated above all was Bose's new method for counting probabilities based on the indistinguishability of identical particles (see Ebeling and Hoffmann 1991, 2014). Einstein successfully applied Bose's new method to derive the quantum statistics of monatomic ideal gases in three papers all printed in the "Sitzungsberichte" of the Prussian Academy of Science in Berlin.

The work in Bose and Einstein's papers was heavily criticized by Ehrenfest, Planck, and other colleagues, since neither Einstein nor Bose gave any deeper foundation to justify the new way of counting. Nernst and Schrödinger were among the first colleagues to support Einstein's new views. It was definitely Einstein who understood the connection between the new statistics and the indistinguishability of identical particles. The new view was a genuine revolution in physics, something that was first clearly understood by Planck and Ehrenfest, who expressed serious protests against Einstein's new views. The reason for these protests was in fact that these scientists immediately understood that the independence of the quantum gas particles was lost and that Einstein's method introduced as yet unknown quantum correlations between noninteracting particles.

The first physicist who understood the general physical principle behind the new mysterious correlations found by Einstein was Wolfgang Pauli, who formulated his exclusion principle in 1925. The first application of the new quantum statistics to the electron gas was given in 1926 by Enrico Fermi (1901–1954) and in the same year by Paul Dirac (1902–1984). Fermi–Dirac statistics applies to identical particles with half-integer spin in a system in thermodynamic equilibrium. The particles in this system have negligible mutual interactions. Note that very important applications of the new statistics were soon given by Fowler and Sommerfeld, who were treating electron plasmas with the new Fermi–Dirac statistics.

Today, particles that obey the exclusion principle, such as particles with spin $s = 1/2$, are called fermions, and particles with integer spins which are like the atoms in Einstein's theory are called bosons. Like Bose–Einstein gases, dense Fermi–Dirac gases also behave at low temperatures in a completely different way to the standard classical ideal gas. In order to demonstrate this, we consider the energy density, defined as the energy per unit of volume $\rho_E = E/V$. For Boltzmann gases, the energy density and the pressure increase linearly with density n and temperature

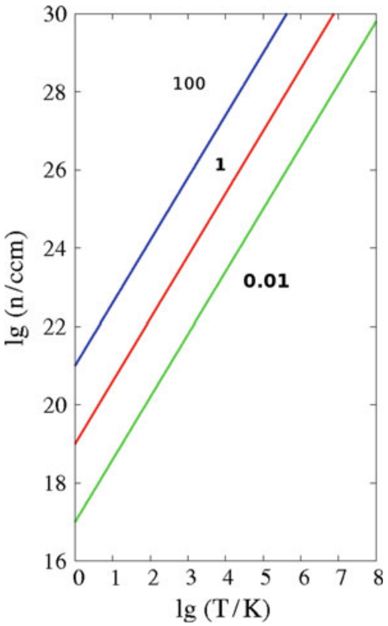

Fig. 1.5 Density–temperature plane for an electron gas on a log-scale, including the lines $n\Lambda^3 = 100, 1, 0.01$ separating strongly degenerate (*above upper line*) from moderately degenerate (*between lines*) from non-degenerate (*below lower line*)

T. For degenerate Fermi gases, the temperature dependence is rather weak, but the energy density and the pressure increase strongly with the density:

$$\rho_E = Cn^{4/3}, \qquad p = Cn^{4/3}. \tag{1.18}$$

As we will show later, due to the high pressures and energy densities in dense systems, all bound states will be destroyed at higher densities. Very dense fermion systems behave like Fermi–Dirac gases. The transition, which is rather sharp, occurs at a density where the thermal de Broglie wavelength begins to overlap (see Fig. 1.5).

We note that the behavior of a quantum gas changes at the transition from non-degenerate gas to degenerate gas, and the masses play a big role here. Typical Fermi systems consist of light electrons which soon reach degeneracy and heavy particles like nuclei which need extreme densities to become degenerate. For Bose gases, the changes at the degeneracy line may be even more dramatic. This was already observed by Einstein, who predicted a new condensation phenomenon in a second talk at the academy, given on 8 January 1925. As a consequence of the theory, he described the phenomenon now known as Bose–Einstein condensation. We note as a matter of fact that the prediction of a condensation phenomenon belongs clearly only to Einstein (Ebeling and Hoffmann 2014). The negative reaction to the idea of Einstein condensation changed only later, when Uhlenbeck, Bogolyubov, and others succeeded in including interactions in the theory, and finally, 70 years later, when experimentalists succeeded in reaching low enough temperatures.

