Abstract

This paper gives a short review of the history of statistical physics starting from D. Bernoulli’s kinetic theory of gases in the 18th century until the recent new developments in nonequilibrium kinetic theory in the last decades of this century. The most important contributions of the great physicists Clausius, Maxwell and Boltzmann are sketched. It is shown how the reversibility and the recurrence paradox are resolved within Boltzmann’s statistical interpretation of the second law of thermodynamics. An approach to classical and quantum statistical mechanics is outlined. Finally the progress in nonequilibrium kinetic theory in the second half of this century is sketched starting from the work of N.N. Bogolyubov in 1946 up to the progress made recently in understanding the diffusion processes in dense fluids using computer simulations and analytical methods.

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In the 17th century the physical nature of the air surrounding the earth was established. This was a necessary prerequisite for the formulation of the gas laws. The invention of the mercuri barometer by Evangelista Torricelli (1608–47) and the fact that Robert Boyle (1627–91) introduced the pressure $P$ as a new physical variable where important steps. Then Boyle–Mariotte’s law $PV = \text{const.}$ for constant temperature, where $V$ is the volume, was formulated.

**First Kinetic Theory of Gases**

Daniel Bernoulli (1700–82) who had been born in Groningen in the Netherlands and moved to Basle in Switzerland gave in 1738 in a treatise on hydrodynamics a derivation of the gas laws from a “‘billiard ball’” model. He assumed that the gas consists of a very large number of small particles in rapid motion. He already identified heat with kinetic energy (living force). He then derived Boyle–Mariotte’s law for the gas–pressure at constant temperature on a movable piston from the impact of the gas molecules onto the piston just in the same way as it is still done today in elementary text books. He also used the principle of conservation of mechanical energy and concluded that, if the temperature changes, the pressure will also change so that it is proportional to the square of the velocities of the gas–particles and thus, for constant volume, will rise with rising temperature. At that time mechanical energy was still called vis viva in Latin or living force in English. Bernoulli was, however, about a century ahead of his time with his kinetic theory of gases. His model was almost forgotten. At that time only his Swiss copatriots J.A. De Luc (1727–1817) and George–Louis Le Sage (1724–1803) in Geneva and M.V. Lomonossov (1711–65) in Russia mentioned it. As Stephen Brush points out in his book on the kinetic theory “The man who persuades the world to adopt a new idea has accomplished as much as the man who conceived that idea.”

The reason why Bernoulli’s kinetic theory received so little attention was that most scientists at that time believed in the so–called caloric theory of heat.

**The Caloric Theory**

In the caloric theory heat was a substance called ”‘caloric’”. Caloric was considered to be a fluid composed of particles which repel each other. Like the earth is surrounded by its atmosphere each matter particle was thought to be surrounded by an atmosphere of caloric whose density increases with temperature. Thus at small distances matter particles repel each other due to the repulsion of their caloric atmospheres. In those days one did not know that matter is held together by electrical forces but one thought that the attractive forces between matter particles are of gravitational origin just as the forces between the sun and the planets. At a certain distance between matter particles there would be equilibrium between the caloric repulsion and the gravitational attraction. As the temperature rises more caloric is added to each matter particle and consequently the caloric repulsion increases shifting the equilibrium point outwards. In this way one could explain the thermal expansion of matter including gases. It should be mentioned that such reputed scientists as Pierre Simon, Marquis de Laplace (1749–1827) gave a very sophisticated derivation of the gas laws within the caloric theory.

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2S.G. Brush: Kinetic Theory, vol. 1. The Nature of Gases and of Heat, Pergamon Press, London 1965, p. 9. Bernoulli’s paper and most other historic papers quoted below are reprinted in vol. 1 or in vol.2: Irreversible Processes (1966) by S.G. Brush.
At the end of the 18th century various arguments against the caloric theory appeared. For instance: Does caloric have weight? In 1798 Benjamin Thompson (1753–1814) could show that the expected additional weight when a body was heated could not be detected. Another argument against the caloric theory was raised by Rumford Humphry Davy (1778–1829). He remarked that an indefinite amount of heat can be produced from matter by mechanical work, for instance by friction. If caloric was a substance only a limited amount should be available in matter. But these arguments did not really convince the fans of the caloric theory.

