BOGOLIUBOV CHOH UHLENBECK THEORY: CRADLE OF MODERN KINETIC THEORY

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(dedicated to the memory of Soon-Tahk Choh)

The Choh Uhlenbeck equation was the first successful generalization of the Boltzmann equation to include triple collisions in a systematic manner. Detailed analysis of its triple collision term has led to the important concept of ring collisions, which create dynamic correlations between particles with a common collision history. This review shows how the ring collisions have been at the root of most major developments in kinetic theory of the last 40 years, both for continuous fluids as well as for lattice gas automata. In present times they have become the standard tool to analyze long spatial and temporal correlations in simple and complex fluids.

1 Historical perspective

In the sixties many efforts were made to generalize the Boltzmann equation to dense liquids. The historical importance of the Bogoliubov Choh Uhlenbeck theory and the Choh Uhlenbeck equation is well expressed by the following quote from Brush’s book on the history of kinetic theory: “At Michigan, Soon-Tahk Choh, a Korean student of Uhlenbeck, was doing apparently similar but ultimately more fruitful work. Early in 1958 he completed his dissertation, The kinetic theory of phenomena in dense gases, a work never published but frequently cited by later physicists who heard about it”.

In an effort to put Choh’s work in perspective I briefly review some important events, relevant for the development of the kinetic theory of dilute and dense fluids. In a small variation on Cohen’s classification in his Fifty years of kinetic theory I divide the history of kinetic theory into four periods:

- Classic Era 1855-1945
- Renaissance 1946-1964
- Modern Era 1965-1985
- Post-modern Era > 1985

The selection of important developments is based on Brush’s book, the overview in Choh’s thesis, and on review papers of personal preference.

The Classical Era started with Maxwell’s derivation in 1859 of the velocity distribution in thermal equilibrium: the birth of kinetic theory. Soon
afterwards, in 1872 Boltzmann formulated his famous equation for the time evolution of the single particle distribution function, \( f(x, t) = f(r, v, t) \), in a *dilute gas* outside equilibrium,

\[
\partial_t f + v \cdot \nabla f = I(ff).
\] (1)

The collision term on the right hand side, which is quadratic in \( f \), represents the change in \( f \) through binary collisions. It is based on the assumption of *molecular chaos*, expressing the absence of precollision correlations between two particles involved in a binary collision. In other words, the Boltzmann equation takes only sequences of uncorrelated binary collisions into account. This implies that the pair distribution function \( f^{(2)}(x_1, x_2, t) \), just before particles 1 and 2 enter each other interaction range, factorizes into

\[
f^{(2)}(x_1, x_2, t) \to f(x_1, t)f(x_2, t) \approx f(r, v, t)f(r, v_2, t).
\] (2)

The Boltzmann equation shows the arrow of time; it is an irreversible equation, which is lacking the time reversal invariance of the mechanical equations of motion. In fact, \( f(x, t)dx \) represents the average number of particles in a small element, \( dx = dr dv \) of phase space. The Boltzmann equation *neglects fluctuations* and can be considered as a mean field theory. Boltzmann was able to prove the \( H \)-theorem and discuss the approach of \( f(x, t) \) towards thermal equilibrium, described by Maxwell’s velocity distribution function.

The remaining problems were to derive the Navier Stokes equation and to calculate the transport coefficients. The possibility of an explicit calculation of viscosity and heat conductivity was realized in 1917 when Chapman and Enskog developed the *Chapman Enskog method* for solving the Boltzmann equation. This multi-time scale method assumes that transport processes, which occur on time scales large compared to the mean free time \( t_0 \), are described by the *normal solution*, \( f(r, v, t) = f(v|n, u, T) \), which depends on space and time variables \( (r, t) \) only through the first five moments of the distribution function, \( a(r, t) = \{ n(r, t), u(r, t), T(r, t) \} \), i.e. the local density \( n \), the local flow velocity \( u \) and the local temperature \( T \).

In this time regime, the temporal and spatial variations over a mean free time \( t_0 \) and a mean free path \( \ell_0 = \frac{v}{\sqrt{\pi}} \), provide a small parameter, the *non-uniformity parameter*, \( \mu \sim \ell_0 \nabla \), which can be used as a systematic expansion parameter. Time derivatives, \( \partial_t f \sim (\partial f / \partial a) \partial_t a \), can be calculated by carrying out a \( \mu \)-expansion of the local conservation laws for \( a(r, t) \), where \( \partial_t a \) is at least of \( O(\mu) \). Then, the Boltzmann equation can be solved by a \( \mu \)-expansion, *i.e.* \( f = f_0 + \mu f_1 + \ldots \), where \( f_0 = n(m/2\pi kT)^{d/2} \exp[-m|v - u|^2/2kT] \) is the local equilibrium distribution with \( d \) the dimensionality of the system. The
Chapman Enskog method yields a linear integral equation for the deviation $f_1$, which is proportional to the gradients of $T$ and $u$, and provides explicit expressions for the heat conductivity and viscosity.

In 1922 Enskog proposed a rather accurate, though approximate, generalization of the Boltzmann equation, to account for transport processes in a dense fluid of hard spheres. This was achieved by replacing Boltzmann’s molecular chaos assumption (2) by

$$f^{(2)}(x_1, x_2, t) \longrightarrow g(|r_{12}| = \sigma)f(r_1, v_1, t)f(r_1 - \sigma, v_2, t).$$

The local equilibrium function for two spheres at contact, $g(\sigma)$, accounts for static correlations in a hard sphere fluid, and the different space dependence of the two $f$’s accounts for the difference in position of the two colliding spheres, and represents the new transport mechanism of collisional transfer, i.e. instantaneous transfer of momentum and energy over the hard sphere diameter $\sigma$ through the interaction. This is in general the dominant transport mechanism at high densities. The original Boltzmann equation takes only kinetic transport into account.

