

### INTERACTING SYSTEMS FAR FROM EQUILIBRIUM

# Interacting Systems far from Equilibrium Quantum Kinetic Theory

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Printed and bound by CPI Group (UK) Ltd, Croydon, CR0 4YY Simplicity is the ultimate sophistication. Leonardo da Vinci

### Preface

With this book a current gap should be filled between standard textbooks on many-body theory and monographs on specific topics. The need for such a summarising overview arises first due to the current interest in describing nonequilibrium processes in different fields and secondly because of the inherent demand of theoretical physics to develop an easy and transparent language to condense many complicated developments into a straight and simple notation. The final aim is to provide a concise textbook which enables students to learn the method of nonequilibrium Green's functions.

Atoms in gases, electrons in crystals or nucleons in nuclear matter behave as independent particles in many aspects so that we can understand the properties of these systems from statistical considerations. We will follow the original question of Ludwig Boltzmann as to how one can describe the motion of many-body systems from individual collisions. In this respect the philosophy is to consider motion versus force and to distinguish between large- and small-angle collisions, where the first one leads to dissipation and collision delays and the second one to the mean field and more complex effects on the drift. In dense systems the motion of particles is not only affected by the surrounding medium but feeds back to the embedding medium which allows us to describe Bose-Einstein condensation and superconductivity on the same footing.

In the course of study there are two ways to become acquainted with a new subject. One consists of developing the theory from phenomenological findings as a bottom-up or inductive way towards the abstract formulation with the upmost simplicity in notation and compression. The second way is to learn the final theory directly and to deduce all different phenomenon as specific applications. Here both possibilities are provided, offering students the ability to learn the quantum kinetic theory in terms of Green's functions using their experience in different fields and at the same time experienced researchers offer a framework to develop and apply the theory straight to the phenomena. Reflecting the versatile applications of nonequilibrium Green's functions, examples are collected ranging from solid state physics (impurity scattering, systems with spin-orbit coupling and magnetic fields, diffraction on organic barriers, semiconductors, superconductivity, Bose-Einstein condensation, ultrafast phenomena, graphene), plasma physics (screening and ultrashort-time modes), quenches of cold atoms in optical lattices up to heavy ion collisions and relativistic transport.

Given the intricate matter and the versatile recent developments, many different views exist on how to present a theory consistently. As the old motto of the University of Rostock said: 'Doctrina multiplex veritas una'. Though preparing collectively to avoid misprints and errors, the alert reader is kindly thanked in advance for bringing any of them to my attention.

Klaus Morawetz

Dresden, 14 May 2017

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From a common book (Lipavský, Morawetz and Špička, 2001*b*) I could adapt parts into the chapters 3, 13, 14, 23 and appendix C, D for which copyright permission by EDP science is thanked for. I would have liked to convince Pavel Lipavský to be a coauthor, since he contributed main parts of sections 2.1, 2.2.2, 2.4, 2.5.1–2, 4, 5, 6.1, 6.3 and 16.1., 16.5–6. Especially the proof in appendix D has been composed in the book (Lipavský, Morawetz and Špička, 2001*b*) by him. The many enlightening discussions with Michael Männel are acknowledged who has worked out the Bose condensation of section 12.2 and 12.5 within his PhD thesis.

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# Part I Classical Kinetic Concepts

The classical concepts of distribution functions are introduced from elementary principles. The motion of single particles is contrasted with the forces and the account of short- and long-range correlations in kinetic theory is explored. The division of collisional correlations into mean-fields and into nonlocal collisions is presented and the concept of quasiparticles is derived. One can learn about virial theorems and viral corrections and entropy production as well as hidden latent heat in collisions.

# Historical Background

#### 1.1 Introduction

Nonequilibrium phenomena are the essential processes which occur in nature. Any evolution is built up of involved causal networks which may render a new state of quality in the course of time evolution. The steady state or equilibrium is rather the exception in nature, if not a theoretical abstraction. The objective of statistical mechanics is to explain and predict the properties of macroscopic matter from the properties of its microscopic constituents. The equilibrium properties of macroscopic systems, with a given microscopic Hamiltonian, can be obtained as suitable averages in well-defined Gibbs ensembles. Our understanding of nonequilibrium phenomena is much less than satisfactory at the present time (Ernst, 1983). The aim of nonequilibrium statistical mechanics is to determine how macroscopic properties of matter evolve with time, in terms of the laws of quantum mechanics that govern the motion of its constituents—atoms, molecules, etc.

One line of approache extends the idea of the Gibbs ensemble to nonequilibrium systems, explicitly specifying the nonequilibrium density operator by a set of relevant observables (Zubarev, 1971; Röpke, 1987). For a modern overview see Zubarev et al. (1996), (Zubarev, Morozov and Röpke, 1997). Besides the great advantage of this method for maintaining the Gibbs ensemble picture and providing a convenient linear response formalism, one has to know in advance the set of relevant observables. In this sense, one has to specify possible evolutions of the system before actually knowing them. The concept of kinetic theory or equation of motions is different.

Kinetic theory tries to find basic evolution equations for the time-dependence of distribution functions with the help of which variables are determined. Kinetic equations for distribution functions ensure the microscopic formulation of hydrodynamics and thermodynamics. Therefore, it is the link between the nonequilibrium statistical mechanics of many particle systems and macroscopic or phenomenological physics.

The kinetic description, which started with the foundation of Ludwig Boltzmann's famous equation (Boltzmann, 1872), has been rapidly developed from important classical contributions made by Chapman and Cowling (1939), Enskog (1917), Kirkwood (1946), Bogoliubov (1946) and Prigogine (1962) to quantum extensions, where the pioneering work along these lines was performed by Bogoliubov and Gurov (1947) and

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Mori and Ono (1952). The quantum Boltzmann equation, called Boltzmann–Uhling– Uhlenbeck (BUU) equation differs from the classical one in the collision term, which takes into account that the final scattering states can be occupied and consequently blocked by the Pauli exclusion principle. Moreover, the quantum-mechanical transition rate, rather than the classical one, is used. Attempts to extend the kinetic theory to higher densities have been fraught with severe difficulties. One might have imagined being able to develop a power series expansion of the transport coefficients in the same way as one expands the equilibrium equation of state in the virial series. In (Cohen and Dorfman, 1965) and (Cohen and Dorfman, 1972) it was proved that such an expansion does not exist. The Navier–Stokes coefficients are non-analytic functions of the density (Evans and Morriss, 1990). We have to search for another expansion schema.

One general starting point in deriving kinetic equations was the coupled set of equations of motion for the reduced density operators. This set was first derived by Irving and Zwanzig (1951). The formal structure is similar to the so-called Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy for reduced distribution functions in classical statistical physics, see Bogoliubov (1946), Born and Green (1946), Kirkwood (1946) or (Balescu, 1978). The reduced density of the BBGKY hierarchy expressed in the mixed Wigner representation becomes a function of the position in phase space like the Boltzmann distribution. The Wigner distribution of quantum theory has thus a close analogy to its classical precursor, the Boltzmann distribution. A quantum particle, however, has a property which disturbs such a classical picture: it can tunnel into regions where the local potential exceeds the energy of the particle, and similarly, it can reach momenta which don't correspond to its kinetic energy. It became necessary to distinguish particles having an energy corresponding to the classical expectation (particles on the energy shell) from those which have a different energy (particle off the energy shell). As Köhler and Malfliet (1993) show, the off-shell contributions are necessary to describe the high-momenta tails of the Wigner distribution and to distinguish the mean removal energy from the quasiparticle one. While the classical picture treats the energy as a property of the particle that is determined by the phase space point, the new concept of quantum statistics known as Green's function treats the energy as an independent variable.

The method of the quantum statistical Green's function was introduced by Matsubara (1955). The Green's functions used by him are also called imaginary-time Green's functions because their time arguments stands for the imaginary inverse temperature. For this reason they can only be used to describe equilibrium many-body systems. In 1959 Martin and Schwinger introduced another Green's function technique for the description of many-body systems (Martin and Schwinger, 1959). As starting point they constructed a hierarchy of equations of motion for the imaginary-time Green's functions, nowadays known as Martin–Schwinger hierarchy. The real-time Green's functions (Schwinger, 1961) have been presented in the textbook by their students Kadanoff and Baym (1962).

An important ingredient in the real-time Green's functions is the analytic continuation of the Green's function from imaginary times to real times in order to describe nonequilibrium situations. Both Keldysh (1964) and Craig (1968) used this concept and formulated a Dyson equation on the time contour.

The real-time Green's functions provide a unifying many-body theory. They allow us to consistently investigate properties of many-particle systems from the ground state, over a finite temperature equilibrium state, to nonequilibrium situations. Applications of real-time many-body methods range from problems of quantum chromodynamics (Landsman and van Weert, 1987), through nuclear physics (Botermans and Malfliet, 1990, 1988; Tohyama, 1987; Danielewicz, 1984a), to the theory of liquid helium (Serene and Rainer, 1983), physics of plasmas (Bezzerides and DuBois, 1972), physics of condensed matter (Rammer and Smith, 1986), astrophysics (Keil, 1988) and cosmology (Calzetta and Hu, 1988). Moreover there are many investigations in classical relativistic treatment (Manzke and Kremp, 1979; Groot, a. van Leeuwen and van Weert, 1980) and quantum relativistic treatments can be found in (Brown, Puff and Wilets, 1970; Poschenrieder and Weigel, 1988; de Jong and Malfliet, 1991). Several papers are devoted to the formulation of transport equations in quantum field theory (Botermans and Malfliet, 1990; Ivanov, 1987; Mrowczynski and Danielewicz, 1990; Elze and et. al., 1987). The real-time Green's function technique is indeed a universal method to describe quantum many-particle systems under extreme conditions like nuclear matter or condensed stellar objects. For reviews see (Botermans and Malfliet, 1990; Danielewicz, 1990, 1984b; Itzykson and Zuber, 1980; Kremp, Schlanges and Bornath, 1985).

#### **1.2** Virial corrections to the kinetic equation

The very basic idea of the Boltzmann equation to balance the drift of particles with dissipation is used both in gases and condensed systems like metals or nuclei. In both fields, the Boltzmann equation allows for a number of different improvements that make it possible to describe phenomena far beyond the range of the validity of the original Boltzmann equation.

In the theory of gases, the focus of the improvements was on a finite volume of molecules. The Boltzmann equation now includes a contradiction. The scattering cross sections used within the Boltzmann equation reflect the finite volume of molecules and their other interactions, however, the instant and local approximation of scattering events implies the equation of state of an ideal gas. To achieve consistency and to extend the validity of the Boltzmann equation to moderately dense gases, Clausius and Boltzmann included the space nonlocality of binary collisions (Chapman and Cowling, 1990). After a century, virial corrections won new interest as they can be incorporated into Monte-Carlo simulation methods (Alexander, Garcia and Alder, 1995).

In the theory of condensed systems modifications of the Boltzmann equation are rather different being determined by the quantum mechanical nature of the singleparticle motion and by quantum mechanical statistics. A headway in this field is covered by the Landau concept of quasiparticles (Baym and Pethick, 1991). There are three major modifications: the Pauli blocking of scattering channels; the underlying quantum-mechanical dynamics of collisions; and the quasiparticle renormalisation of a single-particle dispersion relation. With all these deep modifications, the scattering integral of the Boltzmann equation still remains local in space and time. In other words,

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the Landau theory does not include a quantum-mechanical analogy of virial corrections studied in the theory of gases.

Even if one reinterprets the Boltzmann equation in the spirit of Landau's theory of Fermi liquids incorporating all known quasiparticle renormalisations, the Boltzmann equation still does not cover all known basic features of bulk matter. The structure of the quasiparticle kinetic equation is deduced from the system of weakly coupled particles, while dense matter like nuclear matter exhibits implicit correlations due to strong interactions. These correlations demand to include the virial corrections which are absent in Landau's theory.

