

TIME DEPENDENT CORRELATION FUNCTIONS AND MODE—MODE COUPLING THEORIES

Y. POMEAU

*Service de Physique Théorique, Centre d'Etudes Nucléaires de Saclay,
BP no. 2 – 91190 – Gif-sur-Yvette, France*

and

P. RÉSIBOIS

Faculté des Sciences, Université libre de Bruxelles, Belgique



NORTH-HOLLAND PUBLISHING COMPANY – AMSTERDAM

TIME DEPENDENT CORRELATION FUNCTIONS AND MODE–MODE COUPLING THEORIES

Y. POMEAU

*Service de Physique Théorique, Centre d'Etudes Nucléaires de Saclay,
BP no. 2 – 91190 – Gif-sur-Yvette, France*

and

P. RÉSIBOIS

Faculté des Sciences, Université libre de Bruxelles, Belgique

Received October 1974

Abstract:

We critically discuss the various tools and methods which are used to describe the role of long wave length hydrodynamical processes in the analysis of time-dependent correlation functions. We also review the various physical problems (long time behavior of Green–Kubo integrands, 2 dimensional hydrodynamics, transport properties of the Van der Waals fluid, critical phenomena ...) where these methods have received fruitful applications.

Contents:

1. Introduction	65	4.1. Asymptotic behavior of the Green–Kubo integrands	109
2. The tools	70	4.2. Higher order terms in the Enskog expansion and in the asymptotics of time correlation functions	112
2.1. Phenomenological approach	70	4.3. Mode–mode coupling in 2d fluids	116
2.2. The fluctuating hydrodynamics approach	74	4.4. Transport properties of the Van der Waals fluid	119
2.3. The kinetic approach	82	4.5. Critical dynamics	122
3. Mode–mode coupling illustrated	90	5. Final remarks	125
3.1. Generalization of classical Brownian motion theory	90	Appendix A. Derivation of eq. (2.81)	130
3.2. The phenomenological (or Landau–Placzek) method	95	Appendix B. Formal density expansion of the collision operator $\tilde{C}_0(p, z)$	131
3.3. The method of fluctuating hydrodynamics	99	Appendix C. Structure of the collision operator	135
3.4. Kinetic theory method	101	References	136
4. The applications	108		

Single orders for this issue

PHYSICS REPORTS (Section C of PHYSICS LETTERS) 19, No. 2 (1975) 63–139.

Copies of this issue may be obtained at the price given below. All orders should be sent directly to the Publisher. Orders must be accompanied by check.

Single issue price Dfl. 23.50, postage included.

1. Introduction

The first important step towards an understanding of transport coefficients in terms of time dependent correlation functions goes back to Einstein [1] when he developed his stochastic theory for the diffusion of a Brownian (B) particle; he got the following formula for the diffusion coefficient D :

$$D = \lim_{t \rightarrow \infty} \frac{1}{2t} \langle \Delta r_{1x}^2(t) \rangle \quad (1.1)$$

where $\Delta r_{1x}(t) = r_{1x}(t) - r_{1x}(0)$ denotes the random displacement of the B-particle along the x -axis in the time interval t , while the bracket $\langle \dots \rangle$ means an average over this random motion.

Let us cast this formula into a form which is closer to modern language. To this end, we write:

$$\Delta r_{1x}(t) = \int_0^t v_{1x}(t') dt' \quad (1.2)$$

where $v_{1x}(t')$ denotes the velocity of the B-particle. Inserting this into (1.1) and assuming that the random process is stationary:

$$\langle v_{1x}(t') v_{1x}(t'') \rangle = \langle v_{1x}(t' - t'') v_{1x}(0) \rangle \quad (1.3)$$

we get:

$$D = \lim_{t \rightarrow \infty} \frac{1}{2t} \int_0^t dt' \int_0^t dt'' \langle v_{1x}(t' - t'') v_{1x}(0) \rangle. \quad (1.4)$$

With $\tau = t' - t''$ as a new integration variable and assuming that $\langle v_{1x}(\tau) v_{1x}(0) \rangle$ decays faster than τ^{-1} for large τ , the limit indicated in (1.4) can be taken and leads to:

$$D = \int_0^\infty d\tau \langle v_{1x}(\tau) v_{1x}(0) \rangle. \quad (1.5)$$

More information can be obtained if we assume that $v_{1x}(t)$ satisfies the Langevin equation [2]:

$$\frac{dv_{1x}(\tau)}{d\tau} = -\frac{\xi}{m_1} v_{1x}(\tau) + \frac{F_{1x}(\tau)}{m_1} \quad (1.6)$$

where ξ is the friction coefficient, m_1 the mass of the B-particle and $F_{1x}(\tau)$ is the random force describing the fluctuating collisions of the Brownian particle with the fluid. Supposing $F_{1x}(\tau)$ uncorrelated with the velocity at time $\tau = 0$ (i.e., $\langle F_{1x}(\tau) v_{1x}(0) \rangle = 0$ for $\tau > 0$), we immediately obtain an exponential decay for the velocity correlation function:

$$\langle v_{1x}(\tau) v_{1x}(0) \rangle = \exp\{-\xi|\tau|/m_1\}. \quad (1.7)$$

This, in turn, leads to the well-known Einstein relation $D = k_B T / \xi$ (k_B is Boltzmann constant, T is the absolute temperature).