2 BBGKY-hierarchy

The Renaissance began in 1946 with Bogoliubov’s article Problems of a dynamical theory in statistical physics. The fundamental basis was the BBGKY-hierarchy, which is named after Bogoliubov, Born, Green, Kirkwood and Yvon, and reads

$$(\partial_t + v_1 \cdot \nabla_1) f_1 = \int dx_2 \theta_{12} f^{(2)}_{12},$$

$$(\partial_t + L(12)) f^{(2)}_{12} = \int dx_3 (\theta_{13} + \theta_{23}) f^{(3)}_{123}$$

and so on, where $\theta_{12}$ is the weak scattering operator,

$$\theta_{12} = \frac{\partial V(r_{12})}{\partial r_{12}} \cdot \frac{1}{m} \left( \frac{\partial}{\partial v_1} - \frac{\partial}{\partial v_2} \right),$$

with pair potential $V(r)$, and two-particle Liouville operator

$$L(12) = L^0(12) - \theta_{12} \equiv v_1 \cdot \nabla_1 + v_2 \cdot \nabla_2 - \theta_{12}. $$

a’rather accurate’, that is in moderately dense systems where the mean free path $\ell_0$ is larger than the hard core diameter $\sigma$. In dense liquids, where $\ell_0 << \sigma$, the Enskog equation is inadequate for describing spatial variations with wavelength $\lambda$ in the range $\ell_0 < \lambda < \sigma$. These wavelengths are relevant for analyzing dynamic structure factors as measured in neutron scattering experiments. However, the revised Enskog equation of section 12 is very adequate.
This set of equations is an open hierarchy of coupled equations that expresses the time rate of change of the \(s\)-particle distribution function \(f^{(s)}\) in terms of the \((s+1)\)-particle distribution function, provided the interactions are pairwise additive.

Bogoliubov and Kirkwood were interested in non-equilibrium properties of fluids and dense gases\(^1\). Uhlenbeck considered Bogoliubov as the originator of modern methods in kinetic theory, as he introduced the basic concepts of systematically approximating the dynamics of moderately dense gases in terms of small groups of two, three, four,... isolated particles, just like in Mayer’s cluster expansion for the equation of state in thermal equilibrium. This set the stage in 1954 for Choh’s thesis work.

The main goal of this paper is to analyze the impact of the Bogoliubov Choh Uhlenbeck theory on later developments. Consequently I will refer to links with later developments in kinetic theory for Lattice Gas Automata (LGA), in which the BBGKY-hierarchy has been used as well\(^10\).

An extremely important parallel development occurred also in 1954, which led to the Green Kubo formulas or time correlation function method for transport coefficients in fluids\(^1\). The shear viscosity, for instance, is given by

\[
\eta = \frac{1}{V k_B T} \int_0^\infty dt \langle J_{xy}(t) J_{xy}(0) \rangle, \tag{7}
\]

where \(J_{xy}(t)\) is the microscopic \(N\)-particle momentum flux, which contains both kinetic as well as collisional transfer contributions. The generic form of a Green Kubo formula is a time integral over an equilibrium time correlation function, such as the stress correlation function in (7). It involves in fact two limits: first the thermodynamic limit \(\langle \ldots \rangle/V\) is taken, followed by a time integral over an infinite time interval\(^11\). Similar Green Kubo formulas for LGA were derived by Dufty and Ernst\(^13\), in which the time integrals are replaced by time sums and the initial term in the summand has a weight one half.

\(^b\) LGA are fully discretized models for non-equilibrium fluids\(^9\), defined on a regular space lattice, where time is discrete, where point particles live on the nodes of a lattice, and have a small set of allowed velocities corresponding to the \(b\) nearest neighbor lattice vectors. The dynamics consists of a collision step, followed by a propagation step. If \(\ell\) particles \((\ell = 2, 3, \ldots, b)\) are on the same node (zero range interactions), then they suffer \(\ell\)-tuple collisions according to well defined collision rules, which are obeying momentum conservation in fluid models, and lacking it in purely diffusive or reactive models. As the interactions in LGA are not pairwise additive, but involve genuine \(\ell\)-tuple collisions, the right hand side of the first hierarchy equation for LGA involves already all distribution functions \(f^{(\ell)}\) with \(\ell = 2, 3, \ldots, b+1\). Of course, a similar structure occurs in continuous fluids with non-additive \(b\)-body interactions.
This section will only give an outline of the basic ideas of this theory. The interested reader is referred to Cohen’s lectures about this subject.

The system of interest is a moderately dense gas under conditions of standard temperature and pressure, composed of particles interacting through short range, strictly repulsive forces. Here the typical duration of a collision is $\tau_0 = 10^{-12}$ seconds, whereas the mean free time is $t_0 = 10^{-9}$ seconds. The new concept is that the existence of well separated time scales brings about a contraction of the description in terms of fewer variables, as time progresses.

There exist three time stages: initial stage, kinetic stage and hydrodynamic stage. In the initial stage ($t < \tau_0$) the full Liouville equation is required to describe the fast variation of the $N$-particle distribution function. In the subsequent kinetic stage ($\tau_0 < t < t_0$), which is the first coarse grained time scale, the single particle distribution function $f(x, t)$ is the only slow variable, and the higher order function $f^{(s)}(\ldots | f(t))$ of $f(x, t)$, which implies a loss of memory about the initial state. Once $f^{(2)}(x, x_2 | f(t))$ is determined, one has a closed kinetic equation, the generalized Boltzmann equation. The perturbative calculation proceeds by performing a formal density expansion. In the final hydrodynamic stage ($t > t_0$), which is the second coarse grained time scale, a further contraction of the description occurs. Here the only slow variables are the hydrodynamic fields $a(r, t) = \{n(r, t), u(r, t), T(r, t)\}$ and $f(x, t)$ becomes a time- and space-independent functional of these fields, $f(r, t) = f(v| a(r, t))$. This assumption is a generalization of the normal solution in the Chapman Enskog method. Once $f(v| a(r, t))$ has been determined, one has obtained a closed set of hydrodynamic equations, which contains the Navier Stokes equations, and generalizations thereof, as well as explicit expressions for the transport coefficients. The perturbative calculation proceeds by performing a formal $\mu$-expansion, where $\mu \sim \ell_0 \nabla$ is the non-uniformity parameter.