#### 1.2.1 Classical gas of hard spheres

Beside nonlocalities, Enskog has also introduced static correlations (Enskog, 1972; Chapman and Cowling, 1990; Hirschfelder, Curtiss and Bird, 1964; Schram, 1991) and later Weinstock (1963*a*; 1963*b*; 1965) has discussed dynamic correlations. Although our focus will be on the nonlocalities, it is useful to recall the different kinds of virial corrections.

The first kind of correction beyond the original Boltzmann equation is the collisional transfer of momentum and energy. When two particles undergo a collision, the momentum and energy transferred from one particle to another suddenly jump over the distance between both particles. This process is instant and only two particles are involved. Accordingly, the nonlocal corrections are nothing but a more careful description of an isolated two-particle collision.

The second kind of correction takes into account that particles of finite volume scatter more frequently as is apparent when the density approaches a closely packed system. There are two effects that change the frequency of collisions. Firstly, a particle of a finite volume flies over a shorter distance to meet another partner in a point-like model. Secondly, the particles shield each other. These corrections can be taken into account by introducing static statistical correlations into the scattering integral. The shorter meanfree path and shielding effect appear only if collisions are treated as a process in the many-body surrounding. Accordingly, the static statistical correlations are of a threeparticle nature.

The third kind of correction takes into account the factm that any collision creates a perturbation in the vicinity of a particle. Indeed, the energy and momentum which a particle lost at a certain collision is carried by particles in its neighbourhood. This excess energy and momentum influence an initial condition for its next collision. Apparently, this is a dynamic process by its nature and also needs more than two particles to make it happen.

For the hard-sphere gas the nonlocal correction is trivial; therefore the main theoretical focus was on the statistical correlations (Enskog, 1972; Chapman and Cowling, 1990; Hirschfelder, Curtiss and Bird, 1964; Schram, 1991; Cohen, 1962; Weinstock, 1963*a*,*b*, 1965; Kawasaki and Oppenheim, 1965; Dorfman and Cohen, 1967; Goldman and Frieman, 1967; van Beijeren and Ernst, 1979). It turned out that the treatment of higher-order contributions is far from trivial, as the dynamical statistical correlations result in divergences that are cured only after resummation of an infinite set of contributions. Naturally, this resummation leads to non-analytic density corrections to the scattering integral (Weinstock, 1965; Kawasaki and Oppenheim, 1965; Dorfman and Cohen, 1967; Goldman and Frieman, 1967; van Beijeren and Ernst, 1979). The essence of these hard-sphere studies is that beyond the nonlocal corrections one has to sum up an infinite set of contributions, the plain perturbative expansion leads to incorrect results.

# **1.2.2 Hard-sphere corrections to the quantum Boltzmann** equation

Simulation codes of the Boltzmann equation and similarly the quantum Monte-Carlo dynamics assume the local and instant scattering. Halbert has discussed nonlocal corrections already in 1981, within the cascade model, Malfliet (1983) proposed to include the nonlocal Enskog-type corrections into simulation codes and Kortemeyer et al. (1996) incorporated the nonlocal corrections into the Monte-Carlo codes for the BUU equation using a method developed within the classical molecular dynamics (Alexander, Garcia and Alder, 1995). All these studies treat the nonlocality of two-particle collisions as if particles are classical hard spheres.

The basic idea of nonlocal corrections is that two colliding particles do not occupy the same space point but are displaced by the sum of their radii. For hard spheres, the direction of this displacement is easily identified with the direction of the transferred momentum. The numerical trick of building this displacement into Monte-Carlo simulations consists of a space displacement of the colliding particles after the collision. The classical molecular dynamics (Alexander, Garcia and Alder, 1995) show that the nonlocal corrections might be similarly implemented into quantum-molecular dynamics.

The hard-sphere corrections, however, didn't improve the agreement between numerical simulations and experimental data in nuclear collisions. This is because of their principal natures. As shown by Danielewicz and Pratt (1996) nucleons don't expel each other as hard spheres do, but tend to stay in the collision state as a short-living twonucleon cluster. This effective 'molecule' lasts for a certain time called the collision delay. As known from gases, the formation of molecules reduces the pressure because it reduces the number of particles which carry a momentum. In contrast, hard-sphere interaction leads to the excluded volume of the van der Waals equation which increases the pressure. For realistic simulations it is thus necessary to leave intuitively formulated nonlocal corrections and derive their value from microscopic theory.

#### 1.2.3 Quantum nonlocal corrections in gases

The microscopic theory of nonlocal corrections to the collision integral has been pioneered within the theory of gases by many authors (Waldmann, 1957, 1958, 1960; Snider, 1960, 1964; Bärwinkel, 1969*a*; Thomas and Snider, 1970; Snider and Sanctuary, 1971; Rainwater and Snider, 1976; Balescu, 1975; McLennan, 1989; Laloë, 1989; Tastevin, Nacher and Laloë, 1989; Nacher, Tastevin and Laloë, 1989; Loos, 1990*a*,*b*; de Haan, 1990*b*,*a*, 1991; Laloë and Mullin, 1990; Snider, 1990, 1991; Nacher, Tastevin and Laloë, 1991*a*,*b*; Snider, 1995; Snider, Mullin and Laloë, 1995).

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Snider (1960, 1964) generalised Waldmann's equation in such a way that it includes the nonlocality of collisions. Since then a number of similar theories have been developed. It was generally believed that this approach covers virial corrections until Laloë, Mullin, Nacher and Tastevin analysed the so-called Waldmann-Snider theory to conclude that Snider's equation in its original form is not consistent with the second-order virial correction to the equation of state (Laloë and Mullin, 1990; Nacher, Tastevin and Laloë, 1991a). In a series of papers (Laloë, 1989; Tastevin, Nacher and Laloë, 1989; Nacher, Tastevin and Laloë, 1989; Nacher, Tastevin and Laloë, 1991a, 1991b) these authors have introduced a new concept of 'free Wigner transform which wipes out the effect of the potential at short distances'. The main idea of their approach is identical to the idea of quasiparticles in that the kinetic equation is not constructed for the Wigner distribution but for a subsidiary function, the free Wigner transform, that is free of the correlated motion. The Wigner function is constructed then from the free Wigner transform in the final step. Since the free Wigner transform includes only the on-shell contributions, as far as we can see, the free Wigner transform is identical to the quasiparticle distribution. The intuitive theory of Laloë, Tastevin and Nacher has been confirmed by de Haan (1990b,a, 1991) who used Balescu's formal derivation of kinetic equations (Balescu, 1975).

This theory made headway in the field as it allows one to describe quasiparticle renormalisations including off-shell processes. It gives a nonlocal scattering integral as being consistent with second-order virial corrections. It is important that all nonlocal corrections are presented in terms of derivatives of the scattering phase shift. This provides a clear link between the virial corrections and observable quantities. On the other hand, this approach is limited to dilute systems with non-degenerate statistics, which makes it inapplicable to dense Fermi systems. This is because technically the concept of the free Wigner transform as well as Balescu's method become too complicated for degenerated systems, in particular with in-medium effects.

#### 1.3 Quantum nonlocal corrections in dense Fermi systems

A convenient perturbative expansion for degenerate systems is well established within Green's functions. The pioneering Green's function treatment of non-instant and non-local corrections to the scattering integral was done by Bärwinkel (1969*a*) who also discussed the thermodynamical consequences of these corrections 1969*b*. His studies are limited to low-density particles. Nevertheless, his work was the most important contribution to Green's functional approach to virial corrections.

The physics behind these virial corrections are strong-interaction correlations. In the weak-coupling limit the scattering rate of two particles is given by the matrix element of the interaction potential between the plain waves of initial and final states. For a strong potential, the wave function cannot completely penetrate a strongly repulsive potential being expelled from the particle core, but contrarily it can be enhanced at moderately short distances by short-range attractive forces. In the strong-coupling case one thus has to take into account the reconstruction of the wave functions by the interaction potential. This reconstruction is usually called the internal dynamics of collisions as it is

reflected in the finite duration of collision. The build-up of the wave function means that the particles can be found at a given distance with an increased probability. Within the ergodic interpretation of probability it means that they have to spend a longer time at this distance than would result from an uncorrelated motion. This interpretation corresponds to the concept of dwell time, see (Hauge and Støvneng, 1989). Accordingly, unlike in Landau's theory, the collision has to be treated as non-instant and nonlocal.

These internal dynamics have thermodynamic consequences. For instance, with a finite collision duration, the density of quasiparticles differs from the density of real particles. The difference is the so-called correlated density. The Fermi momentum (of quasiparticles) differs then from the Fermi momentum defined by the density of particles (Schmidt, Röpke and Schulz, 1990; Morawetz and Röpke, 1995; Bornath, Kremp, Kraeft and Schlanges, 1996). We note that within Landau's theory of Fermi liquids the Fermi momentum is not affected by the interaction and these two values are equal according to the Luttinger theorem (Luttinger, 1960). The shift of the Fermi momentum now reflecting the collision delay leads to second-order virial corrections to the law of mass action (Bornath, Kremp, Kraeft and Schlanges, 1996). A discussion about thermodynamic consequences and applications of this mass-action law can be found in (Kraeft, Kremp, Ebeling and Röpke, 1986). Therefore the contradictory predictions of the virial correction to the mass-action law concern the violation of Luttinger's theorem and are traced back to the question of whether a correlated density appears or not. As shown by Farid (1999), Luttinger's proof of the Fermi liquid ground state of any perturbatively treated many-fermion system is a tautology in the sense that the correlated density is neglected as a definition of a Fermi liquid which obeys, then of course the Luttinger theorem. Similarly, the assumption of the Fermi liquid ground state is a part of Craig's approach. We believe that the zero result of Craig (1966a) and a similar study by Ivanov et al. (2000) are not correct in spite of the employed  $\Phi$ -derivable approximation. Most Fermi systems do not lead to the Fermi liquid ground state, but provide e.g. a superconducting transition. In the superconducting state the shift of the Fermi momentum is experimentally confirmed because it leads to the electrostatic potential known as the Bernoulli potential (Lipavský, Koláček, Morawetz, Brandt and Yang, 2007).

The question is now: what approximation is capable of covering the internal dynamics of the collisions. Using the expansion in small scattering rates, Craig (1966*a*) found no virial correction to the density of particles. In contrast, this limit was introduced by Stolz and Zimmermann (1979), Kremp et al. (1984) and Zimmermann and Stolz (1985) to study just this type of virial corrections in a non-ideal plasma. Its implementation for nuclear physics has been considered by Röpke et al. (1982*a*), Röpke et al. (1982*b*; 1982*c*) and Schmidt et al. (1990) who have shown that, for equilibrium, the limit of small scattering rates called the generalised Beth–Uhlenbeck approach (Beth and Uhlenbeck, 1937) provides the correct second-order virial corrections.

#### 1.4 Quantum nonlocal corrections to kinetic theory

In the limit of small scattering rates, the transport equation for the Green's function is converted into the Boltzmann-type kinetic equation by the extended quasiparticle approximation corresponding to the  $\rho[f]$  functional. The ability of the limit of small scattering rates to recover the kinetic equation with non-instant corrections has been discussed by Bornath et al. (1996) although only for non-degenerated systems. Another model study of non-interacting electrons scattered by neutral impurities (Spička, Lipavský and Morawetz, 1997a) demonstrated that the non-instant corrections have to be studied together with the quasiparticle corrections, because they partially compensate each other in many observable quantities. A quantum-kinetic theory which unifies the achievements of transport in dense gases with the quantum transport of dense Fermi systems was derived starting with the impurity problem (Špička, Lipavský and Morawetz, 1997b) and then for arbitrary Fermi systems (Špička, Lipavský and Morawetz, 1998; Lipavský, Morawetz and Špička, 2001*b*; Morawetz, Lipavský and Špička, 2001*c*). The quasiparticle drift of Landau's equation is connected with a dissipation governed by a nonlocal and non-instant scattering integral in the spirit of the Enskog corrections. These corrections are expressed in terms of shifts in space and time that characterise the nonlocality of the scattering process (Morawetz, Lipavský, Špička and Kwong, 1999b). In this way quantum transport can be recast into a quasiclassical picture suited for simulations. The balance equations for the density, momentum, energy and entropy include quasiparticle contributions and the correlated two-particle contributions beyond the Landau theory will also be demonstrated in this book.