Of course, these results have been derived within the frame of the theory of random processes. Yet, it is very easy to guess how eq. (1.5) has to be interpreted in order to give it a purely microscopic meaning.

a) The average $\langle \dots \rangle$ has to be interpreted as an average over the equilibrium ensemble describing a N particle system (the B particle plus $(N-1)$ fluid molecules) with Hamiltonian H_N , in the limit where the system becomes large:

$$\langle \dots \rangle = \lim_{\Omega} \frac{\int dr^N dp^N \dots \exp(-\beta H_N)}{Z_N}. \quad (1.8)$$

Here (r^N, p^N) symbolically denotes phase space coordinates $(r_1 \dots r_N; p_1 \dots p_N)$ and $\beta = 1/k_B T$; moreover \lim_{Ω} denotes the thermodynamic limit $N \rightarrow \infty$, Ω (volume of the system) $\rightarrow \infty$, $N/\Omega = \text{finite}^*$; Z_N is the partition function.

b) The time evolution of the velocity of the B-particle is no longer governed by the Langevin equation (1.6) but by the deterministic Newton's equation:

$$\frac{dv_{1x}(t)}{dt} = -\frac{1}{m_1} \sum_{j=2}^N F_{1j,x}(t) \quad (1.9)$$

where $F_{1j,x}(t)$ denotes the force exerted, at time t , by molecule j on the B-particle.

When interpreted in this way, eq. (1.4) becomes a typical example of a Green-Kubo formula, as developed by Green, Kubo and many others (see for example [3-6]). More generally, one can show that any transport coefficient X can be expressed as the integral of the time dependent correlation function of a microscopic flow operator \hat{J}^X .** One has:

$$X = \lim_{t \rightarrow \infty} \lim_{\Omega} \frac{1}{\Omega k_B T} \int_0^t \langle \hat{J}^X(\tau) \hat{J}^X(0) \rangle d\tau. \quad (1.10)$$

We have, for given \hat{J}^X :

$$\hat{J}^X(\tau) = \exp[iL_N \tau] \hat{J}^X \quad (1.11)$$

where L_N is the Liouville operator:

$$L_N = i\{H_N, \dots\} \quad (1.12)$$

($\{\dots, \dots\}$ denotes the Poisson bracket). Obviously, eq. (1.5) is a particular case of (1.10) with $\hat{J}^D = v_{1x} \sqrt{\Omega k_B T}$.

It is worthwhile to point out that eq. (1.5), which was derived here for a Brownian (large and heavy) particle, remains valid when the observed particle 1 is mechanically identical to the other fluid molecules: eq. (1.5) then gives the self-diffusion coefficient, which will often be used to illustrate our discussion. However, in this case as well as for the other correlation functions, we

*As we shall not be able to say anything mathematically rigorous on this thermodynamic limit, we shall often keep it implicit, assuming that it exists.

**We shall often use the term "operator" for any quantity \hat{A} which depends as a function or as an operator in the usual sense on the dynamical variables of the system: $\hat{A} = \hat{A}(r^N, p^N)$.

have generally no proof of anything like (1.7): this latter result is a consequence of the Langevin equation (1.8) and not of the equation of motion (1.11).

Nevertheless, it was generally believed that a property analogous to (1.7) was valid in general, at least far from the critical region and for uncharged systems. More precisely, defining the Green–Kubo integrand $X(t)$ by:

$$X(t) = \lim_{\Omega} \frac{1}{\Omega k_B T} \langle \hat{J}^X(t) \hat{J}^X(0) \rangle \quad (1.13)$$

we can express this assumption by the following inequality:

$$|X(t)| \leq B \exp(-t/\tau_r) \quad (??) \quad (1.14)$$

where B and τ_r are adequate constants.

It is true that (1.14) was supported by extremely few detailed calculations, and always on very simple models (like the dilute gas [7]). Moreover, the discovery of the non-analytic character of the density expansion of transport coefficient [8] already pointed out that these Green–Kubo integrands did not behave as smoothly as one could hope. Yet, it came as a great surprise when Alder and Wainwright [9, 11] published the result of a computer calculation for the self-diffusion Green–Kubo integrand $D(t)$ of a hard sphere system; they find a very slow decay which, for times t larger than about ten collision times, was well represented by:

$$D(t) \sim t^{-d/2} \quad (1.15)$$

where d denotes the dimensionality of the system ($d = 2, 3$) (see fig. 1.1). At the same time, by carefully looking at the pattern of the molecular motion in their simulated system, they gave a very simple interpretation of (1.15) in terms of hydrodynamics.

Their argument can be put in the following terms: suppose that, at $t = 0$, we give velocity v_{1x} to molecule 1 (fig. 1.2a). This particle interacts with its neighbours and, after a short (microscopic) time τ , its initial momentum is shared by all the molecules lying in a small volume Ω_r around it

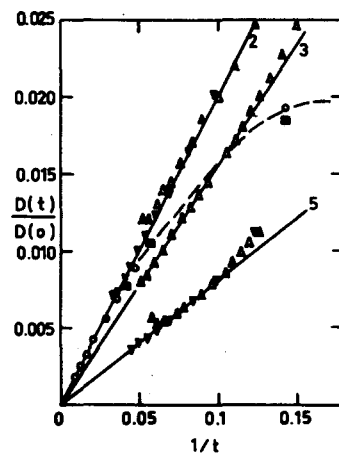


Fig. 1.1. The decay of the velocity autocorrelation function at large times for hard disks at three densities: $A/A_0 = 2, 3$ and 5 . The closed and open triangles refer to molecular-dynamic runs of 986 and 504 particles, respectively (taken from ref. [101]).