How can these ideas be implemented to actually derive the generalized Boltzmann equation? Clearly, in order to solve an open hierarchy, like (3), some kind of closure relation is required. In the present theory closure is obtained by imposing the factorization assumption as a boundary condition on the BBGKY-hierarchy at $t = -\infty$, expressing the absence of correlations in the infinite past. This is technically expressed through the relation

$$\lim_{\tau \to \infty} S_{-\tau} (12) f^{(2)}(x_1 x_2 | S_{-\tau}^0 f(t)) =$$

As will be discussed later on, it is the assumption about the existence of a time-independent functional, to general order in the density, that breaks down and leads to the divergence of the density expansion of transport coefficients, to be discussed in section 5.
Figure 1: Action of streaming operators.

\[ S(12) f(x_1, t) f(x_2, t) \equiv f(x_1^*, t) f(x_2^*, t), \]  

and similar relations for higher order distribution functions. Here \( S_t(12) \) is the streaming operator for two interacting particles, \( S_t(12) = \exp[tL(12)] \), and \( S_0^t(12) \) is the free streaming operator, \( S_0^t(12) = \exp[tL_0(12)] \), where the Liouville operators \( L \) and \( L_0 \) are defined in (6). The streaming operators \( S_t(12) \) and \( S_0^t(12) \) generate the trajectories of two isolated particles with or without interaction respectively. Moreover \( S(12) \) is defined through

\[ S(12) = \lim_{\tau \to \infty} S_{-\tau}(12) S_\tau^0(12). \]  

Both streaming operators \( S(12) \) and \( S_{-\tau}(12) \) act directly on the phases \( x_i \) with \( i = 1, 2 \), by replacing them respectively by \( x_i^* = S(12)x_i \) and \( x_i(-t) = S_{-\tau}(12)x_i \). The latter operator generates backward dynamics. The action of both streaming operators on \( x_1 \) and \( x_2 \) is sketched in Figure 1.

It is exactly the factorized boundary condition at \( t = -\infty \), which introduces the arrow of time into the Boltzmann equation and its generalizations. The BBGKY-hierarchy equations themselves – without the boundary condition – are invariant under time reversal, as required by classical mechanics. The final ingredient in obtaining the generalized Boltzmann equation is the use of the small parameter density, \( n = N/V \), as a systematic expansion parameter. It enables one to perform an \( n \)-expansion of the unknown functionals \( f^{(s)} = f_0^{(s)} + n f_1^{(s)} + \ldots \), of the equations of the BBGKY-hierarchy, and of the boundary condition (8).
The implementation of these ideas were realized in Choh’s thesis, and led to the Choh Uhlenbeck equation in 1958:

$$\left( \partial_t + \mathbf{v} \cdot \nabla \right) f = I(ff) + K(fff) + \ldots$$

(10)

where $I(ff)$ is the binary collision term,

$$I(ff) = \int dx_2 \theta_{12} S(12)f(x_1,t)f(x_2,t),$$

(11)

and $K(fff)$ is the triple collision term, which will be specified below. It is an important new result, that generalizes the Boltzmann equation to include triple collisions. Bogoliubov had already shown in his 1945 article that $I(ff)$ for the case of hard spheres reduces to the collision term in the Enskog Boltzmann equation with $g(\mathbf{r}_{12}) = \sigma = 1$. This binary collision term $I(ff)$ does take into account the difference in position of the colliding particles, the so-called collisional transfer. In the limit of low density, it gives a higher order density correction to the Boltzmann equation.

In the notation of Choh’s thesis, the triple collision operator has the form,

$$K(fff) = \int dx_2 \theta_{12} \int_0^\infty d\tau S_{-\tau}(12) \int dx_3 [\ldots] S_r(12) \Pi_{i=1}^3 f(x_i,t)$$

(12)

with

$$[\ldots] = \int dx_3 [(\theta_{13} + \theta_{23}) S(123) - S(12) \theta_{13} S(13) - S(12) \theta_{23} S(23)].$$

(13)

A more transparent form was obtained in the later cluster expansion methods of Green and Cohen (see review 3), namely

$$K(fff) = \int dx_2 \theta_{12} \int dx_3 [S(123) - S(12) S(13)$$

$$- S(12) S(23) + S(12)] f(x_1) f(x_2) f(x_3).$$

(14)

It is instructive to analyze the different types of contributions from $S(123)$, illustrated in Figure 2. They contain genuine triple collisions, where three particles are simultaneously in each others interaction sphere. Once they have collided, the particles will separate and never recollide again due to the short range repulsive potential. In hard sphere systems, where interactions are instantaneous, this term is vanishingly small.
Moreover, $S(123)$ contains sequences of two uncorrelated successive binary collisions $(12) (13)$ and $(12) (23)$. Such collisions have already been accounted for in the Boltzmann collision term $I(\tau f f^2)$. So, they are subtracted out from the possible sequences of binary collisions among three particles in $(14)$.

Finally $S(123)$ contains sequences of three correlated successive binary collisions, such as the recollision $(12)(13)(12)$ and the cyclic collision $(12)(23)(13)$, generally referred to as ring collisions. A more systematic analysis of the separate terms may be found in Ref. 4.

In the second part of his thesis, Choh obtained the solution to the Choh Uhlenbeck equation in the hydrodynamic stage by following Bogoliubov’s generalization of the Chapman Enskog method, and derived formal expressions for the first density correction to the viscosity and heat conductivity for a moderately dense gas in three dimensions with short range repulsive interactions. The viscosity, for instance, has the form

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

where $\eta_0$ is the low density Boltzmann result and $\eta_1$ is the Choh Uhlenbeck contribution. It is expressed in terms of matrix elements of the triple collision operator, and contains contributions from genuine triple collisions, as well as
from the correlated ring collisions, illustrated in Figure 2. For the special case of hard spheres, Sengers and coworkers have computed $\eta_1$, and found that $\eta_1$ differs only a few percent from the predictions of the Enskog equation.

Similar calculations for the viscosity in LGA have been carried out by Brito et al. Here it was found that the ring collisions give corrections on the order of 10% to the Boltzmann mean field results for all densities, and the resulting viscosities are in excellent agreement with those of computer simulations. I want to stress that the Boltzmann mean field equation and the ring kinetic equation for LGA are not restricted to low densities. The Boltzmann equation for LGA does include apart from binary collisions genuine triple, quadruple, $\cdots$, $b$–tuple collisions, as well as static correlations, accounting for the exclusion principle, which mimics the hard core interactions.

The seven years after the appearance of Choh’s thesis in 1958 may be described as a period of consolidation. Using the cluster expansion method, Green and Cohen derived the formal structure of the $\ell$-tuple collision terms ($\ell = 2, 3, 4, \ldots$) in the generalized Boltzmann equation, in close analogy to the Mayer cluster expansion for reduced distribution functions in thermal equilibrium, and it was believed that transport coefficients could be calculated in the form of a virial expansion where the coefficients $\eta_\ell$ in (15) were determined by the dynamics of $(\ell + 2)$ isolated particles. Similar cluster expansion methods were applied to the Green Kubo formulas for viscosity and heat conductivity. After some initial confusion about a possible difference between the Green Kubo formulas and the Choh Uhlenbeck equation, McLennan was the first to show that both methods yield the same results for the first density correction to the transport coefficients in fluids.