As to special limits, this kinetic theory includes the Landau theory as well as the Beth–Uhlenbeck equation of state which means correlated pairs. The medium effects on binary collisions are shown to mediate the latent heat which is the energy conversion between correlation and thermal energy (Lipavský, Špička and Morawetz, 1999; Lipavský, Morawetz and Špička, 2001b). In this respect the seeming contradiction between particle-hole symmetry and time-reversal symmetry in the collision integral was solved (Spička, Morawetz and Lipavský, 2001). Compared to the Boltzmann equation, the presented form of virial corrections only slightly increases the numerical demands in implementations (Morawetz, Śpička, Lipavský, Kortemeyer, Kuhrts and Nebauer, 1999c; Morawetz, 2000a; Morawetz, Ploszajczak and Toneev, 2000b; Morawetz, Lipavský, Normand, Cussol, Colin and Tamain, 2001b) since large cancellations in the off-shell motion appear which are usually hidden in non-Markovian behaviours. The molecular quantum dynamics and the quantum Boltzmann (BUU) simulations (Morawetz, Špička, Lipavský, Kortemever, Kuhrts and Nebauer, 1999c; Morawetz, Lipavský, Normand, Cussol, Colin and Tamain, 2001b) with nonlocal binary collisions derived from the scattering T-matrix in (Špička, Lipavský and Morawetz, 1998; Morawetz, Lipavský, Špička and Kwong, 1999b) lead to a better agreement of experimental and theoretical distributions of neutrons and protons emitted from reacting nuclei.

Because of the high complexity of the complete quantum-mechanical treatment, the quasiclassical kinetic equation is still beneficial to the study of nonequilibrium manybody systems. In this book we will discuss various aspects of the Green's function approach and very often we will interpret the derived relations and quantities in terms of corresponding features in the quasiclassical picture.

# 2 Elementary Principles

The many-body theory combines ideas of thermodynamics with those of mechanics. In this introductory chapter, the symbiosis of these two different fields of physics is demonstrated on overly simplified models.

#### 2.1 Motion versus forces

Two of Newton's theories have influenced the early microscopic pictures of fluids, the law of motion and the law of gravity. The law of gravity supplied the idea that molecules can act one on each other by forces that range over long distances. Such repulsive forces can explain a finite compressibility of solids, liquids and dense gases. The law of motion,  $\Delta k = F \Delta t$ , says that the change of the momentum is caused by forces and vice versa. This law is sufficient to explain the equations of state of rare gases and provides a link between the heat and the kinetic energy of molecules. The first law of thermodynamics thus became identical with the general law of conservation of energy. This standard interpretation was not so obvious when the heat was viewed as an independent substance.

In the first half of the nineteenth century, the concept based on the law of motion and the concept based on the long-ranged forces were felt to be competitive. The pure theory based on long-ranged forces needed a phenomenological assumption that forces depend on the temperature to explain the equation of state of gases. The pure theory of motion was free of phenomenological assumptions but worked only for rare gases. As often happens, it turned out that the two concepts are not competitive but complementary.

To explain the thermodynamical consequences of molecular motion and of the forces between molecules, we first discuss the pressure in a one-dimensional (1D) classical gas.

#### 2.1.1 Principle of motion

Assume a single particle of mass *m* in a 1D system of volume  $\Omega$ . The particle flies between points  $-\frac{1}{2}\Omega$  and  $\frac{1}{2}\Omega$  with velocity  $\pm v$ . In a single round trip the particle passes the trajectory of length  $2\Omega$  which takes a time  $\Delta t = 2\Omega/v$ . With each encounter of the surface, the momentum of the particle changes by  $\Delta k = 2mv$ . The mean force

needed for these changes of momentum represents the pressure the particle exerts on the surface. According to Newton's law of motion, the pressure

$$\mathscr{P} = \frac{\Delta k}{\Delta t} = \frac{mv^2}{\Omega} \tag{2.1}$$

is proportional to the kinetic energy  $\frac{1}{2}mv^2$  and inversely proportional to the volume.

If there are N non-interacting particles, they move independently. Their individual contributions to the pressure thus add

$$\mathscr{P} = \frac{m}{\Omega} \sum_{i=1}^{N} v_i^2.$$
(2.2)

The sum over single-particle energies divided by volume,

$$\mathscr{E} = \frac{1}{\Omega} \sum_{i=1}^{N} \frac{1}{2} m v_i^2,$$
(2.3)

is the density of energy. The pressure in the non-interacting gas is thus proportional to the density of energy,

$$\mathscr{P} = 2\mathscr{E}.\tag{2.4}$$

Later on, we will establish the relation between the density of energy and the temperature of the system by which 1D Bernoulli's relation (2.4) turns into the equation of state.

#### 2.1.2 Principle of finite-range forces

The long-range forces between particles modify the relation between the pressure and the energy. For the purpose of discussion it is sufficient to assume a model box-like potential

$$\mathscr{V}(r) = \mathscr{V}\theta(R-r), \tag{2.5}$$

where *r* is a distance of particles. The potential is parametrised by range (radius) *R* and strength  $\mathcal{V}$ . We assume a repulsive potential  $\mathcal{V} > 0$  to avoid bounded states.

To describe the effect of collisions on the pressure, we select two neighbouring particles moving one to the other with velocities  $v_1$  and  $v_2$ . When the two particles meet, their velocities change to  $u_{1,2}$  with which they move as long as their distance is smaller than *R*. According to the momentum and energy conservations

$$mv_1 + mv_2 = mu_1 + mu_2, \quad \frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 = \frac{1}{2}mu_1^2 + \frac{1}{2}mu_2^2 + \mathscr{V},$$
 (2.6)

the velocities of interacting particles read

$$u_{1,2} = \frac{v_1 + v_2}{2} \pm \sqrt{\left(\frac{v_1 - v_2}{2}\right)^2 - \frac{\mathscr{V}}{m}}.$$
(2.7)

For a strong potential,  $\mathscr{V} > \frac{1}{4}m(v_1 - v_2)^2$ , the interaction region is not accessible for particles; therefore they get reflected at the very first touch.

After the collision, particles have final velocities  $w_{1,2}$ . In the 1D system, the conservation of momentum and energy,

$$mv_1 + mv_2 = mw_1 + mw_2,$$
  $\frac{1}{2}mv_1^2 + \frac{1}{2}mv_2^2 = \frac{1}{2}mw_1^2 + \frac{1}{2}mw_2^2,$  (2.8)

determines the final states of particles,

$$w_{1,2} = v_{2,1} \qquad \text{for} \quad \mathscr{V} > \frac{1}{4}m(v_1 - v_2)^2 \\ w_{1,2} = v_{1,2} \qquad \text{for} \quad \mathscr{V} < \frac{1}{4}m(v_1 - v_2)^2$$
(2.9)

In the case of strong potentials, particles exchange their momenta. In the case of weak potentials, they end up with their initial momenta.

The two regimes of the collision, reflection or transmission, contribute differently to the pressure. Before we discuss details, it is necessary to note that the pressure corrections appear only for the forces of a finite range. Indeed, for forces of infinitesimal short range,  $R \to 0$ , all collisions are point-like, i.e. local. The characteristic time of the interaction scales with  $R/(v_1 - v_2)$  so that the point collisions are also instant. The value of the internal velocities  $u_{1,2}$  thus does not matter and the collision is characterised fully by the local matching of initial and final velocities (2.9),  $v_{1,2} \to w_{1,2}$ . If all assumed particles are identical, particles 1 and 2 are not distinguishable; therefore the same physical picture is met if they pass each other, as for  $\mathcal{V} < \frac{1}{4}m(v_1 - v_2)^2$ , or if they interchange their momenta, as for  $\mathcal{V} < \frac{1}{4}m(v_1 - v_2)^2$ . For  $R \to 0$ , with no regards whether the interaction is strong, weak or ignored, there are two particles of velocities  $v_1$  and  $v_2$  reaching the point of encounter, and two particles of the velocities  $v_1$  and  $v_2$  leaving this point. Accordingly, all these systems exert the same pressure on the surface. Briefly, the instant and local collisions do not influence the pressure.

*Inaccessible volume* For the potential of finite range, let us assume first a strong potential. The collisions are instant, but at the instant of collision the centres of two colliding particles are displaced by R. Similarly, when reflected by the surface, the centre of the particles is displaced by  $\frac{1}{2}R$  from the surface. Trajectories of three particles are shown in Fig. 2.1. Such 1D particles behave like hard rods. As can be seen, such a system of



**Figure 2.1:** Trajectories of three one-dimensional hard rods colliding three and two times with the wall (left panel). To map this system on a system of point-like particles, we first shift the upper line by  $\frac{1}{2}R$  so that the centre of the first particle is reflected on the surface. Now we shift the middle trajectory and the lower line by R so that the centres of the first and second particles at the instant of collision coincide. Next we shift the lowest trajectory by 2R so that centres of the lowest and the middle particle at collision coincide too. In the right panel we thus obtain an effective system of point-like particles in which particles collide and hit the surface with the same frequency.

hard rods can be mapped on a system of point-like particles in a volume  $\Omega - NR$ . The pressure in the system of hard rods thus is

$$\mathscr{P} = \frac{1}{\Omega - NR} m \sum_{i=1}^{N} v_i^2 = \frac{2\mathscr{E}}{1 - nR},$$
(2.10)

where  $n = \frac{N}{\Omega}$  is the particle density. As (2.4) corresponds to the equation of state of the ideal gas, so (2.10) corresponds to the van der Waals equation of state with the excluded volume *NR*.

Delay time and internal pressure Now we turn to collisions in which particles have enough kinetic energy to pass each other. Such weak-potential collisions are non-instant and nonlocal. At the beginning and at the end of collisions, particles are displaced by R but from opposite sides. Accordingly, during interaction particles travel the relative distance 2R. Since their relative velocity is  $u_1 - u_2$ , the collision process lasts

$$\tau_C = \frac{2R}{u_1 - u_2} = \frac{R}{\sqrt{\left(\frac{v_1 - v_2}{2}\right)^2 - \frac{\gamma}{m}}}.$$
(2.11)

In the absence of interactions, particles would travel the same distance in the time

$$\tau_0 = \frac{2R}{v_1 - v_2}.\tag{2.12}$$

The collision delay that can be attributed to the interaction thus is

$$\Delta_{\tau} = \tau_C - \tau_0. \tag{2.13}$$

The collision delay  $\Delta_{\tau}$  modifies the frequency with which particles hit the surfaces. For simplicity, let us assume for a while that in free motion all particles have the same velocity  $\pm v$ . In this case, only particles with opposite orientations of velocities can collide being always delayed by the same time

$$\Delta_{\tau} = \frac{R}{\sqrt{v^2 - \frac{\gamma}{m}}} - \frac{R}{v}.$$
(2.14)

In a single round trip, each particle collides twice with each other; therefore its motion is delayed by  $2(N-1)\Delta_t$ . Assuming  $N \gg 1$ , we write the time period as

$$\Delta t = 2\frac{\Omega}{v} + 2N\Delta_{\tau}.$$
(2.15)

The internal pressure caused by particles reads

$$\mathscr{P} = N \frac{2mv}{\Delta t} = \frac{2\mathscr{E}}{1 + nR\left(\left[1 - \frac{\gamma}{mv^2}\right]^{-\frac{1}{2}} - 1\right)}.$$
(2.16)

A particularly simple form of the pressure appears for a very weak interaction potential,  $\mathscr{V} \ll mv^2$ . The linear correction in  $\mathscr{V}$  from (2.16) follows as

$$\mathscr{P} = 2\mathscr{E} - \frac{1}{2}n^2 R \mathscr{V}. \tag{2.17}$$

Unlike the excluded volume, the weak potential correction  $-\frac{1}{2}n^2 R \mathscr{V}$  does not depend on the density of energy  $\mathscr{E}$  but only on the square of the density of particles *n*. The internal pressure of the van der Waals equation is exactly of this form.