(fig. 1.2b); it will then be at “local equilibrium” with this volume and move with velocity*:

$$v_{1x}(\tau) \simeq v_{1x}(0)/n\Omega_\tau. \quad (1.16)$$

The further decay of $v_{1x}(t)$ can only occur because this moving volume Ω_t grows larger and larger. Now, how complicated the initial expansion of Ω_t may be, we expect that, for long times, this expansion will be described by hydrodynamics; the velocity field then propagates by two mechanisms:

a) Sound wave propagation, which is a fast process and can be neglected here.

b) Shear mode propagation (or vorticity diffusion), which ensures that the radius R_t ** grows by a diffusion process (see fig. 1.2c):

$$R(t) \sim \sqrt{\nu t} \quad (1.17)$$

where ν is the kinematic viscosity ($\nu = \eta/\rho$; η the shear viscosity; $\rho = nm$; m mass of the fluid particle). Thus

$$\Omega_t \sim (\nu t)^{d/2} \quad (1.18)$$

and

$$v_{1x}(t) \simeq v_{1x}(0)/(\nu t)^{d/2}. \quad (1.19)$$

This last result immediately leads to:

$$D(t) \sim 1/(\nu t)^{d/2}. \quad (1.20)$$

However, in this rough argument, we have assumed that particle 1 was staying at the center of Ω_t ; we should more correctly take its own diffusive motion into account. We get then:

$$D(t) \sim 1/[(\nu + D)t]^{d/2} \quad (1.21)$$

in agreement with (1.15).

As we shall see later, more refined theories confirm this result.

Of course the use of hydrodynamical concepts in the calculation of transport coefficients is not new. It goes back to the thirties, when Debye, Onsager and Falkenhagen [12] computed

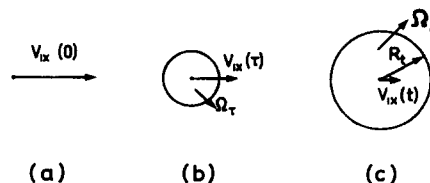


Fig. 1.2. Schematic picture underlying the slow decay of $D(t)$.

*Because the fluid molecules are at thermal equilibrium, with an isotropic velocity distribution which does not contribute to transport phenomena, we may develop the argument as if these molecules were all initially at rest.

**In a more exact calculation, one should take into account that the volume Ω_t is not a sphere (for instance, in 2d, it is bell shaped). Yet our dimensional argument is not affected by this.

the transport properties of dilute electrolyte solutions. Later these ideas were transposed by Fixman [13] followed by Kawasaki [14, 15], Kadanoff and Swift [16] and many others, in the field of dynamical critical phenomena. In these two problems there exists a natural length (respectively the Debye length and the correlation length) which is large compared to molecular dimensions: hydrodynamical effects thus were not unexpected. Yet, as we shall see later, the “long time tails” of the type (1.21) have precisely the same origin – although there is no natural large length in the problem – and they are treated by the same formalisms, which are known as *mode–mode coupling theories*.

The aim of the present report is to give a critical discussion of these various formalisms as well as a general review of their applications. The need of such a synthesis was felt when the authors tried to go through the literature on the subject: indeed, there is a great variety of apparently different starting points; generally – and sometimes quite surprisingly ! – very similar conclusions are reached; but very rarely can one find the interconnection between these different approaches.

Roughly speaking, one finds three types of approaches of increasing mathematical sophistication:

i) *The phenomenological approach* [11, 17, 18]: in this optimistic view point, one is “a priori” confident in the correctness of the picture described above and one puts it in a quantitative form with the help of macroscopic hydrodynamics and equilibrium fluctuation theory.

ii) *The fluctuating hydrodynamics approach* [19, 26]: here, one first remarks that the *linearized* equations of *macroscopic* hydrodynamics, which allow one to define the transport coefficients – and thus the Green–Kubo integrands as well – are the result of the ensemble averaging of the equations of motion for the *fluctuating microscopic* conserved quantities. Difficulties with the Green–Kubo integrands thus manifest corresponding pathologies for the dynamics of these fluctuating quantities; this dynamics is then reconsidered either on a purely stochastic basis or by making suitable hypothesis on the microscopic Langevin type of equation which emerges from the Zwanzig–Mori formalism [27, 28]. In both cases, an essential feature is that these fluctuating conserved quantities obey coupled *non linear* equations.

iii) *The kinetic approach* [29, 36]: here, the program is, at least in principle, to make a detailed many-body analysis of the Green–Kubo integrands. The hydrodynamical effects appear here as contributions, dominant in the long wave length limit, to the “propagator” describing the exact dynamics of the particles in the system.

Of course any classification of this type has some degree of arbitrariness; for example, some works on critical dynamics [14, 16] are somewhat on the border line between (i) and (ii) while taking the “microscopic” Langevin equation as a starting point still allows one a kinetic discussion [26]. However, this distinction will be pedagogically useful in sections 2 and 3 where we shall respectively summarize the *tools* and the *methods* followed in these different approaches. The methods will be illustrated by considering the velocity correlation function, already discussed above. In section 4, we take a different view point and we try to summarize the type of *results* which have been obtained by these various mode–mode coupling approaches; there we discuss the different properties of the Green–Kubo integrands which have been discovered in normal fluids (including the surprising non-existence of transport coefficient in $2d$) as well as applications to critical phenomena and to the transport properties of the Van der Waals fluid. Some conclusions, in particular concerning the relevance of these calculations with respect to experiments, are presented in section 5.

Let us add one remark about the references given at the end of the paper; we have tried

to give a complete list as far as the mode–mode coupling problems are concerned. However, as will appear clearly in the following, we shall also touch upon a great variety of related problems; there, we have not attempted to be exhaustive by any means and, very often, we refer to existing textbooks or review articles rather than to the original papers.