Now let me mention the attempts for a revival of the kinetic theory.

**The Revival of the Kinetic Theory**

In 1820 in England John Herapath, born 1790 at Bristol, criticised the derivation of the gas laws by Laplace and gave an account of the kinetic theory, but his paper was not accepted for publication in the Philosophical Transactions of the Royal Society because it was considered to be too speculative. It finally appeared in 1821 in the Philosophical Transactions and would have been forgotten if James Prescott Joule (1818–89) would not have been influenced by it and by Herapath’s book on Mathematical Physics published in 1847.

In 1847 Joule published a paper in the Manchester Courier with the title “On Matter, Living Force, and Heat” where he stated the principle of conservation of energy. From his experiments he concluded in this paper that heat is not a substance but a form of energy: “Experiment has shown that whenever living force [kinetic energy] is apparently destroyed or absorbed, heat is produced. The most frequent way in which living force is thus converted into heat is by means of friction.” Furthermore he gave the amount of heat equivalent to the converted kinetic energy. A year later he read another paper in Manchester where he used Herapath’s kinetic theory. It was not published until 1851 and at first got very little attention until Clausius quoted it in 1857.

The real breakthrough for the kinetic theory started in Germany after Karl Krönig (1822–79) published a paper about it in Poggendorfs Annalen der Physik in 1856. Contrary to the widespread belief that molecules of gas merely oscillate around definite positions of equilibrium he assumed that they move with constant velocity in straight lines until they strike against other molecules, or against the surface of the container. Krönig was actually a chemist but he had a great reputation because he was editor of Fortschritte der Physik, an annual review of physics, and he had great influence in the German Physical Society. Krönig’s paper apparently motivated Rudolf Clausius (1822–88) to publish on the kinetic theory. In fact Clausius writes that already before his first paper on heat in 1850 he had a very similar conception of heat as Krönig but in his former papers he intentionally avoided mentioning this conception, because his conclusions were deducible from general principles and did not depend on these special conceptions. Clausius was already well known from his papers on thermodynamics. In 1850 he had given his verbal formulation of the second law that there exists no thermodynamic transformation whose sole effect is to extract a quantity of heat from a colder reservoir and to deliver it to a hotter reservoir. In the years until 1854 he had worked out its mathematical formulation. Since 1855 he was professor at the ETH in Zürich. When Clausius started to work on the kinetic theory it became fashionable. In 1857 he published his first paper on the kinetic theory with the title “The Nature of the Motion which we call Heat” where he quoted the papers of Krönig and of Joule. The English
translation of his paper appeared in the same year in the Philosophical Magazine. Two important arguments against the kinetic theory of heat were the following:

How can heat traverse a vacuum if it is just irregular motion of matter particles? There is no matter in the vacuum which could propagate heat while the particles of caloric could easily penetrate through the vacuum.

C.H.D. Buys–Ballot (1817–90) argued that since gas particles in the kinetic theory move with velocities of a few hundred meters per second one would expect that gases diffuse and mix much more rapidly than observed.

In 1858 Clausius published a paper in which he could cope with the second of these objections by introducing the mean free path of a gas molecule. Gas molecules move at speeds of a few hundred meters an hour but they undergo collisions with other gas molecules which change their direction after a very short time of flight. The actual distance they can move on the average freely along a straight line in one direction is the mean free path \( l \) given by

\[
l = \frac{3}{4} \frac{1}{n \pi \sigma^2} \quad n = \frac{N}{V}
\]

where \( n \) is the number density of gas molecules and \( \sigma \) is the diameter of the hard sphere particles which approximate the gas molecules. For his estimate of the mean free path Clausius made the drastic approximation that only one particle is moving and all others are at rest. His result differs less than 10 per cent from the result in Eq. (3) obtained by Maxwell one year later from a much more refined derivation. Clausius who in 1865 introduced the concept of entropy continued to work on the kinetic theory.