5 Discovery of the divergence

The cluster expansion method of Green and Cohen or the alternative inversion method of Zwanzig made it feasible to investigate the fundamental assumption of the Bogoliubov Choh Uhlenbeck theory about the rapid decay of initial correlations within a time $t_o$. This assumption provided the formal justification for the rapid approach of the pair- and higher order distribution functions $F^{(s)}(x_1, x_2, \ldots, x_3, t)$ to the time independent functionals $f^{(s)}(x_1, x_2, \ldots, x_3, f(t))$.

In 1965 Dorfman and Cohen, Weinstock, as well as Goldman and Frieman were the first to make phase space estimates of the triple and higher order collision terms, and to show that the virial expansion contains coefficients $d$ No reviews on the kinetic theory beyond the Boltzmann mean field equation are available for LGA. Therefore I refer in each section to the original LGA publications to show the parallel developments.
that are *divergent* with increasing time; more specifically

\[
\eta = \begin{cases} 
\eta_0 + \eta_1 n + \eta_2(t)n^2 + \ldots & (d = 3) \\
\eta_0 + \eta_1(t)n + \ldots & (d = 2)
\end{cases}
\]  

(16)

where the quadruple collision contribution \( \eta_2(t) \) in three dimensions and the triple collision contribution \( \eta_1(t) \) in two dimensions are logarithmically divergent as \( t \to \infty \). Kawasaki and Oppenheim were the first to sum the ring diagrams. Subsequently the divergences and resummations were consolidated by more detailed calculations of van Leeuwen and Weijland, Swenson and McLennan, Haines together with Dorfman and Ernst, Sengers, and Fujita.

It is of interest to elaborate on this fundamental discovery, which marks the advent of the *Modern Era* in kinetic theory, where collective effects determine the behavior of transport coefficients, even at low densities. To do so, I present the derivation of the log \( t \) divergence, as given in Ref. for hard sphere models and Lorentz gases.

Consider the \( x_3 \)-integral in (14) at fixed \( x_1, x_2 \). Let \( \int^* dx_3 \) denote the phase space where the integrand of the recollision term (12)-(13)-(12) is non-vanishing, and let \( \sigma \) be the range of the repulsive interaction. The configuration with \( dx_3 = dv_3 dr_3 \) for the occurrence of a recollision can be simply estimated in the coordinate system used in Figure 3.

![Figure 3: Phase space for recollisions.](image)

The solid angle \( d\hat{v}_3 \), in which particle 3 has to hit particle 2, such that particle 2 will recollide with particle 1 after a time \( t_1 \), is proportional to \( d\hat{v}_3 \sim (a/v_12t_1)^{d-1} \). For particle 3 to perform this well-aimed collision its position has to be inside a small collision cylinder \( dr_3 \sim a^{d-1}v_3 dt_1 \). The total phase
space for the recollision event is then obtained by integrating over all possible intermediate times, yielding for large times $t$:

$$
\int_{\tau_0}^{t} dx_3 \sim \int_{\tau_0}^{t} dt_1 \left( \frac{a}{v_{12} t_1} \right)^{d-1} \sim \begin{cases} 
\log t & (d = 2) \\
\text{const} + t^{2-d} & (d \neq 2)
\end{cases}
$$

(17)

This estimate illustrates that the triple collision term in the Choh Uhlenbeck equation in three-dimensional systems approaches a finite limit, implying that $\eta_1$ in (16) exists, and that the initial state is indeed forgotten, in agreement with Bogoliubov’s assumption about the existence of a time-independent functional. However all three conclusions, valid for three dimensions, break down in two dimensions, where the Choh Uhlenbeck term diverges as $\log t$.

Next, I consider a similar phase space estimate for the ring collisions in the quadruple collision term, for instance $(12)(23)(24)(12)$. The additional $x_4$-integration yields an extra factor $t_1$ in (17). Consequently the relevant phase space,

$$
\int_{\tau_0}^{t} dx_3 \int_{\tau_0}^{t} dx_4 \sim \int_{\tau_0}^{t} dt_1 t_1 t_1^{d-3} \sim \begin{cases} 
\log t & (d = 3) \\
\text{const} + t^{3-d} & (d \neq 3)
\end{cases},
$$

(18)

diverges logarithmically in three dimensions as $t \to \infty$, and a virial expansion of transport coefficients does not exist in three dimensions either. Therefore, the memory of the initial state is not completely lost.

The above estimates show that dynamic correlations create long time correlations so that the initial and kinetic stage are not well separated anymore. This observation invalidates the first part of Bogoliubov’s assumption about the existence of well separated time scales. These long time correlations are created by unrestricted free motion, which is possible in isolated groups of 3, 4, ... particles. However infinitely long free paths between collisions are unphysical in a real gas. The free motion of a particle will on average be on the order of the mean free path $l_0 \sim \tau_0 \sim 1/n$. Therefore, the collective effect of the other particles, i.e. the surrounding fluid, provides an effective cut off which replaces $t$ in (17) and (18) by $t_0$. Consequently, the transport coefficients for moderately dense gases exhibit a non-analytic term $n \log t_0 \sim n|\log n|$ in the density, i.e.

$$
\eta = \begin{cases} 
\eta_0 + \eta_1 n + \eta_2 n^2 \log n & (d = 3) \\
\eta_0 + \eta_1' \log n & (d = 2)
\end{cases}
$$

(19)

where the coefficients $\eta_1'$ and $\eta_2'$ have been calculated for hard sphere fluids[^4] and Lorentz gases[^9].

[^4]: The Lorentz gas is a simple model for diffusion and consists of independent light particles moving through a random array of fixed scatterers.
The analytical results (19) for transport coefficients can be considered as well established for fluids with short range repulsive interactions, and are believed to be valid for realistic interparticle potentials as well. The low density expansion (19) appears to be consistent with experiment but so is the virial expansion (15). However, up to the present time there are no compelling direct experimental observations for the appearance of a logarithmic term \( n^2 \log n \) in the density expansion of the transport coefficients.

6 Necessity of log n singularities?

The divergence of the ring collision integrals, discussed in (17) and (18), holds for \textit{continuous} velocity variables, and so does the logarithmic singularity (19) in the low density limit. However in systems with \textit{discrete} velocity directions, such as the Ehrenfest wind-tree model and \( d \)-dimensional LGA, and even one-dimensional continuous velocity models, the ring collision integrals diverge algebraically, instead of logarithmically. This can have very surprising effects.