2. The tools

2.1. Phenomenological approach

In transport theory of fluids with a single component, a fundamental role is played by the five conserved macroscopic quantities, namely the particle density $n(r, t)$, the momentum density $g(r, t)$ and the energy density $\bar{\epsilon}(r, t)$ (this latter involves both the internal energy $\epsilon(r, t)$ and the kinetic energy $mn(r, t)v^2(r, t)/2$). These conservation laws are formally expressed by*:

$$\partial_t n(r, t) + \frac{1}{m} \nabla \cdot g(r, t) = 0, \quad \partial_t g(r, t) + \nabla \cdot \tau(r, t) = 0, \quad \partial_t \bar{\epsilon}(r, t) + \nabla \cdot j^{\bar{\epsilon}}(r, t) = 0 \quad (2.1)$$

where $\tau(r, t)$ is the stress tensor and $j^{\bar{\epsilon}}$ is the energy flow. These equations tell us that the number of particles, the momentum and the energy contained in a given volume ω can only vary by flowing through the boundary of ω ; yet, the detailed description of this flow requires supplementary assumptions on the currents τ and $j^{\bar{\epsilon}}$ in order to make (2.1) a closed system of equations [37, 38].

Here, we limit ourselves to a system which is very close to absolute equilibrium; this allows us to linearize all quantities around this equilibrium state. For example, we write:

$$n(r, t) = n + \delta n(r, t), \quad \epsilon(r, t) = \epsilon + \delta \epsilon(r, t) \quad (2.2)$$

with the convention that when the (r, t) dependence of a given quantity is not indicated, its equilibrium value should be taken. We also assume that thermodynamic properties can be defined in this slightly out of equilibrium fluid and that they are interrelated in the same way as at equilibrium; this so-called *local equilibrium* assumption will be used over and over again in the following. For example, the local pressure $p(r, t)$ still exists and is

$$p(r, t) = p(n(r, t), \epsilon(r, t)) \quad (2.3)$$

where $p = p(n, \epsilon)$ is the function of (n, ϵ) which defines the equilibrium pressure. Finally we take for τ and $j^{\bar{\epsilon}}$ the usual macroscopic expressions:

$$\tau_{ij}(r, t) = p(r, t)\delta_{ij} - \eta \left(\frac{\partial v_i(r, t)}{\partial r_j} + \frac{\partial v_j(r, t)}{\partial r_i} \right) - \delta_{ij} \left(\zeta - \frac{2}{3}\eta \right) \sum_{l=1}^3 \frac{\partial v_l(r, t)}{\partial r_l} \quad (2.4)$$

(Newton hypothesis) and

$$j^{\bar{\epsilon}}(r, t) = hv(r, t) - \kappa \nabla T(r, t) \quad (2.5)$$

(Fourier law).

*Throughout this paper vector symbols will not be explicitly displayed and scalar products will be denoted by a dot, as in $v \cdot w$ or $\nabla \cdot g$.

In these formulas, η , ζ and κ respectively denote shear viscosity, bulk viscosity and thermal conductivity; h is the equilibrium enthalpy density and $v(r, t)$ is the velocity field which, in our linear approximation, is simply:

$$v(r, t) = g(r, t)/\rho; \quad (2.6)$$

moreover the local temperature $T(r, t) = T + \delta T(r, t)$ is defined by:

$$\delta\epsilon(r, t) = nC_v\delta T(r, t) + \left(\frac{\partial\epsilon}{\partial n}\right)_T \delta n(r, t) \quad (2.7)$$

(C_v is the specific heat per particle at constant volume).

Collecting these results, we easily arrive at the following *equations of linearized hydrodynamics*:

$$\partial_t \delta n(r, t) + n \nabla \cdot v(r, t) = 0, \quad (2.8a)$$

$$\partial_t v(r, t) + \frac{1}{\rho} \left(\frac{\partial p}{\partial n}\right)_T \nabla \delta n(r, t) + \frac{1}{\rho} \left(\frac{\partial p}{\partial T}\right)_n \nabla \delta T(r, t) - \nu \nabla^2 v(r, t) - \left(\frac{\zeta + \eta/3}{\rho}\right) \nabla (\nabla \cdot v(r, t)) = 0, \quad (2.8b)$$

$$\partial_t \delta T(r, t) + \frac{T}{nC_v} \left(\frac{\partial p}{\partial T}\right)_n \nabla \cdot v(r, t) - \frac{\kappa}{nC_v} \nabla^2 \delta T(r, t) = 0. \quad (2.8c)$$

In order to get an explicit solution of these equations, we define the Fourier-Laplace transform with respect to space and time; for example:

$$n_{q,\omega} = \int_0^\infty dt \exp(-i\omega t) n_q(t) \quad (2.9)$$

$$n_q(t) = \int_\Omega d^3r \exp(iq \cdot r) \delta n(r, t) \quad (2.10)$$

etc. ... and we arrive at the linear system of algebraic equations:

$$\begin{aligned} -i\omega n_{q,\omega} + iq \cdot v_{q,\omega} &= n_q(t=0), \\ -i\omega v_{q,\omega} + iq \left[\frac{1}{\rho} \frac{\partial p}{\partial n} \right]_T n_{q,\omega} + iq \left[\frac{1}{\rho} \frac{\partial p}{\partial T} \right]_n T_{q,\omega} + \left\{ \nu q^2 v_{q,\omega} + \frac{(\zeta + \eta/3)}{\rho} q [q \cdot v_{q,\omega}] \right\} &= v_q(t=0), \\ -i\omega T_{q,\omega} + i \left[\frac{T}{nC_v} \frac{\partial p}{\partial T} \right]_n q \cdot v_{q,\omega} + \frac{\kappa}{nC_v} q^2 T_{q,\omega} &= T_q(t=0). \end{aligned} \quad (2.11)$$