James Clerk Maxwell (1831–79), best known from his electromagnetic field theory which he developed in the years from 1855 to 1873, read his first paper on the kinetic theory in 1859 at a Meeting of the British Association at Aberdeen. With the title “Illustration of the Dynamical Theory of Gases” it appeared 1860 in print in the Philosophical Magazine. While in earlier treatments the absolute value of the velocities of the molecules was considered to be rather uniform he was the first to assume a random motion for the molecules. For thermal equilibrium he could then derive from symmetry considerations his famous velocity distribution function which in modern notation is given by

\[
f_0(\vec{v}) = n \left( \frac{m}{2 \pi kT} \right)^\frac{3}{2} \exp \frac{m \vec{v}^2}{2kT}
\]

where \( \vec{v} \) is the velocity and \( n \) the density of the molecules, \( m \) their mass, \( k \) Boltzmann’s constant and \( T \) the absolute temperature. For the mean free path he then obtained

\[
l = \frac{1}{\sqrt{2} n \pi \sigma^2}
\]

and for the viscosity of a dilute gas

\[
\eta_0(T) = \frac{1}{3} n m l \vec{v} \quad \text{with} \quad \vec{v} = \left( \frac{8kT}{\pi m} \right)^\frac{1}{2}
\]
where $\bar{v}$ is the mean absolute value of the velocity. Inserting $l$ into the last equation he obtained a value independent of the density and because of $\bar{v}$ proportional to the square root of the absolute temperature

$$
\eta_0(T) = \frac{1}{3\sqrt{2\pi\sigma^2}} m\bar{v}.
$$

(5)

The density independence of the viscosity was quite unexpected since for a fluid the viscosity in general increases with increasing density. After its experimental verification this result served as a strong argument in favour of the kinetic theory.

**THE BOLTZMANN EQUATION**

In 1872 Ludwig Boltzmann in Graz generalized Maxwell’s approach for the kinetic theory of dilute gases to nonequilibrium processes, so that he could investigate the transition from nonequilibrium to equilibrium. His non–equilibrium single particle distribution function $f = f(\vec{x}, \vec{v}, t)$ gives the average number of molecules in a dilute gas at the position $\vec{x}$ with velocity $\vec{v}$ at time $t$. The temporal change of this distribution function consists of two terms, a drift term due to the motion of the molecules and a collision term due to collisions with other molecules. In the absence of an external field of force this equation, which is now called Boltzmann equation, reads:

$$
\frac{\partial f}{\partial t} = -\vec{v} \cdot \frac{\partial f}{\partial \vec{x}} + J_B(ff).
$$

(6)

Here $J_B(ff)$ is the binary collision term which takes only two particle collisions into account, a good approximation for a dilute gas. A further assumption in Boltzmann’s expression for the collision term is that the velocities of the colliding molecules must be uncorrelated, which was later called the assumption of “molecular chaos” by Jeans.

Now Boltzmann introduced the functional

$$
H[f] = \int d^3 x \int d^3 v f(\vec{x}, \vec{v}, t) \log f(\vec{x}, \vec{v}, t)
$$

(7)

for which he could show under very general assumptions for the intermolecular interaction that if $f$ is a solution of Eq. (6) the time derivative of $H$ is always smaller than zero or at most zero:

$$
\frac{dH[f]}{dt} \leq 0.
$$

(8)

Furthermore for an ideal gas in equilibrium he could show that the entropy $S$ is up to a sign proportional to $H$. For nonequilibrium this is a generalization of the thermodynamic entropy now called Boltzmann entropy

$$
S(t) = -kH[f]
$$

(9)

and Eq. (8) is nothing but the second law of thermodynamics for a closed system

$$
\frac{dS(t)}{dt} \geq 0.
$$

(10)

This is Boltzmann’s famous $H$–theorem.