Consider, for instance, the self diffusion coefficient \( D \) in a one-dimensional gas of hard rods, which has been calculated exactly. Calculating \( D \) from a formal density expansion yields \( nD = d_0 + d_1(t)n + \ldots \), where \( d_1(t) \sim t \) for large \( t \). By taking the collective effects of the surrounding fluid into account, \( t \) is effectively replaced by the mean free time \( t_0 \sim 1/n \). The renormalized low density behavior of the diffusion coefficient becomes \( nD = (d_0 + d'_1) \) for small \( n \), i.e. the ring collisions modify the leading order Boltzmann contribution. Exactly the same renormalization of the Boltzmann diffusion coefficient through ring collisions has been found in stochastic lattice Lorentz gases with back scattering. The exact low density diffusion coefficient for these models, which is very different from the Boltzmann value, has been calculated by van Beijeren and Ernst through an exact enumeration method.

These two examples have been chosen in order to illustrate (i) that the behavior of transport coefficients, even at low or moderate densities, is not necessarily determined by the dynamics of small isolated groups of 2,3,4,... particles, as had been assumed in the Bogoliubov Choh Uhlenbeck theory, but that it is strongly influenced by \textit{collective effects}, and (ii) that the ring collisions not necessarily lead to (logarithmic) \textit{singularities} at small densities. It all depends on the structure of the relevant phase space.

The previous discussion may suggest that in principle the transport properties in two- and three-dimensional systems are well understood. We know the coefficient of the dominant singularity \( n^{d-1} \log n \) in \( d \) dimensions (\( d = 2,3 \)). We know how to renormalize all divergent terms of the \( n \)-expansion into finite contributions by resumming the most divergent ring diagrams. It looks as if
only technical difficulties are stalling further progress.

However, we do not know the total coefficient of $O(n^{d-1})$. It was Pomeau\cite{Pomeau}, who first realized that the total coefficient of the $O(n^2)$–term in two dimensions was divergent as well, and that there was something fundamentally wrong with the Navier Stokes equations and transport coefficients in two-dimensional fluids, whereas the hydrodynamic equations in three dimensions are still well defined to Navier Stokes order.

To conclude this section, it is worth mentioning that calculation of terms beyond the dominant $n^2 \log n$–term in three dimensions, for instance the $O(n^2)$–contribution, is exceedingly difficult, and general results are lacking. In fact, no progress along these lines has been made since the early eighties. The systematic kinetic theory for fluids has reached an impasse, and the high goals of the modern era have unfortunately not been realized. The reader, interested in further details, is referred to the review by Dorfman and van Beijeren\cite{Dorfman}. Although twenty years old, this review still gives the best account of the current status of the systematic kinetic theory.

## 7 Long time tails

In 1970 Alder and Wainwright\cite{Alder} made their famous discovery of the long time tails in the velocity correlation and other current correlation functions in equilibrium fluids, although a first indication of the existence of long time tails in three dimensions was already present in a paper of 1966 by Goldman\cite{Goldman}. Computer simulations on hard sphere systems\cite{Alder, Walther} show that the velocity correlation function (VAF) of a tagged particle, $\langle v_x(t)v_x(0) \rangle$, has a positive long-time tail, proportional to $t^{-d/2}$, which is caused by the following mechanism\cite{Alder}. The initial momentum of the tagged particle is transferred in part to the surrounding fluid particles. This sets up a flow of vortices around the tagged particle, which transfers some of its momentum back to the tagged particle ("kick in the back"), thus yielding a positive correlation between $v(0)$ and $v(t)$. This correlation extends over hydrodynamic time scales. In LGA similar long time tails have been observed with much higher statistical precision and over much longer time intervals, using Frenkel’s moment propagation method\cite{Frenkel}. The long time tails are a convincing illustration of the important role that computer simulations have played in unraveling the complex dynamics of classical fluids.

The hydrodynamic picture can be cast into a more quantitative form by using the mode coupling theories, developed for critical dynamics\cite{Hohenberg, Witten}, to fluids away from critical points. As an example consider $\langle v_x(t)v_x(0) \rangle$ for a tagged particle. To describe the long time behavior on a coarse grained
spatial and temporal scale, I decompose the total tagged particle current, \( v(t) \simeq \int dr n_s(r,t)u(r,t) \) in terms of the two slow modes: tagged particle density \( n_s(r,t) \) and fluid flow velocity \( u(r,t) \). The relevant Fourier modes decay as \( \hat{n}_s(k,t) \simeq \exp(-Dk^2t)\hat{n}_s(k,0) \) and \( \hat{u}(k,t) \simeq \exp(-\nu k^2t)\hat{u}(k,0) \), where \( D \) is the coefficient of self diffusion and \( \nu = \eta/\rho \) the kinematic viscosity. Consequently, the total current decays as

\[
v_x(t) \sim \int \frac{dk}{(2\pi)^2} \exp[-(D + \nu)k^2t] \sim [4\pi(D + \nu)t]^{-d/2}.
\] (20)

This leads to the quantitative explanation of long time tails, as given by the author, Hauge and van Leeuwen. A more fundamental approach through resummation of ring collision events was given by Dorfman and Cohen. The former theories are valid for general densities, the latter are restricted to low and moderate densities. I also want to point out that the kinetic theory approach of Pomeau, together with that of Dorfman and Cohen, in which the ideas of Pomeau’s 1968 articles were incorporated and clarified, might be considered as the origin of ring kinetic theory, as it is used at the present times.

The predicted asymptotic long time tails in the stress correlation function in (7) and in the other Green Kubo integrands have never been observed in computer simulations in hard core fluids. They are overshadowed by the molasses tails, which are present on intermediate time scales, and are related to the cage effects (see section 11). However in LGA with only on-node interactions the mechanism for “building cages from surrounding hard objects” is absent, and the observed long time tails agree reasonably well with theoretical predictions.

In purely diffusive models, such as Lorentz gases, the correlation function decays as \( \langle v_x(t)v_x(0) \rangle \sim -t^{-1-d/2} \), i.e. after a long time \( t \) the moving particle returns to its point of origin on average moving in a direction opposite to its initial velocity, instead of parallel as in the fluid case. Hence, the correlations are negative at large times and weaker than in fluids. In continuous Lorentz gases, as well as in LGA the observed long time tail phenomena were quantitatively explained by means of mode coupling theory as well as by ring kinetic theory. No new fundamental problems seem to arise here.