The solution of (2.11) can obviously be reduced to the calculation of the five eigenvalues λ_α^q ($\alpha = 1, \dots, 5$) and eigenvectors of the (non-Hermitian) homogeneous problem associated with these equations. In the small q limit, which is of interest to us here, one readily finds:

$$\lambda_{1,2} = \pm icq - \Gamma q^2, \quad \lambda_{3,4} = -\eta q^2/\rho, \quad \lambda_5 = -\kappa q^2/nC_p \quad (2.12)$$

where:

$$\Gamma = \frac{1}{2} \left[\frac{4\eta/3 + \zeta}{\rho} + \left(\frac{1}{C_v} - \frac{1}{C_p} \right) \frac{\kappa}{n} \right] \quad (2.13)$$

and c is the sound velocity:

$$c^2 = \frac{C_p}{C_v} \left(\frac{\partial p}{\partial n} \right)_T. \quad (2.14)$$

Clearly, $\lambda_{1,2}$ describe damped sound-wave propagations, $\lambda_{3,4}$ express the viscous damping of the transverse (or divergence free) velocity and λ_5 corresponds to the damping of the thermal mode [38].

The corresponding eigenvectors are easily written down also but we shall not display them here. Transforming back to the time variable, one then derives the explicit form of $n_q(t)$, $v_q(t)$ and $T_q(t)$. For example, we get for the transverse component of the velocity field:

$$v_{q\perp}(t) \equiv v_q(t) - q(q \cdot v_q(t))/q^2 = v_{q\perp}(0) \exp(-q^2 \nu t) \quad (2.15a)$$

and for the longitudinal part:

$$v_{q\parallel}(t) = q(q \cdot v_q(t))/q^2 = \cos(cqt) \exp(-\Gamma q^2 t) v_{q\parallel}(0). \quad (2.15b)$$

Let us stress that the above derivation was done at the level of *macroscopic physics*; its range of applicability is thus limited to phenomena which are slowly varying in space and time. The way in which such a hydrodynamic description can be used in the analysis of the Green–Kubo integrand (1.11) which involves an equilibrium average over *microscopic* time dependent fluctuations, is by no means trivial and will only be discussed in section 3.

Yet, to suggest the possibility of using macroscopic concepts in a microscopic problem, it is worthwhile to recall briefly here a somewhat analogous though much simpler problem, namely the regression of the density–density correlation function $S_q(t)$ defined by:

$$S_q(t) = \left\langle \frac{1}{N} \hat{n}_q(t) \hat{n}_{-q}(0) \right\rangle \quad (2.16)$$

where \hat{n}_q is the Fourier transform of the microscopic density $\hat{n}(r)$:

$$\hat{n}(r, t) = \sum_{i=1}^N \delta(r - r_i(t)), \quad \hat{n}_q(t) = \sum_{i=1}^N \exp(iq \cdot r_i(t)) \quad (2.17)$$

and depends on the detailed motion of all the particles in the system. In order to analyze (2.16), we use a somewhat modernized version of the Landau–Placzek theory [39, 40]. We perform the trace (see (1.8)) in two steps (such partial averages have been used in various contexts: see for example [27, 41]):

- i) we make a partial phase space average with prescribed density fluctuation (n_q),*
- ii) we then average over these fluctuations.

*To be complete, we should also prescribe four other conserved quantities: the velocity v_q and, for example, the temperature T_q defined in terms of the observable fluctuations n_q and ϵ_q with the help of (2.7). However, these variables fluctuate independently of n_q and we shall neglect them from the beginning.

With the help of (1.12), we write thus*:

$$S_q(t) = \lim_{\Omega} \frac{1}{N} \left\{ \int dn_q P_N(n_q) n_q \left[\int dr^N dp^N \hat{n}_{-q} \exp(-iL_N \tau) \rho_N^l(n_q) \right] \right\} \quad (2.18)$$

where

$$\rho_N^l(n_q) \equiv \frac{\delta(n_q - \hat{n}_q) \exp(-\beta H_N)}{\int dr^N dp^N \delta(n_q - \hat{n}_q) \exp(-\beta H_N)} \quad (2.19)$$

$$P_N(n_q) \equiv \int dr^N dp^N \delta(n_q - \hat{n}_q) \exp(-\beta H_N) / Z_N. \quad (2.20)$$

It is clear from (2.19) that $\rho_N^l(n_q)$ represents an equilibrium state except for the constraint that the local density $\hat{n}(r)$ (or \hat{n}_q) is prescribed. If q is *small enough*, we can split our system in cells of size R such that $q \ll R^{-1} \ll (\text{molecular length})^{-1}$ and, in each of these cells, we find an equilibrium situation with constant density. Hence, the only time evolution of ρ_N^l comes about because the density is not uniform from cell to cell. Identifying the density in each cell with the *macroscopic* local density, we can suppose that its time evolution is governed by the equation of hydrodynamics (2.8). At any time, we then assume that the distribution function ρ_N^l adapts itself to the local equilibrium state characterized by the density $n_q(t)$; we write thus for large N :

$$\rho_N^l(n_q; t) = \exp[iL_N t] \rho_N^l(n_q) = \rho_N^l(n_q(t)) \quad (2.21)$$

with $n_q(t)$ determined by (2.9, 11). Inserting this result into (2.18), we readily obtain:

$$S_q(t) = \lim_{\Omega} \frac{1}{N} \int dn_q n_q n_{-q}(t) P_N(n_q), \quad (2.22)$$

a remarkable result, though only valid in the small wavenumber limit: indeed it no longer depends on the details of the microscopic motion of the molecules in the system.