The $H$–theorem and the Boltzmann equation met with violent objections from physicists and from mathematicians. These objections can be formulated in the form of paradoxes. The most important ones are the reversibility paradox formulated in 1876 by Boltzmann’s friend Josef Loschmidt (1821–95) and the recurrence paradox formulated in 1896 by Ernst Zermelo (1871–1953).
The Reversibility Paradox

In a paper in 1876 Loschmidt gave a recipe of how one can prepare an initial condition with decreasing entropy for any system which follows a motion with increasing entropy. One need only reverse all its velocities at a certain instant of time: $\vec{v}(t) \rightarrow -\vec{v}(t)$. This procedure is equivalent to time reversal and the argument is usually called the reversibility paradox because the equations of classical mechanics are invariant under time reversal while the Boltzmann equation is not. The procedure of time reversal violates the hypothesis of “molecular chaos” since it is like a film which runs backwards. All molecules which have just had a collision will collide again and thus their velocities are correlated. This paradox represented a severe objection to the mechanical interpretation of the second law of thermodynamics. Apparently there are just as many initial conditions which lead at least for a short time to a decrease in the entropy of the system as there are initial conditions leading to an increase in the entropy. Why do we never observe a decrease in entropy for large isolated systems? For very small systems one can easily observe a decrease of entropy in the form of statistical fluctuations, e.g. density fluctuations, local pressure fluctuations or local temperature fluctuations in very small regions of a gas. For very large systems this is not the case because the small local fluctuations average out. Statistical physicists have coined the term typicality for the usual behaviour of macroscopic systems. If one pours, for instance, a dye into a liquid it will gradually spread through the whole liquid. This behaviour is typical whenever you make such an experiment. It is easy to tell the sequence in which snapshots of a spreading dye were taken, even after their original order has been deranged. How does this unidirectional behaviour in time come about? For a very large system, by far the largest number of states corresponds to equilibrium- and quasi-equilibrium-states. The latter are states which differ very little from the equilibrium state with maximum entropy and cannot be distinguished macroscopically from the equilibrium state. In our example of the liquid containing a dye they correspond to a practically uniform distribution of the dye through the whole liquid with very small local intensity fluctuations of the dye. With increasing size of the system, the preponderance of the equilibrium- and quasi-equilibrium-states becomes ever more overwhelming. If for every possible state of a large system we put a marked sphere into an urn and afterwards drew spheres from the urn indiscriminately, we would practically always draw an equilibrium- or quasi-equilibrium-state. The transition from nonequilibrium to equilibrium thus corresponds to a transition from exceptionally rare nonequilibrium-states to extremely probable states. This is Boltzmann’s statistical interpretation of the second law.

Statistical Mechanics

Loschmidt’s reversibility paradox led to a very fruitful discussion between Boltzmann and Loschmidt about the second law and motivated Boltzmann to work out his statistical interpretation of the second law in detail. To handle the reversibility paradox Boltzmann investigated the entire phase space of a dynamical system consisting of $N$ particles or molecules. He found that the volume in the $6N$ dimensional phase space of the system which represents all possible values of the three coordinates and the three momentum components of each particle can be subdivided into regions corresponding to macroscopic states of the system which we shall call macrostates.

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3 J. Loschmidt, Sitzungsber. Kais. Akad. Wiss. Wien, Math. Naturwiss. Classe 73, 128–142 (1876).
4 J. L. Lebowitz: Boltzmann’s Entropy and Time’s Arrow, Phys. Today 46 (9), 32 (1993).
In his paper of 1877 entitled “On the relation between the second law of the mechanical theory of heat and the probability calculus with respect to the theorems on thermal equilibrium”\(^5\), Boltzmann now presented a probabilistic expression for the entropy. He could show that the entropy \( S \) is proportional to the \( 6N \)-dimensional phase space volume \( \Omega \) occupied by the corresponding macrostate of an \( N \)-particle system:

\[
S \propto \log \Omega. \quad (11)
\]