Experimental confirmation of the long time tails for air and gaseous argon has been obtained by Kim and Matta, and for latex spheres in water by Ohbayashi et al., using the photon correlation method. Neutron scattering experiments on liquid argon and sodium also offer indirect evidence for the existence of long time tails (for references see).
8 Renormalized fluid dynamic equations

The most dramatic consequence of the long time tails in fluids is the non-
existence of the Navier Stokes equations in two dimensions. As the trans-
port coefficients of viscosity, heat conductivity and self-diffusion are expressed
through Green Kubo formulas as time integral over current correlation func-
tions, these time integrals are diverging as log $t$, and transport coefficients do
not exist in two-dimensional fluids. In purely diffusive systems, like Lorentz
gases, on the other hand, Fick’s law is still valid in two-dimensions, since
$\langle v_x(0)v_x(t) \rangle \sim 1/t^2$ for large $t$, and the diffusion coefficient $D$ is finite.

In three dimensions conventional hydrodynamics involves constitutive re-
lations where (Fourier transforms of) fluxes are linear in the gradients or in the
wave number $k$ and the coefficients of proportionality are the Navier Stokes
transport coefficients. In the same conventional picture one expects that the
fluxes can be expanded systematically in powers of $k$, where the coefficients
of proportionality in the $O(k^2)$-terms are the Burnett coefficients. This sys-
tematic expansion in the non-uniformity parameter, $\mu \sim \ell_0 \nabla$, was the basis of
Bogoliubov’s generalization of the Chapman Enskog method in section 3.

However, explicit calculations using mode coupling theory or ring kinetic
theory show that the Burnett coefficients in three dimensions are diverging
logarithmically. This is a consequence of the occurrence of algebraic long
time tails, which show that the kinetic and hydrodynamic time stages are not
well separated. This observation invalidates the second part of Bogoliubov’s
assumption about the existence of well separated time scales.

We observe that there is in fact a close parallel between on the one hand
the non-existence of the density expansion in (16), which resulted in a non-
analyticity in the low density behavior of the transport coefficients, and on
the other hand the non-existence of the $\mu$–expansion, i.e. the non-existence of the
Navier Stokes equations in two dimensions, and the non-existence of the
Burnett equations in three dimensions.

The legitimate question is then: Are there any singularities in the reno-
malized $\mu$-expansion? If the Navier Stokes equations do not exist in two di-
dimensions, what is the structure of the renormalized hydrodynamic equations
in two-dimensional fluids? Similarly, what is the structure of the renormalized
fluid dynamic equations in three dimensions? Mode coupling theory as well as kinetic theory provide partial answers.

Suppose one calculates the dispersion relation for the relaxation rate $z_\perp(k)$
of transverse velocity excitations (shear modes). Conventional hydrodynamics
gives $z_\perp(k) = -\nu k^2 + \cdots$, where $\nu = \eta/\rho$ is the kinematic viscosity. The new
theory yields:

\[
z_{\perp}(k) = \begin{cases} 
-\nu k^2 + \nu' k^{5/2} + \ldots & (d = 3) \\
-\nu k^2 \log k + \ldots & (d = 2)
\end{cases}
\] (21)

The small-\(k\) singularity in the dispersion relation suggests that the constitutive relations between fluxes and gradient fields involve transport kernels which are nonlocal in space and time. There exist also more complex systems with intrinsic length scales larger than \(\ell_0\) (e.g., dense fluids) where generalized hydrodynamics with wavenumber dependent elastic and dissipative response functions are relevant. The same holds for LGA.

The general structure of the renormalized fluid dynamic equations in two and three dimensions is still an open problem. A clear resolution of their structure is hampered by the apparently complicated non-local structures produced by the long range spatial and temporal correlations, as well as by the smallness of the effects that these correlations produce when they are calculated or hunted for experimentally. As the effects of long time tails are very small in three dimensions, the use of the conventional Navier Stokes equations should of course continue in the foreseeable future.

9 Long range correlations in nonequilibrium stationary states

The first author to analyze already in 1978 long range spatial correlations in non-equilibrium fluids in terms of ring collision events was Onuki. He calculated the pair distribution function in a steady laminar flow using the Boltzmann-Langevin equation, and showed that the pair correlation function has a very long range, exhibiting Coulomb-type behavior, and is proportional to \(\log r\) for \(d = 2\) and to \(1/r\) for \(d = 3\). Kirkpatrick et al. (see review) used in 1982 ring kinetic theory to calculate long range correlations in fluids with an imposed temperature gradient (here the range is even longer than in the laminar flow case), and calculated the dynamic structure factor, which is measured in light scattering experiments.

Such spatial correlations occur in open systems that are kept out of equilibrium by reservoirs or by external driving fields. The objects of interest here are the spatial correlations between fluctuations in the local density \(\delta n(r, t) = n(r, t) - \langle n \rangle\) or in the local flow velocity \(\delta u(r, t) = u(r, t) - \langle u \rangle\). The correlation functions are taken at equal or at unequal times. The spatial Fourier transforms of the former are the static structure factors; the spatial and temporal Fourier transforms of the latter are the dynamic structure factors. The correlations and structure factors related to density fluctuations are studied in light and neutron scattering experiments; those related to
fluctuations in the flow field are studied in homogeneous turbulence \textsuperscript{43}. The theoretical and experimental results for non-equilibrium stationary states in fluids with externally imposed gradients in temperature or flow field have been recently reviewed in \textsuperscript{43}. Those for driven diffusive systems are discussed in a recent monograph by Schmittmann and Zia \textsuperscript{44}.

Also here it is instructive to discuss a simple example: I consider the density-density correlation function \( G(r) \) and corresponding susceptibility or structure factor \( \chi(k) \) in the stationary state of a spatially uniform driven system, where the driving field violates the conditions of detailed balance and breaks the spatial isotropy, \textit{i.e.}

\[
G(r) = \frac{1}{V} \int d\mathbf{r}' \langle \delta n(\mathbf{r} + \mathbf{r}') \delta n(\mathbf{r}') \rangle = \frac{1}{(2\pi)^d} \int d\mathbf{k} \chi(k) \exp(i\mathbf{k} \cdot \mathbf{r}). \tag{22}
\]

Clearly, for the correlation function \( G(r) \) to have an algebraic tail, the susceptibility \( \chi(k) \) needs to have a singularity at small wave number \( k \). The singularities discussed in section 8 are branch points of the form \( \log k \) or \( k^\alpha \) with non-integer \( \alpha \); the same holds in section 7 for the time correlation functions with \( r \) replaced by the time \( t \) and \( k \) by the frequency \( \omega \). However, the singularities need not be branch points.