The Einstein condition for condensation is this: in a cube with length equal to 10 thermal de Broglie wavelengths should be more than 2 612 gas particles. Here the thermal de Broglie wavelength is the wavelength corresponding to the thermal momenta at temperature T. Erwin Schrödinger found this role of the De Broglie matter waves very interesting and inspiring, and exchanged letters with Einstein which were important for his formulation of wave mechanics. But Schrödinger could not believe that such conditions could be reached for real gases. The experimental verification of Einstein's prediction of a condensation of atomic gases at low temperatures was confirmed only 70 years after the prediction, in 1995. At the International Conference of Laser Spectroscopy on the island of Capri, Eric Cornell reported experiments at the University of Boulder which confirmed Einstein's prediction, as did parallel experiments by Wolfgang Ketterle's group at MIT. Nowadays, many groups around the world work in that field, and several Nobel Prizes have been attributed. Note that the effects we have discussed here, from the destruction of bound states in fermion gases to the condensation phenomena in boson systems, are clearly strong correlation effects.

1.3.2 Quantum Statistics of Interacting Gases

One of the difficulties in confirming experimentally the early theories of quantum gases was that the particles in real gases or plasmas are always interacting. The models by Einstein and Fermi, based on additive Hamiltonians, were just an abstraction. So the need to include at least weak interactions as a perturbation was seen immediately. For weakly degenerate systems, i.e., when the gas is still below the degeneracy line, in order to go from classical statistics to the quantum case only a few changes are needed in the classical theory. To see this, we study the mean potential energy, which in quantum statistics is expressed by an expectation value and given by a trace, viz.,

$$U = \langle V \rangle = \frac{1}{2}\mathrm{Tr}\big[U(12)\hat{\rho}_2(1,2)\big] , \tag{1.19}$$

where $\hat{\rho}_2$ is a two-particle density operator. An easy way to proceed is by using the coordinate representations. The pair probability given classically by a Boltzmann factor is to be replaced by its quantum-statistical counterpart, the Slater sum of pairs. In this way, as shown by Beth and Uhlenbeck, the classical expressions remain valid if we simply replace the Boltzmann factor by binary Slater sums (Uhlenbeck and Beth 1936). The second virial coefficient expressed in terms of the binary Slater function or Slater sum is

$$B_2(T) = \frac{1}{2}\int \mathrm{d}\mathbf{r}\big[S_{ab}(\mathbf{r}) - 1\big] , \tag{1.20}$$

where **r** is the displacement vector between the two particles. In the classical case, the Slater sum is identical to the Boltzmann factor. The pioneers Uhlenbeck and Beth represented the Slater sum in terms of the wave functions, including bound and scattering states. They thus expressed the second virial coefficient in terms of the energy spectrum and the density of states $n_l(k)$. The density of states may be expressed in terms of the scattering phase shifts or the Jost functions, using the relations between scattering phase shifts and the Jost functions of scattering theory (Uhlenbeck and Beth 1936; Kraeft et al. 1986; Kremp et al. 2005; Ebeling et al. 1976; Blaschke et al. 2014).

The extension of the statistical theory to strongly degenerate quantum gases can be attributed to several scientific schools. We mention, for example, Alexei A. Abrikosov, Nikolai N. Bogolyubov, Richard Feynman, Vitaly L. Ginzburg, Ryogo Kubo, Walter Kohn, Lev D. Landau, Elliot Montroll, and Julian Schwinger (Abrikosov et al. 1962; Bogolyubov and Bogolyubov 1992; Feynman 1972; Martin and Schwinger 1959; Montroll and Ward 1958). Among them, Nikolai N. Bogolyubov holds a special place in our view. Coming originally from the Kiev school of nonlinear mechanics and mathematics, he turned to statistical physics in the 1940s and 1950s, in particular to the method of distribution functions, where he developed with others the method of the BBGKY hierarchy to derive the kinetic equations. He then turned to the theory of superfluidity and superconductivity, formulated the microscopic theory of superfluidity, and made other essential contributions. Later he worked on quantum field theory, introduced the Bogolyubov transformation, and formulated and proved several theorems now named after him.