Transition from weak to strong potential The effect of the interaction on the pressure depends on the value of the potential. For the potential smaller than the kinetic energy  $\mathcal{V} < mv^2$ , the interaction decreases the pressure. In the limit  $\mathcal{V} \to mv^2$ , the pressure goes to zero,

$$\lim_{\mathscr{V}-mv^2 \to 0_-} \mathscr{P} = 0, \qquad (2.18)$$

because  $\tau_C$  becomes infinite. At  $\mathscr{V} = mv^2$ , the potential dependence of the pressure is non-analytic. From the zero value (2.18), the pressure suddenly jumps to the hard-rod

value (2.10). For all strong potentials  $\mathscr{V} > mv^2$  the pressure is given by the hard-rod value, i.e. in this region it is independent of the actual value of the potential.

The sharp transition from weak to strong potential regimes follows from non-realistic assumptions of the box-like potential and equal velocities; nevertheless, this discussion shows that the strong and weak forces act principally in a different manner. The strong repulsive forces lead to the inaccessible volume since they simply do not allow two particles to be closer than the sum of their radii. The weak forces modify velocities of particles during their encounter leading to the internal pressure.

#### 2.1.3 Summary

The naive derivation of the van der Waals equation of state shows that the motion of particles is responsible for the basic structure of the equation of state and forces appear only via corrections. The free motion is the dominant and explains why all gases behave identically when sufficiently diluted. On the other hand, the force contribution is the interesting part if we want to learn about molecules composing the gas. The internal pressure and the excluded volume can be used to infer the interaction potential from thermodynamic measurements. For this model, the range R of the interaction is readily obtained from the excluded volume at low temperatures when the thermal velocity does not allow the particles to penetrate each other, and the strength  $\mathcal{V}$  is found at high temperatures from the mean-field correction  $\sim R\mathcal{V}$ . So finally one obtains a relation reminding us of the familiar van der Waals equation of state,

$$\left(\mathscr{P} + a\frac{N^2}{\Omega^2}\right)(\Omega - Nb) = 2\mathscr{E}.$$
(2.19)

The (mean-field) corrections to drift result in the internal pressure  $a_{\Omega^2}^{N^2}$ . The nonlocal correction to the collisions results in the effect of the molecular volumes *Nb*. The importance of these two corrections depends on the range of the interaction. The weak interaction dominantly contributes to the drift. The strong interaction leads to nonlocal collisions. Realistic interactions are strong on short distances and weak on long distances. Both groups of corrections are thus needed.

#### 2.2 Random versus deterministic

So far we have assumed that velocities and coordinates of individual particles are known. In reality it is not possible and even not desirable to characterise any many-body system by so many numbers as there are coordinates and velocities of all its particles. From experience we know that in equilibrium all systems of the same density of particles and energy behave so similar that the actual shape of the container and also the actual set of coordinates and velocities are irrelevant. It is sufficient to know the total energy E, the volume  $\Omega$  and the number of particles N.

The fact that actual coordinates and velocities of particles do not matter can be utilised in two ways. The first one is used within numerical simulations. The system is represented by some randomly selected initial condition that complies with the prescribed total energy. Solving the trajectories of particles numerically with this initial condition one can evaluate e.g. the force on the surface. Although this force fluctuates differently for different initial conditions, its mean value is always the same.

The second way to benefit from the low sensitivity of the system to the actual initial condition is to average it over all possible initial conditions. The averaging wipes out most of the dynamics in the system. For example in equilibrium, any physical quantity averaged over the full set of initial conditions remains time independent. Of course, instead of exact predictions one is able to obtain only the most probable values of observables which are just the mean values independent of initial conditions.

#### 2.2.1 Chaos

The equivalence of different initial conditions is limited to observables which include large numbers of single-particle events. Easily observable physical effects which do not meet this condition are rather rare but exist. A simple example is the Brownian motion of pollen seeds. Each actual initial condition results in a different trajectory of pollen seed.

It is reasonable to assume that each particle in the system moves along a zigzag path as shown in Fig. 2.2. The abrupt changes of direction are caused by collisions. Let us try to understand to what extent the initial condition influences the actual behaviour of the system. The sensitivity of the system to the initial condition can be demonstrated on two particles scattering at three Lenard–Jones impurities with minimal initial displacement shown in Fig. 2.2. The particle is scattered by the walls of the container and by the impurities. The numerical solution shows that two close initial conditions lead after a



**Figure 2.2:** The trajectories of two 2D particles displaced initially by 0.01Å interacting with Lennard-Jones-type impurities (Green, 1952),  $V(r) = -\frac{a}{r^6} + \frac{b}{r^{12}}$  with  $a = 0.63 \text{ eVÅ}^6$  and  $b = 220 \text{ eVÅ}^{12}$ fitted to helium. The weak attractive long-range potential bends trajectories towards the impurity; the strong repulsive short-range potential bounces particles off in a rather abrupt way. In spite of nearly identical initial conditions, the trajectories become soon very dissimilar. Right: Lyapunov exponent (2.20) for the infinitely mirrored middle figure.

short time to two very different positions and velocities of the particle. This can be measured by an exponential divergence of the difference in position as

$$\lambda = \frac{1}{t} \log |r_1(t) - r_2(t)|$$
(2.20)

called the Lyapunov exponent plotted in Fig 2.2. In other words, two close initial conditions diverge quickly into two well separated ones.

The divergence of the initial conditions is so strong that one can vaguely say that the system can reach any state from any initial condition. If an ensemble of particles starts with initial conditions from a small interval  $(x, x + dx) \times (y, y + dx) \times (\phi, \phi + d\phi)$ , where  $\phi$  denotes a direction of velocity, they will soon cover the whole space with all possible directions of velocities. For this reason, the averaging over a small interval of initial conditions results in the same observables as the averaging over all initial conditions. The averaging over small intervals is necessary at least because of experimental errors. The averaging over all initial conditions is a powerful theoretical tool. In equilibrium the averaging over time agrees with the ensemble averaging.

It is clear that with such a high sensitivity to the initial condition we cannot solve the actual trajectory of the system, because any small error, either in establishing the initial condition or in numerical treatment of the time evolution, necessarily leads to a completely different trajectory of the particle. Accordingly, it is more reasonable to deal with conserving quantities and to treat the non-conserving degrees of freedom as random. One can see that chaotic evolution leads to a basic paradox of the many-body physics: the evolution of the system is so sensitive to the initial condition of non-conserving degrees of freedom that their actual initial values do not matter.

#### 2.2.2 Velocity distribution

The interaction of particles in the three-dimensional (3D) system results in a randomisation of the single-particle energies. If we assume that the interaction has no other effect than to randomise the positions and velocities of particles, we can treat the system as a system of non-interacting particles; however, averaged over all possible states.

*N*-particle distribution in a 1D system To average over all states, assume N particles with the total energy E. Since all states have equal statistical weights, a probability to find the system in one particular state is given only by the restriction that this state corresponds to the energy E,

$$F_N(r_1, \dots, r_N, v_1, \dots, v_N) = A_N \delta \left( E - \frac{1}{2} m \sum_{i=1}^N v_i^2 \right).$$
(2.21)

The norm

$$A_N = (N-1)! \frac{1}{3\Omega^N} \Gamma\left(\frac{3}{2}N+1\right) m\left(\frac{2\pi E}{m}\right)^{1-\frac{3}{2}N}$$
(2.22)

is chosen so that the sum over all states is unity<sup>1</sup>

$$\frac{1}{N!}\int dr_1\dots dr_N dv_1\dots dv_N F_N = 1.$$
(2.23)

To obtain the analogue for N' particles in 3D system, one takes N = 3N' so that the number of degrees of freedom is the same.

Single-particle distribution Although the N-particle distribution is as simple as the  $\delta$  function, it escapes our intuition as any N-dimensional function would. Let us take a look at an intuitively simpler function f(r, v), the probability to find at a point r a particle of velocity v. The function f is the local distribution of velocities known as the Boltzmann distribution.

To evaluate the probability that a single particle is at r with v while positions and velocities of the other particles can be any, we fix the 1-th, the 2-nd, ..., N-th, argument of the N-particle distribution,  $r_i = r$  and  $v_i = v$ , and integrate over the others. Since

<sup>1</sup> From (2.21) the norm follows as

$$A_N^{-1} = \frac{1}{N!} \int dr_1 \dots dr_N dv_1 \dots dv_N \,\delta\left(E - \frac{1}{2}m\sum_{i=1}^N v_i^2\right).$$

First, we integrate out space variables which yield the factor  $\Omega^N$ . Secondly, in the velocity space, we substitute into 3*N*-dimensional spherical coordinates  $w^2 = \sum_{i=1}^N v_i^2$ ,

$$A_{N}^{-1} = \frac{1}{N!} \Omega^{N} \int dS_{3N} \int_{0}^{\infty} dw w^{3N-1} \delta\left(E - \frac{1}{2}mw^{2}\right).$$

The angle element in the 3*N*-dimensional sphere  $S_{3N}$  does not enter the  $\delta$  function and can be readily integrated out giving 3*N*-times the volume of the 3*N*-dimensional unitary sphere [formula (4.632) in (Gradshteyn and Ryzhik, 2014)]

$$\int dS_{3N} = 3N \frac{\pi^{\frac{3}{2}N}}{\Gamma\left(\frac{3}{2}N+1\right)}.$$

The  $\delta$  function reduces as

$$\delta\left(E-\frac{1}{2}mw^2\right) = \frac{1}{mw}\delta\left(w-\sqrt{\frac{2E}{m}}\right),$$

giving the integral over w

$$\int_0^\infty dw w^{3N-1} \delta\left(E - \frac{1}{2}mw^2\right) = \frac{1}{m} \left(\frac{2E}{m}\right)^{\frac{3}{2}N-1}.$$

The combination of these formulae yields (2.22).

all particles are identical, the contributions of all particles are equal. Therefore the sum over all particles is N-times the contribution of the 1-th one,<sup>2</sup>

$$f(r,v) = \frac{1}{(N-1)!} \int dr_2 \dots dr_N dv_2 \dots dv_N F_N(r,r_2,\dots,r_N,v,v_2,\dots,v_N).$$
(2.24)

The integration is similar to the evaluation of the norm  $A_N$ , see Footnote 1. The space integration is (N-1)-dimensional giving the factor of  $\Omega^{N-1}$ ,

$$f(r,v) = \frac{\Omega^{N-1}}{(N-1)!} A_N \int dv_2 \dots dv_N \delta \left( E - \frac{1}{2} m v^2 - \frac{1}{2} m \sum_{i=2}^N v_i^2 \right).$$
(2.25)

The velocity integration is also similar to the norm  $A_N$  except that one has to subtract the kinetic energy of the selected particle from the total energy, because only the energy  $E - \frac{1}{2}mv^2$  is left for particles 2,..., N. The velocity integral is a 3(N-1)-dimensional one. In parallel with the evaluation of the norm  $A_N$ , one finds

$$f(r,v) = A_N \frac{3\Omega^{N-1}}{(N-2)!} \frac{1}{m} \frac{\left(2\pi \left(\frac{E}{m} - \frac{1}{2}v^2\right)\right)^{\frac{3}{2}N - \frac{3}{2}}}{\Gamma\left(\frac{3}{2}N - \frac{1}{2}\right)}$$

 $^{2}$  In a more careful formulation one can introduce the probability P to find any of the particles in the interval

$$(r, r+dr) \times (v, v+dv) \equiv (x, x+dx) \times (y, y+dy) \times (z, z+dz) \times (v_x, v_x+dv_x) \times (v_y, v_y+dv_y) \times (v_z, v_z+dv_z).$$

For infinitesimal dr and dv, this probability is proportional to drdv so that P = f(r, v)drdv.