As a matter of fact, even the calculation of $P_N(n_q)$ (see (2.20)) does not require statistical mechanics at a microscopic level. Indeed, in the small wavenumber limit, we can argue that n_q is a macroscopic deviation from the average density; $P_N(n_q)$ can then be calculated from the well known thermodynamic fluctuation theory [41–43]. One gets:

$$P_N(n_q) = \left(\frac{1}{2\pi\Omega k_B T^2 n^2 \chi_T} \right)^{1/2} \exp(-|n_q|^2 / 2\Omega k_B T^2 n^2 \chi_T) \quad (2.23)$$

where χ_T is the isothermal compressibility. Incidentally, let us point out a similar formula for the probability distribution of the velocity fluctuations:

$$P_N(v_q) = \left(\frac{nm}{2\pi k_B T \Omega} \right)^{1/2} \exp(-|v_q|^2 nm / 2\Omega k_B T) \quad (2.24)$$

which will be used in section 3.

From (2.17), $\hat{n}_q = \hat{n}'_q + i\hat{n}''_q$ is a complex quantity, which satisfies $\hat{n}_q = \hat{n}_{-q}^$; the integral over \hat{n}_q and the Dirac delta functions in (2.18–20) should thus be expressed with the variables n'_q and n''_q . We shall however ignore this point here.

With the help of (2.23) and of the solution of the hydrodynamic equations (2.11) (with the initial conditions $v_q(0) = T_q(0) = 0$; see footnote on page 72), one readily gets the explicit form for $S_q(t)$:

$$S_q(t) = nkT\chi_T \left[\left(1 - \frac{C_v}{C_p}\right) \exp(-q^2\kappa|t|/nC_p) + \frac{C_v}{C_p} \cos(qct) \exp(-\Gamma q^2|t|) \right]. \quad (2.25)$$

It would be out of place here to comment any further on the well-known Landau–Placzek formula (2.25). Let us simply point out that there is a big difference between the correlation function $S_q(t)$ and the Green–Kubo integrand (1.11): the dynamical variable $\hat{n}_q(t)$ is conserved (i.e. $\lim_{q \rightarrow 0} \{H_N, \hat{n}_q\} = 0$), while the flow $\hat{J}^X(t)$ is not ($\{H_N, \hat{J}^X\} \neq 0$); nevertheless, we shall find striking similarities between the ideas leading to (2.25) and the mode–mode coupling treatment of the Green–Kubo integrands, to be presented in section 3.

Before closing this subsection, let us still remark that we have treated here the linearized hydrodynamics of a fluid made of particles of one single species. Later on, we will also need the hydrodynamics of a binary mixture, in the very special case where one of the species is infinitely dilute. Thus the properties of the second species are unaffected and are still described by the above formulas. Yet for the dilute species, we find a single diffusive mode: if we denote by $n_{1,q}$ the Fourier transform of the density of this dilute species, we have:

$$\partial_t n_{1,q}(t) = -q^2 D n_{1,q}(t) \quad (2.26)$$

where D is the self-diffusion coefficient already considered in (1.5).

2.2. *The fluctuating hydrodynamics approach*

As already pointed out for the case of the density (see (2.17)), the macroscopic conserved variables are statistical averages of well defined microscopic operators. The unexpected behavior of transport coefficients, which we indicated in the introduction, makes it worthwhile to reconsider the assumptions underlying this averaging procedure.

That the problem is non trivial can be seen on the following example: consider the microscopic momentum density, defined by:

$$g(r, t) = \sum_{a=1}^N p_a(t) \delta(r - r_a(t)). \quad (2.27)$$

From Hamilton's equations of motion for $r_a(t)$, it is readily seen that:

$$\partial_t g(r, t) = -\nabla \cdot \tau(r, t) \quad (2.28)$$

where the stress tensor operator is defined by:

$$-\nabla \tau(r, t) \equiv i L_N g(r, t). \quad (2.29)$$

Assuming formally that $\tau(r, t)$ is slowly varying over the range of the forces*, we can get the following representation:

*This assumption, which may appear very strong in view of the singular nature of $\tau(r, t)$, is really no more than a mathematical convenience, as shown for example in references [44, 45].

$$\mathbf{r}(r, t) = \sum_{a=1}^N \left[v_a p_a - \frac{1}{2} \sum_{b \neq a} \frac{\partial V}{\partial r_{ab}} r_{ab} \right] \delta(r - r_a(t)). \quad (2.30)$$

Eq. (2.28) is of course the microscopic analog of the conservation law (2.1b) and the connection between these two expressions follows by averaging the former over an arbitrary time independent ensemble. In both cases, apart from expressing the conserved nature of momentum density, these equations are void of physical meaning.

What we really need is the microscopic analog of the Navier–Stokes equation (2.8b) and this can only be obtained at the price of much stronger assumptions, which we now discuss.

Zwanzig and Mori [27, 28] have provided us with a particularly convenient formalism to do this. To simplify, we shall discuss this formalism here for a hypothetical system with only one conserved quantity, denoted $a(r, t)$.* The generalization of the forthcoming results to a realistic fluid, with its five conserved operators, requires no more than the use of a suitable matrix notation.

Following (2.10), we denote by $\hat{a}_q(t)$ the Fourier transform of $\hat{a}(r, t)$. The conserved nature of $\hat{a}_q(t)$ tells us, that in analogy with (2.28):

$$\partial_t \hat{a}_q(t) = i L_N \hat{a}_q(t) \equiv i q \cdot \hat{j}_q(t); \quad (2.31)$$

the explicit form of the current \hat{j}_q will not be specified.