1.4 Ionic Fluids and Dense Low-Temperature Plasmas

1.4.1 Coulomb Forces and Debye–Hückel–Wigner Theories

The law of interaction between charged particles was formulated by Charles Augustin de Coulomb around 1785. The force between two charges e_a and e_b is as a function of the distance r in the radial direction (in Gaussian units)

$$F = -\frac{e_a e_b}{\varepsilon_\mathrm{r} r^2} \,. \tag{1.21}$$

This force is repulsive for equal charges and attractive for opposite charges. We assume here that the two particles belong to species a and b and that ε_r is the relative dielectric constant of the imbedding medium. The corresponding potential was introduced above. The potential at distance r from a charge e and the related field $\mathbf{E}(r)$ decay as $1/r$. In the following, we work in the Gaussian system of units. In the denominator, ε_r is the relative dielectric constant of the medium. In most cases we will assume without comment that the plasma is imbedded in a vacuum, so that

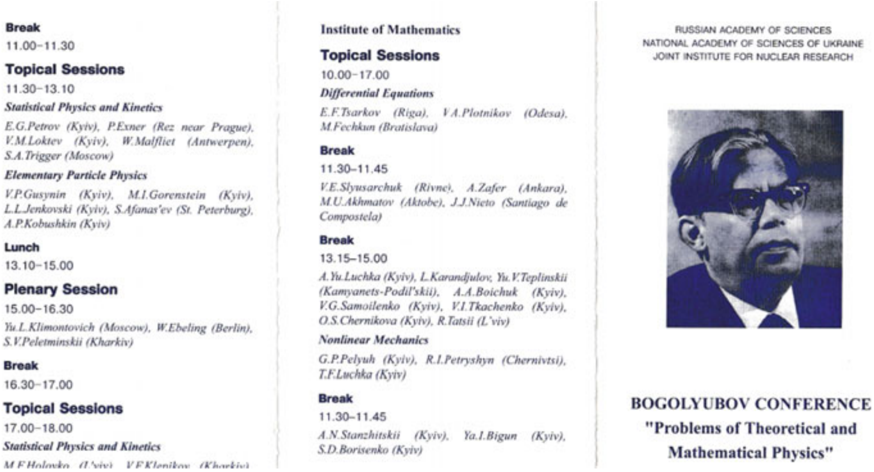

Fig. 1.6 Poster for a conference in 1999 in the Ukrainian capital Kiev, where Nikolai N. Bogolyubov (1909–1992) was educated and begin his career

$\varepsilon_{\mathrm{r}} = 1$. The electric field is source-free, except at the locations of the point charges, which are the sources of the field. This leads to the Poisson equation for the potential, which is the basic tool for the Debye–Hückel theory Fig. 1.6.

The idea due to Milner in 1912 is that free charges in an electroneutral ensemble of charges are always surrounded by opposite charges which screen the Coulomb fields. Milner's theoretical treatment, which used mainly graphical tools, was quite complicated. In 1923, Peter Debye presented a simpler theory based on Poisson's law and showed that the Milner effect is responsible for an exponential screening of the fields. This regularization is needed since the integral over the naked Coulomb potential is divergent, whence direct application of the method of virial expansions fails. All the standard virial coefficients known from the statistical theory of gases diverge for Coulomb potentials. As a consequence, it is known from the work of Milner, Debye, and Debye–Hückel (1923) that the form of the thermodynamic functions for gases or solutions containing particles satisfying Coulomb's law, like plasmas and electrolytic solutions, show essential deviations from those of typical gases. Density expansions of thermodynamic functions fail and completely different series expansions are needed. In particular, the pressure or its analogue in solutions, the osmotic pressure, cannot be expanded in Taylor series with respect to density. In the statistically well founded approach due to Debye and Hückel (Debye 1923; Debye and Hückel 1923; Kelbg 1963, 1972), the modern screening concept was developed. Further important contributions to the classical statistical theory of screening effects were made by Bogolyubov, Mayer, Meeron, Zubarev, Yukhnovsky, Kelbg, and Friedman (Friedman 1962; Bogolyubov and Bogolyubov 1992).

Let us now briefly discuss the concept of Debye screening based on the Poisson equation and some extensions, such as the Bogolyubov theory based on integral