To evaluate the probability *P*, we introduce a condition that the *i*-th particle is from the interval (r, r + dr) by function  $\xi_r(r-r_i) = \theta(r_i - r)\theta(r + dr - r_i)$ . The function  $\xi_r$  equals unity if the *i*-th particle is in the interval and zero otherwise. A similar function  $\xi_v(v-v_i) = \theta(v_i - v)\theta(v + dv - v_i)$  is used for velocities. The probability of finding some of the particles in the given phase-space interval then reads

$$P = \frac{1}{N!} \int dr_1 \dots dr_N dv_1 \dots dv_N F_N \sum_{i=1}^N \xi_r (r-r_i) \xi_v (v-v_i).$$

The velocity distribution  $f = \frac{P}{drdv}$  results sending  $dr \to 0$  and  $dv \to 0$ . Under this limit,

$$\frac{1}{dr}\xi_r(r-r_i) \to \delta(r-r_i) \quad \text{and} \quad \frac{1}{dv}\xi_v(v-v_i) \to \delta(v-v_i),$$

so that

$$f(r,v) = \lim_{drdv\to 0} \frac{P}{drdv} = \frac{1}{N!} \int dr_1 \dots dr_N dv_1 \dots dv_N F_N \sum_{i=1}^N \delta(r-r_i) \delta(v-v_i)$$
$$= \frac{1}{(N-1)!} \int dr_1 \dots dr_N dv_1 \dots dv_N F_N \delta(r-r_1) \delta(v-v_1)$$

which is equivalent to (2.24).

After substitution of the norm  $A_N$  from (2.22), we get

$$f(r,v) = \frac{N-1}{\Omega} \left(\frac{m}{2\pi E}\right)^{\frac{3}{2}} \frac{\Gamma\left(\frac{3}{2}N+1\right)}{\Gamma\left(\frac{3}{2}N-\frac{1}{2}\right)} \left(1-\frac{mv^2}{2E}\right)^{\frac{3}{2}N-\frac{3}{2}}.$$
 (2.26)

*Maxwell distribution* For large numbers of particles,  $N \to \infty$ , the single particle distribution simplifies to Maxwell's distribution. Not to change thermodynamic properties of the system, we have to limit the large number of particles keeping the particle density n and the energy  $\epsilon$  per particle fixed, i.e.  $N, \Omega, E \to \infty$  while  $\frac{N}{\Omega} = n$  and  $\frac{E}{N} = \epsilon$  are constant. From (2.26) the exponential form of Maxwell's distribution of velocities then results,<sup>3</sup>

$$\lim_{N \to \infty} f(r, v) = n \left(\frac{3m}{4\pi\epsilon}\right)^{\frac{3}{2}} \exp\left(-\frac{3mv^2}{4\epsilon}\right).$$
(2.27)

Maxwell's distribution of velocities starts to form for a surprisingly small number of particles. In Fig. 2.3 we show single-particle velocity distributions for systems composed of three, six and an infinite number of particles. At velocities corresponding to the energy per particle, already for the two-particle system, the distribution has the character of a hat. For velocities far exceeding the energy per particle, however, one has to be careful about the number of particles in game; the higher the velocity, the slower the convergence towards Maxwell's distribution. Nevertheless, in the majority of many-body systems, the limit of an infinite number of particles is safely achieved.

<sup>3</sup> From Stirling's formula for the  $\Gamma$  function,  $\ln \Gamma(z) \approx z \ln z - z - \frac{1}{2} \ln z + \ln \sqrt{2\pi} + o(z^{-2})$ , see formula (8.343) in (Gradshteyn and Ryzhik, 2014), we obtain

$$\ln \frac{\Gamma\left(\frac{3}{2}N+1\right)}{\Gamma\left(\frac{3}{2}N-\frac{1}{2}\right)} \approx \left(\frac{3}{2}N+1\right) \ln \left(\frac{3}{2}N+1\right) - \left(\frac{3}{2}N+1\right) - \frac{1}{2} \ln \left(\frac{3}{2}N+1\right)$$
$$- \left(\frac{3}{2}N-\frac{1}{2}\right) \ln \left(\frac{3}{2}N-\frac{1}{2}\right) + \left(\frac{3}{2}N-\frac{1}{2}\right) + \frac{1}{2} \ln \left(\frac{3}{2}-\frac{1}{2}\right)$$
$$\approx \frac{3}{2} \ln \frac{3N}{2}.$$

The  $\Gamma$  factors in the distribution (2.26) thus yield

(2)

$$\frac{\Gamma\left(\frac{3}{2}N+1\right)}{\Gamma\left(\frac{3}{2}N-\frac{1}{2}\right)} \approx \left(\frac{3N}{2}\right)^{\frac{3}{2}}$$

The Gaussian function results from the limit

$$\lim_{N \to \infty} \left( 1 - \frac{2}{N} \frac{mv^2}{4\epsilon} \right)^{\frac{3}{2}N - \frac{5}{2}} = \exp\left( -\frac{3mv^2}{4\epsilon} \right).$$



Figure 2.3: Dimensionless velocity distribution (2.26) for 3, 6 and  $\infty$  particles in the 3D space. With an increasing number of particles the distribution is taller and thinner in the central part and has longer tails. All distributions correspond to the same density and energy per particle.

*Pressure* Having the single-particle distribution one can use probabilistic arguments to evaluate various observables. To connect with the previous discussion we evaluate the pressure.

The force dF exerted by particles on a small area dS of the surface of the container is given by the difference between the momentum flux which particles carry towards the surface and the momentum flux they carry away,

$$dF = \sum_{v_{\perp}>0} mv_{\perp} \frac{dn^{(+)}(v_{\perp})}{dt} - \sum_{v_{\perp}<0} mv_{\perp} \frac{dn^{(-)}(v_{\perp})}{dt}.$$
 (2.28)

The number  $dn^{(\pm)}(v_{\perp})$  of particles which hit/leave the surface during time dt with the perpendicular velocity  $v_{\perp}$  is the sum of the velocity distribution over the parallel velocity,

$$dn^{(\pm)}(v_{\perp}) = |v_{\perp}| dt dS \int dv_{\parallel} f(v).$$
(2.29)

The factor  $|v_{\perp}|dtdS$  appears because during dt all particles from this volume cross the surface. Substituting (2.29) into (2.28) the pressure results as

$$\mathscr{P} = \frac{dF}{dS} = \int dv m v_{\perp}^2 f(v).$$
(2.30)

In the 1D system, where  $v \equiv v_{\perp}$ , the left-hand side of (2.30) equals twice the density of energy,  $\int dv m v_{\perp}^2 f(v) = 2\mathscr{E}$ . Formula (2.30) is thus identical with (2.4). In the 3D system, we can use Maxwell's distribution to obtain the (3D) Bernoulli's formula

$$\mathscr{P} = \int dv m v_{\perp}^2 n \left(\frac{3m}{4\pi\epsilon}\right)^{\frac{3}{2}} \exp\left(-\frac{3mv^2}{4\epsilon}\right) = n \frac{2}{3}\epsilon = \frac{2}{3}\mathscr{E}, \qquad (2.31)$$

with the density of energy

$$\mathscr{E} = \int dv \frac{1}{2} m v^2 f(v) = n\epsilon.$$
(2.32)

*Temperature* In accordance with our assumption that the interaction of particles only randomises the distribution, the pressure (2.31) has no force corrections; i.e., it corresponds to the equation of state of the ideal gas,

$$\mathscr{P}\Omega = Nk_BT, \tag{2.33}$$

where  $k_B$  is Boltzmann's constant and T is a temperature. Comparing with (2.31) we find the energy per particle,

$$\epsilon = \frac{3}{2}k_BT.$$
(2.34)

By this relation, the distribution function f introduced to describe chaotic motion of molecules (2.27) becomes parametrised with a purely thermodynamic quantity, the temperature T. Now the microscopic and macroscopic worlds are connected.

*Summary* In principle, the evolution of the many-body system is covered by Newton's equation, but in reality, the exact state of the system is unpredictable because of chaotic evolution of non-conserving degrees of freedom. In the chaotic regime the time evolution scans the phase space in a manner which reminds a random sampling of the whole allowed subspace. Observables thus can be conveniently evaluated as mean values over this allowed subspace.

#### 2.3 Information versus chaos

#### 2.3.1 Entropy as a measure of negative information or disorder

Any randomisation destroys possible information stored in the system in the specific structure of the distribution. Therefore we will measure the dissipation or randomisation by the Shannon measure of information from information theory which is the opposite of the Boltzmann physical entropy. The aim is now to develop a quantitative formula for such measure *entropy S* which is able to count the information stored in the distribution. Amazingly we can derive an explicit mathematical expression for *S* if we demand only three properties for such a measure:

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1. The entropy should be a positive quantity

$$S \ge 0. \tag{2.35}$$

2. S will not judge about the symmetry of distributions or probabilities  $w_i$ 

$$S(w_1, w_2, w_3, ...) = S(w_2, w_1, w_3, ...) = S(w_3, w_1, w_2, ...) = ....$$
(2.36)

3. We divide our distribution into n rough boxes and then further into m > n fine boxes. Then the total entropy should be the entropy of the rough division plus the entropy of the fine division under the condition that we have any given rough division

$$S(w_{nm}) = S(w_n) + \sum_{\bar{n}} w_{\bar{n}} S(w_{m|\bar{n}}).$$
(2.37)

Here  $w_{nm}$  is the probability to have *n* and *m* divisions and  $w_{m|\bar{n}}$  is the probability of *m* under the condition of  $\bar{n}$  which occurs with probability  $w_{\bar{n}}$ .

The usefulness of property 3. is easily seen if we assume that the fine division is independent of the rough division  $w_{m,|n} = w_m$ . Then the sum in (2.37) about the probability  $w_{\bar{n}}$  is unity, as it should be for a probability and one gets simply the sum of the entropies of both divisions  $S(w_{nm}) = S(w_n) + S(w_m)$ .

Now we hunt for the explicit formula and use the properties 2. and 3. which means that the entropy has to be additive and the sum of an unknown function s(w) of the distribution  $w_n$ 

$$S(w_n) = \sum_n s(w_n) \tag{2.38}$$

since only in this case the interchangeability of any division n into arbitrary intervals is ensured. One gets from property 3.

$$\sum_{nm} s(w_{nm}) = \sum_{n} s(w_n) + \sum_{\bar{n}} w_{\bar{n}} \sum_{m} s(w_{m|\bar{n}}).$$
(2.39)

Since one summation occurs on both sides we can choose a specific  $\bar{n} = n = 1$  to get

$$\sum_{m} s(w_1 w_{m|1}) = s(w_1) + w_1 \sum_{m} s(w_{m|1})$$
(2.40)

where we have employed the formula of Bayes  $w_{1m} = w_{m|1}w_1 = w_{1|m}w_m$  as one checks from the definition of the probability to count events 1 or *m*.

With (2.40) we have arrived at a functional equation for the unknown function s. In fact, the only function which translates an argument of products  $w_1w_{m|1}$  into a sum is

the log function. Therefore using the ansatz  $s(x) = g(x) \ln x$  in (2.40) leads to

$$\ln w_1 \left[ \sum_m g(w_1 w_{m|1}) - g(w_1) \right] + \sum_m \ln w_{m|1} \left[ g(w_1 w_{m|1}) - w_1 g(w_{m|1}) \right] = 0. \quad (2.41)$$

Both parts vanish independently if we choose g(x) = x. Therefore we have reached our goal and have derived an explicit formula for the entropy obeying the properties 1.–3.:

$$S = -k_B \sum_{n} w_n \ln w_n. \tag{2.42}$$

Here the minus sign is chosen according to property 1. and the constant  $k_B$  turns out to be the Boltzmann constant as the comparison with thermodynamic quantities shows in section 2.3.2.

#### 2.3.2 Maximum entropy and equilibrium thermodynamics

As we will see on each level of kinetic theory throughout this book, the entropy is a quantity which will increase with time. This second law of thermodynamics is one of the most fundamental laws of thermodynamics. In fact the maximum of the entropy (2.42) leads to the different known equilibrium distributions  $w_n$  and the thermodynamic quantities.