It is now usually written in the notation of Max Planck

\[
S = k \log W \quad (12)
\]

where \( k \) is the Boltzmann constant and \( W \) is the number of microstates by which the macrostate of the system can be realized. This relation has been called Boltzmann’s Principle by Albert Einstein (1879–1955) in 1905 since it can be used as the foundation of statistical mechanics. It is not limited to gases as Eq. (9) but can also be applied to liquids and solid states. It can be obtained from Eq. (11) by introducing cells of finite volume in phase space as Boltzmann had already done in order to obtain a denumerable set of microstates. It implies that the entropy is proportional to the logarithm of the so-called thermodynamic probability \( W \) of the macrostate which is just the corresponding number of microstates. A macrostate is determined by a rather small number of macroscopic variables of the system such as volume, pressure and temperature. The latter two correspond to averages over microscopic variables of the system. A microstate, on the other hand, is specified by the coordinates and momenta of all molecules of the system. Due to the large number of molecules there is a very large number of different choices for the individual coordinates and momenta which lead to the same macrostate. It turns out, that for a large system by far the largest number of microstates corresponds to equilibrium- and quasi-equilibrium–states as we have already illustrated in the example of the liquid containing a dye. The latter are states which differ very little from the equilibrium state with maximum entropy and cannot be distinguished macroscopically from the equilibrium state. Thus this macrostate is the state of maximal entropy and the transition from nonequilibrium to equilibrium corresponds to a transition from exceptionally improbable nonequilibrium-states to the extremely probable equilibrium–state. In Boltzmann’s statistical interpretation the second law is thus not of absolute but only of probabilistic nature. The appearance of so-called statistical fluctuations in small subsystems was predicted by Boltzmann and he recognized Brownian motion as such a phenomenon. The theory of Brownian motion has been worked out independently by Albert Einstein in 1905 and by Marian von Smoluchowski. The experimental verification of these theoretical results by Jean Baptiste Perrin was important evidence for the existence of molecules.

The term Statistical Mechanics has actually been coined by the great American physicist J. Willard Gibbs (1839–1903) at a meeting of the American Association for the Advancement of Science in Philadelphia in 1884\(^6\) This was one of the rare occasions when Gibbs went to a meeting away from New Haven. He had been professor of mathematical physics at Yale University since 1871 and had served nine years without salary. Only in 1880, when he was on the verge of accepting a professorship at John

\(^5\)L. Boltzmann: Sitzungsber. Kais. Akad. Wiss. Wien, Math. Naturwiss. Classe 76 (1877) 373–435.
\(^6\)M.J. Klein: The Physics of J. Willard Gibbs in his Time, Phys. Today, Sept. 1990, p. 40.
Hopkins University, did his institution offer him a salary. He had realized that the papers of Maxwell and Boltzmann initiated a new discipline which could be applied to bodies of arbitrary complexity moving according to the laws of mechanics which were investigated statistically. In the years following 1884 he formulated a general framework for Statistical Mechanics and in 1902 published his treatise.7

Gibbs started his consideration with the principle of conservation of the phase space volume occupied by a statistical ensemble of mechanical systems. He considered three types of ensembles.

The so-called microcanonical ensemble of Gibbs corresponds to an ensemble of isolated systems which all have the same energy. Boltzmann called this ensemble “Ergoden”. In this case each member of the ensemble corresponds to a different microstate and all microstates have the same probability.

The canonical ensemble of Gibbs corresponds to systems in contact with a heat bath. In this case the energy of the individual systems is allowed to fluctuate around the mean value $E$. If $E_\nu$ is the energy of an individual system $\nu$ of the ensemble, its probability $P_\nu$ is proportional to an exponential function linear in the energy $P_\nu \propto \exp \left( -\frac{E_\nu}{kT} \right)$ which is nowadays often called the Boltzmann factor.