In the present case of a vector field \( \chi(k) \) the singularity turns out to be a \textit{discontinuity} at \( k = \{k_x, k_y, \ldots\} = 0 \). This is shown by explicit calculations based on fluctuating hydrodynamics \textsuperscript{44,43,46} or ring kinetic theory \textsuperscript{48}. The presence of the driving field makes the susceptibility anisotropic, \textit{i.e.}

\[
\lim_{k \to \infty} \chi(k) = \chi_o(\hat{k}) \tag{23}
\]

depends on the direction \( \hat{k} \) along which the origin is approached. The long range part of \( G(r) \) is then given by

\[
G(r) = \frac{1}{(2\pi)^d} \int d\mathbf{k} \chi_o(\hat{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) = \frac{h(\mathbf{r})}{r^d}, \tag{24}
\]

where a rescaling of the \( \mathbf{k} \)-variable shows that the pair correlation function decays algebraically, with a coefficient \( h(\mathbf{r}) \) that only depends on the direction of \( \mathbf{r} \). An illustrative landscape plot of \( G(r) \) can be found in Ref. \textsuperscript{47}. Also, note the importance of the anisotropy. If \( \chi_o \) were to be a constant, independent of \( \hat{k} \), then the correlation function above would reduce to \( G(r) = \chi_o \delta(r) \), and is strictly short ranged. The algebraic tails \( \sim 1/r^d \) are intimately related to the
long time tails $\sim 1/t^{d/2}$, discussed above. In fact, they are driven by the same slow diffusive modes of the ring kinetic equation, where spatial and temporal scales are related by $r^2 \sim t$.

Also in the context of lattice gas automata the long range spatial correlations in velocity and density fields have been observed in simulations over about 1.5 decades on the spatial scale, and the theoretical calculations obtained from ring and repeated ring kinetic theory are in excellent agreement with the results from molecular dynamics simulations.[48]

10 Ring kinetic theory

The "red thread" connecting all sections in this review are the ring collisions, which were born out of the systematic analysis of the triple collision integrals of the Choh Uhlenbeck equation. Hence the name “cradle of modern kinetic theory”. Ring kinetic theory has been at the basis of most major developments in nonequilibrium statistical mechanics over the last 40 years: it explains the breakdown of the virial expansion of transport coefficients in continuous fluids, and their logarithmic density dependence.[4] it explains the algebraic long time tails of Green Kubo current correlation functions in continuous fluids[6] and in lattice gas automata[32], the breakdown of the Navier Stokes equations in two dimensions for very long times, as well as the non-analytic dispersion relations for sound propagation and for relaxation of hydrodynamic excitations.[6] Moreover, it explains the existence of long range spatial correlations in nonequilibrium stationary states, coupled to reservoirs that impose shear rates or temperature gradients.[42, 43], or in driven diffusive systems.[46]

It seems therefore appropriate to give a simple derivation of the ring kinetic equation for hard spheres, as given in Refs.[39, 42]. Under the restriction of low densities, the BBGKY hierarchy for hard spheres with diameter $\sigma$ can be obtained from (4) and (5) by replacing $\theta_{12}$ by the binary collision operator:

$$T_0(12) = \delta(r_{12})\sigma^{d-1} \int_{v_{12} \cdot \hat{\sigma} < 0} d\hat{\sigma} |v_{12} \cdot \hat{\sigma}|(b_\sigma - 1).$$

The vector $\sigma$ connects the centers of the two colliding spheres at contact and hats denote unit vectors. The integration over the solid angle $d\hat{\sigma}$ is restricted to the precollision hemisphere, $v_{12} \cdot \sigma < 0$. The operator $b_\sigma$ replaces the precollision velocities $v_i$ ($i = 1, 2$) by postcollision ones, i.e.

$$v_1^* \equiv b_\sigma v_1 = v_1 + (v_{12} \cdot \hat{\sigma})\hat{\sigma}$$
$$v_2^* \equiv b_\sigma v_2 = v_2 - (v_{12} \cdot \hat{\sigma})\hat{\sigma}.$$  

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The Boltzmann equation for a dilute gas of hard spheres follows from the hard sphere hierarchy by combining the first equation with the molecular chaos assumption (2). As the density increases the ring collisions build up dynamic correlations, which invalidate the molecular chaos assumption.

The method is based on a cluster expansion of the $s$-particle distribution functions, defined recursively as

\[ f_{12} = f_1 f_2 + g_{12} \]
\[ f_{123} = f_1 f_2 f_3 + f_1 g_{23} + f_2 g_{13} + f_3 g_{12} + g_{123}, \quad (27) \]

and so on. Here $g_{12}$ accounts for pair correlations, $g_{123}$ for triplet correlations, etc. The molecular chaos assumption implies $g_{12} = 0$, which is equivalent to (2). The basic assumption to obtain the ring kinetic equation is that pair correlations are dominant and higher order terms in (27) can be neglected, i.e. $g_{123} = g_{1234} = \ldots = 0$.

Setting $g_{12} = 0$ in the first hard sphere hierarchy equation and eliminating $\partial f_i / \partial t$ ($i = 1, 2$) from the second hierarchy equation with the help of the first one, yields the ring kinetic theory of elastic hard spheres:

\[
(\partial_t + L^0(12)) f_1 = \int dx_2 T_0(12)(f_1 f_3 + g_{12}) \\
\{\partial_t + L^0(12) - T_0(12) - (1 + P_{12}) \int dx_3 T_0(13)(1 + P_{13}) f_3\} g_{12} = T_0(12)\{f_1 f_2 + g_{12}\}. \quad (28)
\]

Here $P_{ij}$ is a permutation operator that interchanges the particle labels $i$ and $j$. The second equation is the so called repeated ring equation for the pair correlation function. If the operator $T_0(12)$ on the left hand side of the second equation is deleted, one obtains the simple ring approximation. Formally solving this equation for $g_{12}$ yields an expression in terms of the single-particle distribution functions $f_i$ ($i = 1, 2, 3$), and subsequent substitution into the first hierarchy equation above yields the generalized Boltzmann equation in ring approximation. Essentially all results about singularities and tails, discussed in sections 5 to 9, can be obtained from the ring kinetic equation, as given in (28). However, the convergent Choh Uhlenbeck correction $\eta_1$ to the three-dimensional viscosity in (15) is not correctly accounted for in this approximate equation.

11 Molasses tails

At liquid densities the velocity correlation function shows a negative part at intermediate times, the so-called cage effect. At the same density and in
the same time interval the stress correlation function in (7) appears to have in three dimensions a long time tail, that can be fitted to $t^{-3/2}$, but with a coefficient 400 to 500 times larger than predicted by the mode coupling theory of section 7. This so-called molasses tail occurs in dense liquids with short range hard core interactions, where the mean free path $\ell_0$ is much smaller than the hard core diameter $\sigma$.