For micro-canonical ensembles we assume no further restrictions and consider a closed system. Then the maximum of (2.42) is easily seen form  $\delta S/\delta w_n = 0$  to be  $w_n = 1/N$  which means the equi-partitioning of N events where we used the normalisation

$$1 = \sum_{1}^{N} w_n.$$
 (2.43)

If we allow energy fluctuations between the energy portions  $\epsilon_n$  in each division and demand constant energy on the ensemble average

$$\sum_{1}^{N} w_n \epsilon_n - E = 0, \qquad (2.44)$$

we have to add this boundary condition to (2.42) with a Lagrange multiplier  $\beta$ . Rendering this expression extremal one gets the canonical distribution

$$w_n = \frac{e^{-\beta\epsilon_n}}{z_{can}}; \quad z_{can} = \sum_m e^{-\beta\epsilon_m}$$
 (2.45)

where we have used the normalisation (2.43). The multiplier  $\beta$  turns out to be the inverse temperature  $\beta = 1/k_BT$  as one sees from the comparison with the first law of

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thermodynamics dE = TdS for constant volume and particle number. In fact calculating explicitly the entropy (2.42) with (2.45) one has  $S = \beta k_B E + k_B \ln z$  which leads to the desired identification. Furthermore since the free energy is F = E - TS one has direct access to the free energy by calculating the canonical statistical sum  $F = -k_B T \ln z_{can}$ .

If one allows density fluctuations between the occupation numbers  $n_n$  and demands that the total number conserves,

$$\sum_{1}^{N} n_n \epsilon_n - N = 0, \qquad (2.46)$$

one has to add this boundary with an additional Lagrange multiplier  $\alpha$  and obtains the grand canonical ensemble. By comparison to the first law of thermodynamics, this additional Lagrange multiplier  $\alpha = -\beta\mu$  is identified with the chemical potential  $\mu$  and one has

$$w_n = \frac{e^{-\beta(\epsilon_n - \mu n_n)}}{z_g}; \quad z_g = \sum_m e^{-\beta(\epsilon_m - \mu n_n)}$$
(2.47)

and direct access to the Gibbs potential  $PV = k_B T \ln z_g$ .

This illustrates the importance of the explicit formula for the entropy as the measure of (negative) information or disorder in the system. The kinetic theory as the description of time-dependent distributions will proove the second law of thermodynamics that the entropy (2.42) is a quantity which increase with time due to collisions or dissipation. Consequently, in equilibrium, this provides an extremal principle which allows us to access thermodynamic quantities by microscopic parameters.

#### 2.4 Collisions versus drift

Let us return to Fig. 2.2 which shows a zigzag path of a particle. The path is composed of slightly bent straight lines and sharp curvatures. It is convenient to assume that the collisions are due to centres of fixed positions, such as impurities in semiconductors. The two distinct components of the path follow from the properties of the impurity potential which are strong at short distances and weak at large distances.

The curvature, i.e., the encounter of a large deflection angle, appears only for nearly central events, when the strong part of the potential affects the particle. We will call such an event a collision. In a highly non-central encounter, the particle feels the weak tail of the potential without the strong part. On a short scale, the weak potential of the tails only slightly deviates from a straight motion. These deviations, however, accumulate so that along a longer trajectory the particle slowly changes its velocity or momentum. We will describe the encountering of a low deflection angle as a momentum drift. The momentum drift has to be distinguished from the space drift given by the free motion of particles. Both components together, space and momentum, we call briefly the drift.

#### 2.4.1 Collisions

In Fig. 2.2 one can see that the essential part of the collision happens on the scale which is small compared to the mean distance between impurities. Since the strong potential of the closest impurity dominates, it is possible to solve this short part of the trajectory by neglecting the other impurities. The collision is then approximated by a collision on an isolated impurity.

The dependence of the deflection angle on the impact factor for a Lennard–Jones potential is demonstrated in Fig. 2.4. As expected, large deflection angles appear for impact factors comparable with an atomic radius R. The collision is overly sensitive to an initial condition: nearly the whole sphere of finite directions results from target locations in a region of area  $\sim R^2$ .

The over-sensitivity of collisions allows us to take the target location as a random quantity. Let us assume that a particle of velocity v somewhere in a cylindrical tube of section  $2\pi b^2$  approaches an impurity sitting in the centre of the tube. The target location is given by orientation angle  $\varphi$  of the collision plane and the impact factor b. Accordingly, the particle is in cell  $(\varphi, \varphi + d\varphi) \times (b, b + db)$  with the probability  $\frac{bd\varphi db}{2\pi b_{cut}^2}$ .

From the target location b and  $\varphi$ , the particle is scattered into the final velocity w. Due to the energy conservation, the magnitude of velocity does not change, |w| = |v|. Due to the angular momentum conservation, the particle remains in the same collision plane (we assume spherical potential), i.e.,  $\varphi$  conserves. The deflection angle  $\theta$  depends on the impact factor b. The probability  $p_{vw}d\varphi \sin \theta d\theta$  that the particle will end up with velocity in the direction cell  $(\varphi, \varphi + d\varphi) \times (\theta, \theta + d\theta)$  equals the probability that it has started the collision from the corresponding cell of target locations,

$$p_{vw}d\varphi\sin\theta d\theta = \frac{bd\varphi db}{2\pi b_{cut}^2}.$$
(2.48)



**Figure 2.4:** Classical trajectories of a particle with different impact parameter and same velocity (left) and the corresponding deflection angle as a function of the impact factor (right). The interaction potential is of Lennard–Jones type as in Figure 2.2.

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Accordingly,

$$p_{vw} = \frac{bdb}{\sin\theta d\theta} \frac{1}{2\pi b_{\rm cut}^2}.$$
(2.49)

This probability can be derived from the dependence of the deflection angle on the impact factor presented in Fig. 2.4.

*Boltzmann equation* If one neglects low-angle encounters, the concept of random target location can be used to derive a kinetic equation for a single-particle distribution f(r, v, t). Let us assume a small space and velocity cell  $d\Omega_r \times d\Omega_v$  around the point (r, v). The number of particles in this cell is  $dN = f(r, v, t)d\Omega_r d\Omega_v$ . This number changes with time due to particles which cross the space border of the cell running with velocity v, and due to particles which cross the velocity border being accelerated by the potential of some impurity.

We take a cylindrical space cell,  $d\Omega_r = dldS$ , with the rounded side of area dS perpendicular to velocity v, i.e. the dl follows the direction  $\frac{v}{|v|}$ . During time dt, all particles of velocity v which are in the layer of width |v|dt attached to the cylinder from the upwind side enter the cylinder. Their number is

$$dN_{\text{enter}} = |v| dt dS d\Omega_v f\left(r - \frac{1}{2} \frac{v}{|v|} dl, v, t\right).$$
(2.50)

On the contrary, during dt, all particles of velocity v in the layer of width |v|dt inside the cylinder on the downwind side leave it. Their number is

$$dN_{\text{leave}} = |v| dt dS d\Omega_{v} f\left(r + \frac{1}{2} \frac{v}{|v|} dl, v, t\right).$$
(2.51)

The acceleration by impurity potential is described as a collision. During dt, each particle will scan the volume  $\pi b_{\text{cut}}^2 |v| dt$  reaching some impurity with a probability  $\pi b_{\text{cut}}^2 |v| dt \frac{dN_{\text{imp}}}{d\Omega_r}$ , where  $dN_{\text{imp}}$  is the number of impurities in the volume  $d\Omega_r$ . The probability that during dt some of particles lose their velocity v is

$$dN_{\rm out} = dN\pi b_{\rm cut}^2 |v| dt \frac{dN_{\rm imp}}{d\Omega_r} = f(r, v, t) d\Omega_r d\Omega_v \pi b_{\rm cut}^2 |v| dt \frac{dN_{\rm imp}}{d\Omega_r}.$$
 (2.52)

On the contrary, some particles of velocity w suffer a collision after which they end up in the cell  $d\Omega_v$  around v. The number of particles of velocity |w| = |v| scattered into the cell  $d\Omega_v$  is

$$dN_{\rm in} = \int_{d\Omega_v} dv \times \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta p_{wv} \times \pi b_{\rm cut}^2 |w| dt \frac{dN_{\rm imp}}{d\Omega_r} \times d\Omega_r f(r, w, t).$$
(2.53)

The symbols  $\times$  separate components of the formula. The last term counts particles of velocity w. The last but one term specifies which particles undergo some collision. The second term selects collisions which end up with the velocity v. The first term sums over all velocities in an allowed velocity cell. After substitution from (2.49) we obtain

$$dN_{\rm in} = d\Omega_v d\Omega_r dt \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \sin \theta P_{wv} f(r, w, t), \qquad (2.54)$$

where we have denoted the transition probability

$$P_{wv} = \frac{dN_{\rm imp}}{d\Omega_r} |v| \frac{bdb}{\sin\theta d\theta}.$$
 (2.55)

In terms of the transition probability one can also express the number of particles which leave the cell

$$dN_{\rm out} = d\Omega_v d\Omega dt \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta P_{vu} f(r, v, t), \qquad (2.56)$$

where

$$\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta P_{vw} = \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta d\theta c |v| \frac{bdb}{\sin\theta d\theta} = c|v|2\pi \int_0^b bdb = c|v|\pi b^2.$$
(2.57)

Summing all contributions,  $dN = dN_{\text{enter}} - dN_{\text{leave}} + dN_{\text{in}} - dN_{\text{out}}$ , one finds the time evolution of the distribution. The time derivative results from  $\frac{dN}{dtd\Omega dv} = \frac{\partial f}{\partial t}$ . The space drift is obtained from (2.50) and (2.51) as  $\frac{dN_{\text{enter}} - dN_{\text{leave}}}{dtd\Omega dv} = v \frac{\partial f}{\partial r}$ . The scattering integral results from (2.54) and (2.56) into  $\frac{dN_{\text{in}} - dN_{\text{out}}}{dtd\Omega dv} = \sum_{w} P_{ww} f(r, w, t) - \sum_{w} P_{vw} f(r, v, t)$  and the final form is the kinetic equation,

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial r} = \sum_{w} P_{wv} f(r, w, t) - \sum_{w} P_{vvw} f(r, v, t), \qquad (2.58)$$

known as the Boltzmann equation. Here  $\sum_{w} \equiv \int_{0}^{2\pi} d\varphi \int_{0}^{\pi} \sin \theta d\theta$ . The left-hand side covers a deterministic space drift, the right-hand side covers a random dissipation.

#### 2.4.2 Drift

Deriving the collision integral we have neglected events with the impact factor larger than  $b_{\text{cut}}$ , i.e., with the deflection angle smaller than corresponding to  $\theta_{\text{cut}}$ . Formally it seems that low-angle encounters can be included by a straightforward limit  $\theta_{\text{cut}} \rightarrow 0$ .

This approach fails because the actual choice of  $\theta_{cut}$  determines how many collisions a particle suffers. A mean time  $\tau$  of straight flight is inversely proportional to the cross section  $\pi b^2$ ,

$$\frac{1}{\tau} = \sum_{w} P_{vw} = c |v| \pi b_{\text{cut}}^2, \qquad (2.59)$$

therefore with increasing  $b_{\text{cut}}$  we soon meet a regime in which a particle should scatter again before it leaves the interaction potential of a previous scatterer. To keep binary collisions as independent sequential events, one has to cut collisions at some reasonably selected angle and treat the low-angle encounters in a different manner.

*Effect of potential tails on velocity* Let us assume a particle between collisions. If it would be completely free of interactions, its velocity is v. Since it passes through tails of impurity potentials, its motion,

$$m\ddot{r} = -\frac{\partial\phi}{\partial r},\tag{2.60}$$

is driven by a force from a sum over all potential tails

$$\phi(r) = \sum_{i}' V(r - r_i)$$
(2.61)

of impurities placed at positions  $r_i$ . The prime on the sum denotes that no impurity is closer than  $b_{\text{cut}}$ .