For the grandcanonical ensemble of Gibbs not only the energy but also the number of particles $N_\nu$ of the individual systems is allowed to fluctuate around the mean value $N$.

If we introduce the density in $6N$–dimensional phase space for an ensemble of physical $N$–particle systems

$$\rho = \rho(\vec{x}_1, \vec{p}_1, \vec{x}_2, \vec{p}_2, \ldots, \vec{p}_N, \vec{x}_N, t)$$

the Gibbs entropy can be written in the form

$$S = -k \int d^3 x_1 d^3 x_2 \ldots \int_{-\infty}^{\infty} d^3 p_1 d^3 p_2 \ldots d^3 p_N \rho \log \rho.$$ (14)

Introducing finite cells in phase space the number of microstates becomes denumerable and will be labelled by $\nu = 1, 2, \ldots, W$ where $W$ is the total number of microstates. The expression for the entropy then becomes

$$S = -k \sum_\nu P_\nu \log P_\nu \quad \text{with} \quad \sum_\nu P_\nu = 1$$ (15)

where $P_\nu$ is the probability of the corresponding microstate. Eq. (15) has already the same form as the corresponding expression for a quantum system with discrete energy levels. We may thus use the procedure introduced by John von Neumann (1903–1957) in 1927 to determine the equilibrium distribution $P_\nu$. It can be found by demanding that the entropy Eq. (15) becomes a maximum under certain subsidiary conditions which implies that the variation of $S$ with respect to the $P_\nu$ vanishes.

For the microcanonical ensemble only the sum of all probabilities must be one and if the total number of states is $W$ one obtains the same probability $P_\nu = \frac{1}{W}$ for all microstates which implies that Eq. (15) reduces to Eq. (12).

7J. W. Gibbs: Elementary Principles in Statistical Mechanics. Developed with Especial Reference to the Foundation of Thermodynamics. Yale Univ. Press 1902.

8L. Boltzmann: Über die Eigenschaften monozyklischer und anderer damit verwandter Systeme. Crelles Journal 98 (1884) p.68–94, Über die mechanischen Analogien des zweiten Hauptsatzes der Thermodynamik. ibid 100 (1887) p. 201–212 and Vorlesungen über Gastheorie, II. Teil, J.A. Barth, Leipzig 1898, p. 89.
For the canonical ensemble the fluctuations of the energy $E_\nu$ of the individual systems around the mean value $E$ requires the subsidiary condition

$$\sum_\nu P_\nu E_\nu = E .$$

(16)

The maximum entropy principle then gives for the probabilities

$$P_\nu = \frac{\exp\left(-\frac{E_\nu}{kT}\right)}{Z} \quad \text{with} \quad Z = \sum_\nu \exp\left(-\frac{E_\nu}{kT}\right)$$

(17)

where $T$ is the absolute temperature and $Z$ the canonical partition function.

For the grand canonical ensemble the fluctuations of the number of particles $N_\nu$ of the individual systems around the mean value $N$ require in addition to Eq. (16) the subsidiary condition

$$\sum_\nu P_\nu N_\nu = N ,$$

(18)

which has to be multiplied by a Lagrange multiplier and added to the entropy when the variation of $P_\nu$ is performed. This way one obtains for the grand canonical probability distribution

$$P_\nu = \frac{\exp\left(\frac{\mu N_\nu - E_\nu}{kT}\right)}{\Xi} \quad \text{with} \quad \Xi = \sum_\nu \exp\left(\frac{\mu N_\nu - E_\nu}{kT}\right)$$

(19)

where $\mu$ is the chemical potential and $\Xi$ the grand canonical partition function.