The conventional long time tail $\sim t^{-d/2}$ is controlled by long wavelength modes, and the intermediate time molasses tail by slow modes of intermediate wavelength around $k\sigma \simeq 2\pi$, where the structure factor has its maximum. At these wavevectors the dynamics of fluid excitations is in fact controlled by a single soft (density) mode, also called cage diffusion. At the high densities relevant for liquids, the Fourier modes of momentum and energy density with wave vectors near $2\pi/\sigma$ relax very rapidly through the mechanism of instantaneous collisional transfer over distances of order $\sigma$, whereas kinetic transport, which is operating on scales of $\ell_o$, is much slower. Therefore the density, which can only relax through kinetic transport, is the only slow mode near $k\sigma \simeq 2\pi$. It requires rearrangments of particle configurations over distances of order $\sigma$, i.e. structural relaxation. The detailed explanation was given by Kirkpatrick and van Beijeren, who extended the mode coupling theory of section 7 by including wavenumbers up to $k \simeq 2\pi/\sigma$, i.e. by including the slow cage diffusion mode. This important fundamental result marks perhaps the end of the modern era.

12 Post-modern kinetic theory

By 1985 the results of the modern era: the log $n$–dependence of transport coefficients, the long spatial and temporal tails in correlation functions, and the fact that conventional hydrodynamics breaks down, at least in principle, were generally accepted. However, the experimental consequences of the exciting developments were minute and difficult to observe experimentally.

Where to go from here? The tendency was to combine intuitive classical concepts with the modern concepts of dynamical correlations, originating from mode coupling and ring kinetic theory, and to apply these to more complex problems, such as nonlinear hydrodynamics and porous media, dense fluids, granular flows, mathematical modeling of the Boltzmann equation and ring kinetic equations, and even to the calculation of Lyapunov exponents in non-equilibrium fluids. Simultaneously one sees the development of new methods for numerical simulation of non-equilibrium fluids, such as Lattice Gas Automata (LGA), the Lattice Boltzmann Equation (LBE) method, and Bird-type methods, which are stochastic simulation methods for solving...
nonlinear kinetic equations.

Many of these current developments, such as the LBE method, the Bird-type methods, mathematical modeling of kinetic equations, and Lyapunov exponents, have no direct links with the modern concepts of dynamical correlations and with the Choh Uhlenbeck equation, and will not be discussed any further.

An outburst of renewed interest in kinetic theory occurred in 1986, when Frisch, Hasslacher and Pomeau\cite{Frisch1986} proposed Lattice Gas Automata (LGA), as models for non-equilibrium fluids. This event marks in my view the beginning of the \textit{Post-modern Era}. The LGA, already defined in section 2, are fully discretized statistical mechanical models of $N$–particle systems, which do not involve any new fundamental concepts. The LGA were specially designed for large scale and long time computer simulations of complex hydrodynamic flow problems. As the dynamic description is based on Boolean variables, there are no round off errors. The kinetic theory for these models closely parallels that for continuous fluids, as I have been indicating in all previous sections.

The most important fundamental result from LGA is the excellent confirmation of the theoretical predictions for the long time tails in the velocity correlation function, calculated from mode coupling and ring kinetic theory. Here the tails have been measured with very high statistical accuracy over two decades of mean free times\cite{Rothman1986}.

Moreover, the study of LGA has provided many interesting new results on the dynamics of phase separation and pattern formation, as well as on flows through porous media (see review by Rothman and Zaleski\cite{Rothman1988}). Unfortunately, LGA turned out to be not very suitable to study high Reynolds number flows, because the viscosity of LGA is too large.

A phenomenological equation linked to the modern era, and widely applied in the post-modern era, is the \textit{nonlinear} revised Enskog equation for hard spheres, which is a Markovian approximation, constructed in 1972 by van Beijeren and the author\cite{Beijeren1972} as an exact result for short times. The \textit{linearized} version of this theory has been derived by many authors\cite{Beijeren1972}. These theories are collectively referred to as the \textit{Revised Enskog Theory} (RET) with a collision operator taking non-local short range static correlations into account.

The theoretical and experimental research by de Schepper and collaborators\cite{Schepper1986} on dynamical structure functions of dense liquids with short range hard core interactions has shown that the RET gives a reasonably accurate description of the elementary excitations with wavelengths in the range $\ell_o < \lambda \leq \sigma$. A Fourier mode analysis\cite{Schepper1986} of the revised Enskog equation shows that this equation has only a single slow mode at wavevectors near $k\sigma \simeq 2\pi$, the cage diffusion mode. Although the RET involves only binary collision dynamics, it
mimics the effects of cage diffusion, described in section 11, reasonably well. The classical Enskog equation in (3) is missing this effect.

Further interesting extensions of the RET to non-equilibrium solids have been given by Kirkpatrick et al., who derived the macroscopic equations of motion for the elastic solid from this equation. RET yields in principle a microscopic theory for elastic constants and dissipative coefficients, as well as a dynamic theory for freezing. In the fluid phase there are five slow hydrodynamic modes; in the solid phase there are eight soft modes with vanishing dispersion relations as $k \to 0$, i.e. five conserved densities and three displacement fields (order parameter fields). There are six propagating modes, a thermal diffusion mode and a vacancy diffusion mode. Vacuum diffusion, which involves structural relaxation, occurs on time scales much greater than those occurring in sound phenomena and thermal diffusion, which are controlled by collisional transfer of momentum and energy. This suggests that cage diffusion in the liquid phase and vacancy diffusion in the solid phase may be related to the same slow microscopic excitation. Moreover, the RET has also been applied by Kirkpatrick, Kawasaki and Dufty to study the slow structural relaxation in glasses.

The ring equation of section 10 has still a very complex structure. Dufty, Lee and Brey have proposed a mathematical model with a simpler structure than (28). It would be very interesting to obtain from this simpler model more explicit analytic results for the pair correlation function in non-equilibrium fluids. Finally, a very recent publication by van Noije et al. on long range correlations in rapid granular flows shows that ring kinetic theory or fluctuating hydrodynamics has become the standard tool to analyze long range correlations in complex and simple fluids out of equilibrium.

The central theme of this review has been the importance in non-equilibrium statistical mechanics of the ring collisions, which were born out of a detailed analysis of the Choh Uhlenbeck equation.

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