Some of impurities push the particle to the left and others to the right. Many of these low-angle deflections compensate after a large number of events. If the impurity concentration, however, has a gradient, the particle is more strongly pushed from the side with the higher concentration. In this case, a distortion of the trajectory accumulates which becomes apparent for long trajectories. These distortions can be described by a mean value of potentials affecting the particle, i.e., approximating the actual potential  $\phi$  by a mean field

$$\bar{\phi} = \int_{|r-y| > b_{\text{cut}}} dy c(y) V(r-y).$$
(2.62)

Neglecting the short-range deviations from the locally 'straight' trajectory, one can speak only about a mean coordinate  $\bar{r}$  and mean velocity  $\bar{v} = \frac{d\bar{r}}{dt}$ . From an effective Newton equation,

$$m\frac{d\bar{v}}{dt} = -\left.\frac{\partial\bar{\phi}}{\partial r}\right|_{\bar{r}},\tag{2.63}$$

one finds that an effective energy

$$\epsilon = \frac{1}{2}m\bar{v}^2 + \bar{\phi},\tag{2.64}$$

conserves along the mean trajectory. When the particle enters the impurity-free region, its velocity equals v and the energy is  $\epsilon = \frac{1}{2}mv^2$ . The mean velocity thus differs from the velocity of a completely isolated particle as

$$|\bar{v}| = \sqrt{v^2 - \frac{2\bar{\phi}}{m}} \approx |v| - \frac{\bar{\phi}}{m|v|}.$$
(2.65)

*Vlasov equation* The mean field is easily incorporated into the kinetic equation. Due to forces caused by the mean field, particles can leave the cell  $d\Omega_r \times d\Omega_v$  crossing the velocity border under acceleration  $a = -\frac{1}{m} \frac{\partial \tilde{\phi}}{\partial r}$ . We choose a cubic velocity cell,  $d\Omega_v = dv_a dS_v$ , with a side of area  $dS_v = dv_a dv_a$  perpendicular to *a*; i.e. the explicit  $dv_a$  is the direction of the acceleration  $\frac{a}{|a|}$ . During *dt*, all particles from a layer of width |a|dt attached to the cube from the upwind side are driven into the cube, and all particles from a layer of the same width but in the downwind side of cube are driven out of the cube. These two processes change the number of particles as

$$dN_{\rm accel} = |a| dt dv^2 d\Omega f\left(r, v - \frac{1}{2} \frac{a}{|a|} dv_a, t\right),$$
(2.66)

$$dN_{\text{decel}} = |a| dt dv^2 d\Omega f\left(r, v + \frac{1}{2} \frac{a}{|a|} dv_a, t\right).$$
(2.67)

Summing all contributions,  $dN = dN_{enter} - dN_{leave} + dN_{accel} - dN_{decel} + dN_{in} - dN_{out}$ , one finds the kinetic equation,

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial r} - \frac{1}{m} \frac{\partial \phi}{\partial r} \frac{\partial f}{\partial v} = \sum_{w} P_{wu} f(r, w, t) - \sum_{w} P_{vu} f(r, v, t), \qquad (2.68)$$

known as the Vlasov equation (although more common is the Vlasov equation with the collision term neglected).

#### 2.4.3 Equivalence of low-angle collisions and momentum drift

At first glance, the Vlasov equation differs from the Boltzmann equation (2.58) only via the mean field term, the momentum drift. The difference, however, is much larger. The mean field and the collisions are two different manifestations of forces between particles. The separation of the interaction into these components has been defined artificially with an open parameter  $\theta_{cut}$ . Such a procedure is allowed only if there is a region in which both components are equivalent. Briefly, we have to show that there is a region of small deflection angles which can be described either via mean fields or via collisions, of course, with the same result. It turns out that a more sophisticated approximation of the scattering integral is necessary.

To demonstrate the equivalence of collisions on small angles with the mean field, let us derive the corresponding kinetic equations for a system of particles which interact via

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a soft potential of finite range, e.g., the 3D box potential,  $V(r) = V\theta(R - |r|)$ . Since the potential is soft,  $V \ll \frac{1}{2}mv_{\text{th}}^2 = \frac{3}{2}k_BT$ , all scattering events are on small deflection angles. Accordingly, all interactions can be described via the mean field. Since the range of the potential is finite, the total cross section is finite,  $\sigma = \pi R^2$ . We assume that the range of interactions can be treated as rare events. Accordingly, all interactions can be described as collisions. To show this equivalency of both pictures we derive the mean-field-less Boltzmann-type kinetic equation and rearrange it into the collision-less Vlasov equation.

*Kinetic equation with nonlocal corrections* We have seen in section 2.1.2 that the mean field is connected with the time  $\Delta_t$  by which the particle is delayed in the collision. To introduce the delay time into the kinetic equation, we have to take into account that a particle scattered into the velocity v at time t has started the collision process at  $t - \Delta_t$ . The number of particles scattered into the cell  $d\Omega_r \times d\Omega_v$  thus reads

$$dN_{\rm in} = dt d\Omega_r d\Omega_v \sum P_{wv} f(r, w, t - \Delta_t).$$
(2.69)

The low-angle collisions happen for rather large values of the impact factor b, see Fig. 2.5. Since we identify the position r of the collision with the point on the trajectory where the particle is closest to the impurity, the impurity is displaced at  $r + \Delta r$ . The number of scattered particles thus has to be modified as

$$dN_{\rm in} = dt d\Omega_r d\Omega_v \sum P_{wv}(r + \Delta r) f(r, w, t - \Delta_t), \qquad (2.70)$$

$$dN_{\rm out} = dt d\Omega_r d\Omega_v \sum P_{wv}(r - \Delta r) f(r, v, t).$$
(2.71)

With these modifications, the kinetic equation reads

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial r} = \sum_{w} P_{wv}(r + \Delta r) f(r, w, t - \Delta_t) - \sum_{w} P_{vw}(r - \Delta r) f(r, v, t).$$
(2.72)



**Figure 2.5:** Scattering on the box potential. In the scattering-out (upper trajectory) a particle of initial velocity v is deflected to the velocity w. In the corresponding scattering-in (lower trajectory) a particle goes from w to v. The distance  $\pm \Delta r$  of an impurity centre from the point r attributed to the collision event is mutually reversed for -in and -out processes.

For the soft potential, only small deflection angles and short delay times appear.<sup>4</sup> The free motion of a particle is thus perturbed by two quantities, the deviation of the velocity direction  $\Delta v = w - v$  and the collision delay  $\Delta_t$ . Both these  $\Delta$ 's are small being linear in potential V. The  $\Delta r$  is proportional to the impact factor b which is also small on the scale of gradients in the system.

Expanding (2.72) in  $\Delta$ 's and *b*, one finds<sup>5</sup>

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial r} = \frac{\partial f}{\partial v} \sum_{w} \frac{\partial P_{vv}}{\partial r} \Delta r \Delta v - \frac{\partial f}{\partial t} \sum_{w} \bar{P}_{vv} \Delta_t.$$
(2.73)

<sup>4</sup> In the collision process on the box-like potential, the particle gains three velocities, v before, u during and w after the collision. Since the collision is symmetric, the change of velocity at matching points, |r - y| = R, equal, u - v = w - u. (The impurity sits in y.) It is thus sufficient to solve for u as w = 2u - v.

When the particle makes a contact, the tangential velocity  $v_{\parallel} = |v|\frac{b}{R}$  conserves,  $u_{\parallel} = v_{\parallel}$ . The normal velocity is given by the energy conservation,  $\frac{1}{2}mv_{\perp}^2 = \frac{1}{2}mu_{\perp}^2 + V$  as  $v_{\perp} = |v|\sqrt{1-\frac{b^2}{R^2}}$  and  $u_{\perp} = \sqrt{v_{\perp}^2 - 2\frac{V}{m}}$ . The maximum deflection angle  $\theta_{\max}$  is achieved for the impact factor  $b_{\max}$  at the edge of allowed penetration, where  $u_{\perp} = 0$ . This condition gives

$$1 - \frac{b_{\max}^2}{R^2} = \frac{V}{\frac{1}{2}mv^2}, \quad \text{from which} \quad \theta_{\max} = 2\arccos\frac{b_{\max}}{R} = 2\arcsin\sqrt{\frac{V}{\frac{1}{2}mv^2}} \approx 2\sqrt{\frac{V}{\frac{1}{2}mv^2}}.$$

The collision delay can be estimated in the region of relatively small impact factors from an unperturbed trajectory as

$$\Delta_t = \frac{2\sqrt{R^2 - b^2}}{|u|} - \frac{2\sqrt{R^2 - b^2}}{|v|} \approx \frac{2\sqrt{R^2 - b^2}}{|v|} \frac{V}{mv^2}$$

The velocity change  $\Delta v = v - v = 2(u - v)$  has the dominant contribution in the direction parallel to  $\Delta r$ .

$$\Delta v \approx \frac{\Delta r}{b} \frac{2V}{m|v|} \frac{\frac{b}{R}}{\sqrt{1 - \frac{b^2}{R^2}}} = \frac{\Delta r}{\sqrt{R^2 - b^2}} \frac{2V}{m}.$$

<sup>5</sup> A straightforward expansion of the scattering-in gives

$$\begin{split} &\sum_{w=v+\Delta v} P_{wv}(r+\Delta r)f(r,v+\Delta v,t-\Delta_t) = f(r,v,t) \sum_{w=v+\Delta v} P_{wv}(r) + f(r,v,t) \frac{\partial \ln c}{\partial r} \sum_{w=v+\Delta v} P_{wv}(r)\Delta r \\ &+ \frac{\partial f(r,v,t)}{\partial v} \sum_{w=v+\Delta v} P_{wv}(r)\Delta v - \frac{\partial f(r,v,t)}{\partial t} \sum_{w=v+\Delta v} P_{wv}(r)\Delta_t + \frac{\partial f(r,v,t)}{\partial v} \frac{\partial \ln c}{\partial r} \sum_{w=v+\Delta v} P_{wv}(r)\Delta r\Delta v \\ &= \frac{f}{\tau} - \frac{\partial f}{\partial t} \sum_{w=v+\Delta v} P_{wv}\Delta_t + \frac{\partial f}{\partial v} \frac{\partial \ln c}{\partial r} \sum_{w=v+\Delta v} P_{wv}\Delta r\Delta v = \frac{f}{\tau} - \frac{\partial f}{\partial t} \sum_{w=v+\Delta v} P_{vv}\Delta_t + \frac{\partial f}{\partial v} \frac{\partial \ln c}{\partial r} \sum_{w=v+\Delta v} P_{vv}\Delta r\Delta v. \end{split}$$

We have used that  $P_{vvv}$  depends on the coordinate only via the concentration of impurities. The inverse lifetime is  $\frac{1}{\tau} = \sum_{vv} P_{vvv}$ . Two terms have vanished under the integration over directions: the term  $\Delta r = b \sin \varphi$ ,

$$f\sum_{w} \left(\frac{\partial P_{wv}}{\partial r} + \frac{\partial P_{vw}}{\partial r}\right) \Delta r = f\frac{\partial \ln c}{\partial r} \sum_{w} \left(P_{wv} + P_{vw}\right) \Delta r = f \ 2 \int_{0}^{2\pi} d\varphi \int_{0}^{\pi} d\theta \sin \theta P(|v|, \theta) b \sin \varphi = 0,$$

and from the same reason the term with  $\Delta v \propto \sin \varphi$ .

A straightforward expansion of the scattering-out gives

z

$$\sum_{v=v+\Delta v} P_{vw}(r-\Delta r)f(r,v,t) = \frac{J}{\tau}.$$

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One can see that the correction terms are small if gradients in time and space are small. The higher powers in  $\Delta$ 's would lead to higher powers in gradients and can be neglected. The linear order is proportional to gradients in the same way as the drift terms on the left-hand side; therefore they cannot be neglected as small in gradients.