The quantum mechanical generalization of the framework of statistical mechanics has already been given in 1927 by John von Neumann who was born in Hungary. He introduced the density operator $\hat{\rho} = \rho(\hat{p}_1, \hat{x}_1, ... \hat{p}_N, \hat{x}_N, t)$ where the hat denotes the operator character. The quantum mechanical generalization of Eq. (14) is then given by

$$S = -k \text{Tr}(\hat{\rho} \log \hat{\rho})$$

(20)

where $\text{Tr}$ denotes the trace. If one uses for the trace eigenstates of the Hamiltonian and the energy spectrum is discrete, the expression in Eq. (20) reduces to the form given in Eq. (15). An important difference between classical and quantum statistics is the symmetry of the state under permutations of the particles. While for classical particles permutations of the particles lead to a different state identical quantum mechanical particles can only be in an antisymmetric state if they are fermions or in a symmetric state if they are bosons. An important application of Eq. (20) is the treatment of ferromagnetism.

**Progress in Nonequilibrium Kinetic Theory**

Efforts for a systematic derivation as well as a generalization of the Boltzmann equation have been made by N.N. Bogolyubov in 1946. The starting point for the derivation of the Boltzmann equation is the time reversal invariant Liouville equation for the $N$–particle phase space density in Eq. (13)

$$\frac{\partial \rho}{\partial t} = \{H, \rho\}$$

(21)

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9J. v. Neumann: Göttinger Nachr. (1927) 273.
10N.N. Bogolyubov: J. Phys. (USSR) 10 (1946) 256.
where $\{\cdot,\cdot\}$ is the Poisson bracket and $H$ the Hamiltonian of the system. Eq. (21) follows from the classical equations of motion and expresses the conservation of the probability in phase space. To arrive at the Boltzmann equation which violates time reversal invariance, because the direction of increasing entropy is singled out, some coarse graining is necessary which is done by successively integrating over the coordinates and momenta of $N-1$ particles until one arrives at the one particle distribution function $f = f(\vec{x}, \vec{v}, t)$ which appears in Eq. (6). This way one arrives at the so-called B.B.G.K.Y. chain of equations which stands for the first letters of the physicists Bogolyubov, Born and Green, Kirkwood, Yvon. Then one has to perform the limit of low density, the so-called Boltzmann–Grad–Limit and make the assumption of molecular chaos for the initial distribution which implies factorization of the reduced $n$–particle densities into products of one particle densities. Furthermore one has to assume that the system is large enough so that the influence of the walls of its container is negligible. There exist a number of such derivations of the Boltzmann equation of which I would like to mention the one by O.E. Lanford and one by an Italian group. While Lanford’s derivation holds only for a very short time interval, the Italian derivation implies so low densities that nearly no collisions take place. These restrictions are not surprising since at higher densities correlated collision sequences appear such as the “ring collisions” shown in Fig. 1 which introduce correlations between the colliding particles violating the assumption of molecular chaos. In this way the relaxation to equilibrium is slowed down. In computer simulations of a gas of hard spheres which are often called “relaxation experiments” one can study the approach to the one particle equilibrium distribution. Alder and Wainwright did pioneering experiments of this kind in 1958. Quite recently such experiments have also been performed at Vienna University. Following the analytic methods of Bogolyubov a modified Boltzmann equation of the type

$$\frac{\partial f}{\partial t} = -\vec{v} \cdot \frac{\partial f}{\partial \vec{x}} + J(ff) + K(fff) + L(ffff) + \ldots$$

(22)

is obtained where $J(ff)$ contains the two particle collisions, $K(fff)$ the three particle collisions, $L(ffff)$ the four particle collisions etc.. The solution of this generalized Boltzmann equation with the Chapman–Enskog method then leads to a density or virial expansion for the viscosity

$$\eta(n,T) = \eta_0(T) + n\eta_1(T) + n^2\eta_2(T) + \ldots$$

(23)

which is a power series expansion in the density $n$ with temperature dependent coefficients. For higher densities, however, it turns out that especially due to the “ring collision” terms the Bogolyubov collision integrals $K(fff)$ and $L(ffff)$ become divergent and a cut off for the mean free path has to be introduced. The revised density

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11 For a review see e.g. R. Jancel: Foundations of Classical and Quantum Statistical Mechanics, English translation ed. D. Ter Haar, Pergamon Press, Oxford 1969.

12 O.E. Lanford: Time Evolution of Large Classical Systems, in Dynamical Systems, Theory and Application, edited by J. Moser, Springer, Berlin, 1975.

13 R. Illner and M. Pulvirenti: Global Validity of the Boltzmann Equation for Two- and Three-Dimensional Rare Gas in Vacuum: Erratum and Improved Result, Commun. Math. Phys. 121 (1989) 143–146.

14 B.J. Alder and T. Wainwright, in Transport Processes in Statistical Mechanics, edited by I. Prigogine, Wiley–Interscience, New York, 1958.

15 Ch. Dellago and H.A. Posch: Mixing, Lyapunov instability, and the approach to equilibrium in a hard sphere gas, Phys. Rev. E 55 (1997) R9.
expansion for the viscosity now contains a logarithmic term in the density $n$:  

$$\eta(n, T) = \eta_0(T) + n\eta_1(T) + n^2 \ln n\eta_2'(T) + n^2\eta_2(T) + ...$$  \hspace{1cm} (24)\

Similar expressions result for the other transport coefficients.

**Dense Fluids**

With the development of more powerful computers extensive computer simulations for dense hard sphere fluids have been performed in the last twenty years.\(^{17}\) In this way, and from theoretical considerations, it has been possible to identify two especially relevant collision sequences going on in a dense hard fluid. These are the “cage diffusion” collision sequence in Fig. 2 and the “vortex diffusion” collision sequence in Fig. 3. In “cage diffusion” the particle finds itself trapped in a cage made up by the surrounding particles and it requires several collisions with its neighbours until it finds a hole to sneak out. It leads to a significant change in the volume dependence of the viscosity of a dense fluid as shown in Fig. 4.\(^{18}\) Its importance was discussed by de Schepper and Cohen in 1980.\(^{19}\) In “vortex diffusion” an energetic particle creates a vortex like a macroscopic sphere moving through liquid, see Fig. 3. It was discovered around 1968 by Alder and Wainwright\(^{20}\) and affects the long–time behaviour at about twenty–five mean free times. The above mentioned collision sequences constitute corrections to the Boltzmann equation in dense fluids and provide an understanding of the behaviour of dense fluids through collisions.

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\(^{16}\)For a review see e.g. E.G.D. Cohen: Kinetic Theory: Understanding Nature through Collisions, in Thermodynamics and Statistical Physics – Teaching Modern Physics, ed. M.G. Velarde and F. Cuadros, World Scientific, 1995.

\(^{17}\)W.W. Wood, in Fundamental Problems in Statistical Mechanics, ed. E.G.D. Cohen, North–Holland Pub., Amsterdam 1975.

\(^{18}\)I.M. de Schepper, A.F.E.M. Haffmans and J.J. van Loef: J. Stat. Phys. 57 (1989) 631.

\(^{19}\)I.M. de Schepper and E.G.D. Cohen: Phys. Rev. A 22 (1980) 287; J. Stat. Phys. 27 (1982) 223.

\(^{20}\)B.J. Alder and T.E. Wainwright: Phys. Rev. A1 (1979) 18.
Figure 1: Examples of correlated four particle “ring collision” sequences.

Figure 2: Example of a correlated “cage diffusion” collision sequence.
Figure 3: Example of a correlated “vortex diffusion” collision sequence. (a) Two vortex rings. (b) Left vortex ring in more detail.

Figure 4: The reduced hard–sphere fluidity $\phi^* = \frac{2\eta}{\eta_0}$, which corresponds to the inverse of the viscosity $\eta$ multiplied with the low density limit $\eta_0$ of the viscosity, is plotted as a function of the reduced volume $V^*$ which is the volume of the liquid divided by the volume of the hard spheres. The dashed curve is $\phi^*$ according to the classical Enskog theory and the solid curve according to the mode coupling theory which takes also “cage diffusion” into account. The squares and crosses are from computer simulation experiments.