Space displacements and direction-changing forces The space displacement  $\Delta r$  and the velocity change  $\Delta v$  have the same direction which is perpendicular to the velocity v. Accordingly, the gradients are restricted to a plane perpendicular to v which we denote by a projector operator  $\mathbf{Q}_{xy} = \delta_{xy} - \frac{v_x v_y}{v^2}$ . Clearly,  $\mathbf{Q}\Delta r = \Delta r \mathbf{Q} = \Delta r$  and  $\mathbf{Q}\Delta v = \Delta v \mathbf{Q} = \Delta v$  while  $\mathbf{Q}v = v\mathbf{Q} = 0$ . So far we have parametrised the collision by the final velocity w, as it is customary for the scattering integrals. For low-angle collisions when  $w \approx v$ , this parametrisation becomes clumsy and it becomes more convenient to parametrise the collision by the impact factor b which naturally measures the rate,

$$\sum_{w} \bar{P}_{wv} = \int_{0}^{2\pi} d\varphi \int_{0}^{\pi} d\theta \sin \theta \bar{P}_{wv} = \int_{0}^{2\pi} d\varphi \int db \ bc|v|.$$
$$\Delta v \approx \frac{\Delta r}{b} \frac{2V}{m|v|} \frac{\frac{b}{R}}{\sqrt{1 - \frac{b^2}{R^2}}} = \frac{\Delta r}{\sqrt{R^2 - b^2}} \frac{2V}{m}.$$

Then

$$\sum_{vv} \frac{\partial P_{vv}}{\partial r} \Delta r \Delta v = \mathbf{Q} |v| \frac{\partial c}{\partial r} \int_0^R db \ b \int_0^{2\pi} d\varphi b |\Delta v|$$
$$\approx \mathbf{Q} \frac{\partial c}{\partial r} \frac{4\pi V}{m} \int_0^R db \frac{b^3}{\sqrt{R^2 - b^2}} = \mathbf{Q} \frac{1}{m} \frac{\partial c}{\partial r} V \frac{4\pi R^3}{3}. \tag{2.74}$$

Therefore the effect of the velocity correction is

$$\sum_{vv} \frac{\partial P_{vv}}{\partial r} \Delta r \Delta v = \mathbf{Q} \frac{1}{m} \frac{\partial \phi}{\partial r}$$
(2.75)

and we have arrived at a kinetic equation,

$$\left(1 + \sum_{w} \bar{P}_{vv} \Delta_t\right) \frac{\partial f}{\partial t} + v \frac{\partial f}{\partial r} - \frac{\partial \bar{\phi}}{\partial r} \mathbf{Q} \frac{\partial f}{\partial v} = 0, \qquad (2.76)$$

which reminds us of the Vlasov equation in the absence of a collision. The force perpendicular to v is also the same as in the Vlasov equation. The only peculiar point is that there is no force parallel to v. Instead, we have obtained a strange renormalisation of the time derivative.

*Collision delay and energy-changing forces* The renormalisation of the time derivative can be rearranged into the force parallel to the velocity. To this end we evaluate the correction

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$$\sum_{vv} \bar{P}_{vv} \Delta_t = \int_0^{2\pi} d\varphi \int_0^R db \ bc|v| \Delta_t \approx c \frac{V}{mv^2} \frac{4\pi R^3}{3} = \frac{\bar{\phi}}{mv^2}.$$
 (2.77)

Now we divide the equation with the renormalisation factor,<sup>6</sup>

$$\frac{\partial f}{\partial t} + \bar{v}\frac{\partial f}{\partial r} - \frac{\partial \bar{\phi}}{\partial r}\mathbf{Q}\frac{\partial f}{\partial v} = 0, \qquad (2.78)$$

so that the renormalisation moves into the velocity,

$$\bar{v} = \frac{v}{1 + \frac{\bar{\phi}}{mv^2}} \approx v - v \frac{\phi}{mv^2},$$
(2.79)

which becomes the mean velocity (2.65). The renormalisation changes the amplitude but not the direction of velocity. Therefore it corresponds to forces parallel to v.

To complete the rearrangement, we substitute the mean velocity instead of the asymptotic velocity v,

$$\bar{f}(r, \bar{v}, t) = f(r, v, t).$$
 (2.80)

This substitution results into the complete force term<sup>7</sup>,

$$\frac{\partial \bar{f}}{\partial t} + \bar{v}\frac{\partial \bar{f}}{\partial r} - \frac{1}{m}\frac{\partial \bar{\phi}}{\partial r}\frac{\partial \bar{f}}{\partial \bar{v}} = 0.$$
(2.81)

One can see that  $\overline{f}$  obeys the Vlasov kinetic equation. We have thus proved that the low-angle collisions can be rearranged into the mean field.

 $^{6}$  A renormalisation of the perpendicular force term can be neglected being of the second order in potential V.

<sup>7</sup> With substitution (2.79) we have to make an identical substitution of coordinate and time,  $\bar{r} = r$  and  $\bar{t} = t$ . The derivatives transform as

$$\begin{array}{l} \frac{\partial}{\partial t} \ = \ \frac{\partial}{\partial \overline{t}} \ + \ \frac{\partial |\bar{v}|}{\partial t} \ \frac{\partial}{\partial |\bar{v}|} \ = \ \frac{\partial}{\partial \overline{t}}, \\ \\ \frac{\partial}{\partial r} \ = \ \frac{\partial}{\partial \overline{r}} \ + \ \frac{\partial |\bar{v}|}{\partial r} \ \frac{\partial}{\partial |\bar{v}|} \ = \ \frac{\partial}{\partial \overline{r}} \ - \ \frac{v}{mv^2} \ \frac{\partial \bar{\phi}}{\partial r} \ \frac{\partial}{\partial |\bar{v}|} \\ \end{array}$$

We have used that the potential of impurities is stationary,  $\frac{\partial \tilde{\phi}}{\partial t} = 0$ , so that  $\frac{\partial \tilde{v}}{\partial t} = 0$ . The projection of  $\tilde{v}$  on the derivative in the parallel direction is just  $|\tilde{v}|$ ; therefore

$$\bar{v}\frac{v}{mv^2}\frac{\partial\bar{\phi}}{\partial r}\frac{\partial}{\partial\bar{v}} = \frac{1}{m}\frac{\partial\bar{\phi}}{\partial r}\left(1-\mathbf{Q}\right)\frac{\partial}{\partial\bar{v}}$$

Finally, we join both gradient contributions,

$$\frac{\partial \bar{\phi}}{\partial r} \mathbf{Q} \frac{\partial \bar{f}}{\partial \bar{v}} + \frac{\partial \bar{\phi}}{\partial r} \left( \mathbf{1} - \mathbf{Q} \right) \frac{\partial \bar{f}}{\partial \bar{v}} = \frac{\partial \bar{\phi}}{\partial r} \frac{\partial \bar{f}}{\partial \bar{v}}$$

*Energy bottom* The kinetic equation with the nonlocal and non-instant collision integral can be rearranged into the kinetic equation with the mean field for sufficiently highenergy particles. At low energies, however, they differ substantially. Let us assume that the mean potential is repulsive,  $\bar{\phi} > 0$ . Writing (2.79) in the form of energy conservation,

$$\frac{1}{2}m\bar{v}^2 + \bar{\phi} = \frac{1}{2}mv^2,$$
(2.82)

one can see that slow particles,  $\frac{1}{2}mv^2 < \bar{\phi}$ , correspond to a negative kinetic energy within the mean-field picture. Accordingly, the slow particles are not allowed to penetrate into this region. Within the nonlocal and non-instant picture, no such limitation appears.

For the model assumed, the mean field is an incorrect approximation for low energies and the energy bottom corresponds to v = 0. On the other hand, for the Coulomb potential which is truly of long range, there is no space between particles that would be free of the potential of particles around. Accordingly, the mean-field energy bottom is more appropriate to the Coulomb interaction. The optimal separation of the interaction into the mean field and the nonlocal and non-instant collisions thus has to be guided by the actual interaction potential and the density of particles in questions.

#### 2.4.4 Summary

The effects of interaction on the trajectories of particles can be separated into two groups. Firstly, infrequent collisions with a large deflection angle and secondly rather frequent encounters with deflections on small angles. The collisions randomise the trajectory of particles. The low-angle encounters act as a mean field.

These two effects of the interaction naturally appear in the kinetic equation as the mean-field drift and the collision integral. The simplest collision integral of Boltzmann type is local and instant. It describes only the randomisation of directions. In Part IV we discuss the kinetic theory in which collisions are nonlocal and non-instant and thus carry a share of forces.

#### 2.5 Explicit versus hidden forces

Previously we have restricted the deflection angle by an artificial cutoff. In many systematic approaches one never meets the demand to set any cut-offs. In these cases the separation of low- and high-angle collisions happens automatically as a byproduct of binary correlations. Let us demonstrate how binary correlations split the interaction potential into a strong short-range potential core responsible for the high-angle deflections and a weak long-range tail acting like a mean field.

*Binary correlation* Naturally, fast particles can penetrate into the repulsive potential deeper than slow ones. The radius of the core thus shrinks with an increasing temperature. Let us evaluate the probability that in a system of N particles interacting by a

potential  $\mathcal{V}(r-r')$ , two particles are found at a distance |r-r'|. The N-particle distribution

$$F_N(r_1, \dots, r_N, v_1, \dots, v_N) = A_N \delta \left( E - \frac{1}{2} m \sum_{i=1}^N v_i^2 - \sum_{i< j}^N \mathcal{V}(r_i - r_j) \right),$$
(2.83)

integrated over velocities provides a probability that all N particles are in the prescribed coordinates,

$$n_N(r_1,\ldots,r_N) = \frac{3(2\pi)^{\frac{3}{2}-1}A_N}{(N-1)!\;\Gamma\left(\frac{3}{2}N+1\right)m^{\frac{3}{2}N}} \left(E - \sum_{i< j}^N \mathscr{V}(r_i - r_j)\right)^{\frac{3}{2}N-1}.$$
 (2.84)

This is called the *N*-particle space-correlation function.

To find the probability  $n_2(r, r')$  that there are two particles at r and r' with no regards to the coordinates of the others, we associate r with some  $r_i$  and r' with some  $r_j$ ,  $j \neq i$ , and integrate over the remaining coordinates. There are N(N-1) ways how to select i and j. For identical particles, we can take i = 1 and j = 2 and multiply them with factor N(N-1); for all other choices,

$$n_2(r,r') = \frac{3(2\pi)^{\frac{3}{2}-1}A_N}{(N-1)!\,\Gamma\left(\frac{3}{2}N+1\right)m^{\frac{3}{2}N}}N(N-1)$$
(2.85)

$$\times \int dr_3 \dots dr_N \left( E - \mathscr{V}(r-r') - \sum_{2 < i}^N \mathscr{V}(r-r_i) - \sum_{2 < i}^N \mathscr{V}(r'-r_i) - \sum_{2 < i < j}^N \mathscr{V}(r_i-r_j) \right)^{\frac{1}{2}N-1}.$$

The two-particle probability  $n_2$  cannot be evaluated exactly; however, already a simple approximation provides physically interesting results. If we neglect interactions of three and more particles, the interaction of the remaining particles can be neglected which yields<sup>8</sup>

$$n_2(r, r') = n^2 \exp\left[-\frac{\mathscr{V}(r-r')}{k_B T}\right].$$
 (2.86)

<sup>8</sup> From the norm  $A_N$  of non-interacting particles (2.22) and the limit of a large number of particles,  $N \to \infty$  while,  $\frac{N}{\Omega} = n$  and  $\frac{E}{N} = \epsilon = \frac{3}{2}k_BT$ , one finds

$$\begin{split} n_2(r,r') &\approx \frac{3(2\pi)^{\frac{N}{2}-1}A_N}{(N-1)!\,\Gamma\left(\frac{3}{2}N+1\right)m^{\frac{3}{2}N}}N(N-1)\int dr_3\dots dr_N\left(E-\mathscr{V}(r-r')\right)^{\frac{3}{2}N-1} \\ &= \frac{3(2\pi)^{\frac{3}{2}-1}A_NN\Omega^{N-2}}{(N-2)!\,\Gamma\left(\frac{3}{2}N+1\right)m^{\frac{3}{2}N}}\left(E-\mathscr{V}(r-r')\right)^{\frac{3}{2}N-1} \\ &= \frac{N(N-1)}{\Omega^2}\left(1-\frac{\mathscr{V}(r-r')}{E}\right)^{\frac{3}{2}N-1} = n^2\exp\left[-\frac{3}{2}\frac{\mathscr{V}(r-r')}{E}\right] = n^2\exp\left[-\frac{\mathscr{V}(r-r')}{k_BT}\right]. \end{split}$$