We then define an operator in phase space denoted by \hat{P}_q :

$$\hat{P}_q \dots = \hat{a}_q \langle \hat{a}_{-q} \dots \rangle / \langle \hat{a}_{-q} \hat{a}_q \rangle \quad (2.32)$$

where the bracket $\langle \dots \rangle$ has been defined in (1.8). Thus, for any phase function \dots , \hat{P}_q transforms it into a function proportional to $\hat{a}_q \equiv \hat{a}_q(0)$. One readily verifies that \hat{P}_q is a *projection operator*:

$$\hat{P}_q^2 \dots = \hat{P}_q \dots \quad (2.33)$$

which projects any function on the subspace of the dynamical variable \hat{a}_q . In particular

$$\hat{P}_q \hat{a}_q = \hat{a}_q. \quad (2.34)$$

We now use the identity:

$$i L_N \hat{a}_q(t) = i q \cdot \exp(i L_N t) \hat{j}_q \quad (2.35)$$

with $\hat{j}_q = \hat{j}_q(0)$, as well as:

$$\hat{U}_q(t) \equiv \exp\{i(1 - \hat{P}_q)L_N t\} = \exp(i L_N t) - i \int_0^t \exp(i L_N(t - \tau)) \hat{P}_q L_N \hat{U}_q(\tau) d\tau \quad (2.36)$$

which is readily verified by differentiation.

Inserting (2.36) into (2.35), we get after a little algebra:

$$\partial_t \hat{a}_q(t) - i \omega_q \hat{a}_q(t) = - \int_0^t \Phi_q(t - t') \hat{a}_q(t') dt' + \hat{F}_q(t) \quad (2.37)$$

*If the reader wants to make the following analysis more concrete, he can think of $\hat{a}(r, t)$ as being the magnetization in an isotropic spin system, or the transverse velocity field in an incompressible fluid.

where the frequency ω_q is defined by:

$$\omega_q = -q \cdot \langle \hat{a}_{-q} \hat{j}_q \rangle / \langle \hat{a}_{-q} \hat{a}_q \rangle \quad (2.38)$$

and describes the non-dissipative part of the transport of a_q .

With only one conserved variable, we have identically, as a consequence of the equations of motion (and possibly of the symmetries of the system):

$$\omega_{q=0} = 0 \quad (2.39)$$

although this is not true in general. For simplicity, we shall however always assume (2.39) in the following. Moreover, the dynamical variable $\hat{F}_q(t)$ is given by:

$$\hat{F}_q(t) = \hat{U}_q(t)(1 - \hat{P}_q)(-iq \cdot \hat{j}_q). \quad (2.40)$$

Finally, the so-called memory function $\Phi_q(t)$ is given by:

$$\Phi_q(t) = \langle \hat{F}_{-q}(0) \hat{F}_q(t) \rangle / \langle \hat{a}_{-q} \hat{a}_q \rangle. \quad (2.41)$$

Although (2.37) is an exact consequence of the Liouville equation much as (2.31) is, it is nevertheless very useful because it is written in a way that suggests approximations. Indeed, we remark that the structure of this equation is very similar to the Langevin equation (1.6); for this reason (2.37) is often called the ‘‘generalized Langevin equation’’. In particular, $\hat{F}_q(t)$ is analogous to the random force of Brownian motion theory and one can easily check that it satisfies the familiar requirements*:

$$\langle \hat{F}_q(t) \rangle = 0 \quad (2.42)$$

$$\langle \hat{F}_{-q}(t) \hat{a}_q(0) \rangle = 0. \quad (2.43)$$

Moreover (2.41) is the fluctuation dissipation theorem [38, 41].

This analogy becomes even closer if we make an approximation on (2.37) whose eventual validity will be crucial to the usefulness of this theory: let us remark that $\hat{F}_q(t)$ is defined in a space which is orthogonal to \hat{a}_q (because $(1 - \hat{P}_q)\hat{a}_q = 0$); similarly the memory function $\Phi_q(\tau)$ is also defined by an average over quantities orthogonal to \hat{a}_q . Thus if we assume that for small q , \hat{a}_q is the only slowly varying operator of our problem, we expect that $\Phi_q(t)$ will be very rapidly decaying, at least in the thermodynamic limit, on the time scale characterizing the decay of $\hat{a}_q(t)$. With this assumption, eq. (2.37) exactly reduces to the Langevin equation:

$$\partial_t \hat{a}_q(t) = -\Phi_q \hat{a}_q(t) + \hat{F}_q(t) \quad (2.44)$$

with

$$\Phi_q \equiv \int_0^\infty \Phi_q(\tau) d\tau \quad (2.45)$$

*Notice that (2.43) is not a trivial consequence of (2.42) because the two ‘‘random’’ variables $\hat{F}_q(t)$ and $\hat{a}_q(0)$ are defined in the same sample space, i.e. in phase space.

and

$$\langle \hat{F}_{-q}(0) \hat{F}_q(t) \rangle = 2\Phi_q \langle \hat{a}_{-q} \hat{a}_q \rangle \delta(\tau). \quad (2.46)$$

What is the relevance of this result to transport theory? As we already pointed out the macroscopic variable $a_q(t)$ is defined by:

$$a_q(t) = \int dr^N dp^N \hat{a}_q(t) \rho_N(r^N, p^N) \quad (2.47)$$

where $\rho_N(r^N, p^N)$ is the initial non equilibrium N -particle distribution function in the system and, for small initial deviations from equilibrium, we expect that in the long term we will have a hydrodynamic behavior:

$$a_q(t) \underset{\substack{q \rightarrow 0 \\ q^2 t \text{ finite}}}{=} \exp(-q^2 t \mu) a_q(0) \quad (2.48)$$

where μ is the transport coefficient associated to the diffusion process for a_q . Yet for arbitrary initial conditions, eq. (2.37) is not very useful because:

$$F_q(t) = \int dr^N dp^N \hat{F}_q(t) \rho_N(r^N, p^N) \quad (2.49)$$

is non zero, and presumably a very complicated function of time. Nevertheless we may hope that after a long time the role of the initial preparation of the system will be completely forgotten (see discussion leading to (2.44)) and we are thus free of choosing the most convenient initial state; then we take ρ_N as describing a *small local equilibrium deviation* from absolute equilibrium

$$\rho_N = \rho_N^{\text{eq}} + \hat{a}_{-q} b_q \rho_N^{\text{eq}} \quad (2.50)$$

where ρ_N^{eq} denotes the canonical equilibrium distribution and b_q is the parameter conjugate to \hat{a}_q , which we do not need to specify here. Then (2.47) becomes

$$a_q(t) = \langle \hat{a}_q(t) \hat{a}_{-q}(0) \rangle b_q \quad (2.51)$$

and we get immediately from (2.37) the following kinetic equation for the correlation function $\langle \hat{a}_q(t) \hat{a}_{-q}(0) \rangle$:

$$\partial_t \langle \hat{a}_q(t) \hat{a}_{-q}(0) \rangle = - \int_0^t \Phi_q(t-t') \langle \hat{a}_q(t') \hat{a}_{-q}(0) \rangle dt'. \quad (2.52)$$

It is now easy to see how (2.52) may lead to (2.48) with an explicit definition of μ ; indeed taking the Laplace transform of (2.52) (see the notations defined in (2.9)), we have:

$$\langle \hat{a}_{q,\omega} \hat{a}_q(0) \rangle = \frac{\langle \hat{a}_q \hat{a}_{-q} \rangle}{i\omega + \Phi_{q,\omega}}. \quad (2.53)$$

Because the random force (2.40) is proportional to q , we can write:

$$\Phi_{q,\omega} = q^2 \mu_{q,\omega}. \quad (2.54)$$

with:

$$\mu_{q,\omega} = \int_0^{\infty} e^{-i\omega t} dt \langle \hat{j}_{-q}(1-\hat{P}_{-q})\hat{U}_q(t)(1-\hat{P}_q)\hat{j}_q \rangle / \langle \hat{a}_q \hat{a}_{-q} \rangle \quad (2.55)$$

and this tells us immediately that, for small q , the singularities of (2.53) closest to the real axis are only at a distance of order q^2 from this axis. Because we have assumed that $\Phi_q(t)$ was rapidly decaying in time, we have

$$\mu_{q,\omega} \sim q^2 = \mu_{q,0} (1 + O(q^2)) \quad (2.56)$$

and this leads us indeed to the exponential decay (2.48) with the following definition of μ :

$$\mu \equiv \lim_{\substack{q \rightarrow 0 \\ \omega \rightarrow 0}} \mu_{q,\omega} \quad (2.57)$$

provided that this limit exists. Now, from our assumption (2.39), we have

$$\lim_{q \rightarrow 0} (1-\hat{P}_q)\hat{j}_q = \hat{j}_0 \quad (2.58)$$

and the conserved nature of \hat{a}_q implies that:

$$\lim_{q \rightarrow 0} (1-\hat{P}_q)L_N \equiv L_N. \quad (2.59)$$

Defining now the static susceptibility

$$\chi_q = \langle \hat{a}_q \hat{a}_{-q} \rangle \quad (2.60)$$

(which must not be confused with the isothermal compressibility χ_T) we can cast eqs. (2.55, 57) into the following form:

$$\mu = \int_0^{\infty} d\tau \frac{\langle \hat{j}_0 \exp(iL_N \tau) \hat{j}_0 \rangle}{\chi_0}. \quad (2.61)$$

This is precisely the Green-Kubo formula (1.11) for our hypothetical model.

Yet our main objective is not so much to rederive the Green-Kubo expressions, but rather to find the flaws which might occur in their derivation. One such difficulty now clearly appears: we have assumed that \hat{a}_q was the only slowly varying quantity in our system: this is wrong because, for small enough wavenumber, products of a like $\hat{a}_q \hat{a}_{q-q'}$, $\hat{a}_{q'} \hat{a}_{q'-q''}$, $\hat{a}_q \hat{a}_{q'-q''}$... are also slowly varying. Yet the part of these operators orthogonal to \hat{a}_q have nevertheless been included in the "rapidly" varying $\Phi_q(t)$ and $\hat{F}_q(t)$! Let us stress that this remark does not contradict the validity of the exact equations (2.37) and (2.52); still, it now appears as plausible that the Markoffian approximations made in deriving (2.44) and (2.61) are unjustified. Notice moreover that this statement may be too strong because the weight of the contributions of these products of \hat{a}_q to $\hat{F}(t)$ and $\Phi_q(t)$ may very well be negligible. As we shall see later, this latter possibility is partly supported for transport coefficients in three dimensional fluids far from the critical point where, for

example, the Green–Kubo formulas (2.61) indeed define well behaved transport coefficients. Nevertheless, the point made here indicates that we have to be extremely careful in dealing with these non-linear effects.

One of the beauties of the Zwanzig–Mori formalism is that it can easily be adapted to take care at least formally of the present difficulty. The basic idea [15, 46] is to derive a generalized Langevin equation but now with the help of a projector which also eliminates products of modes a_q . In order to do this, we define a vector of infinite dimensions, \hat{A}_q , whose component $A^i_{\{q_i\}}$ is given by the product:

$$\hat{a}_{q-\sum_i q_i} \prod_i \hat{a}_{q_i} \quad (2.62)$$

minus some linear combination of products of $(j-1)$, $(j-2)$... operators \hat{a}_q . This linear combination is uniquely defined by the condition $\langle \hat{A}^j_q \hat{A}^{j'-q} \rangle = 0$ if $j \neq j'$; moreover the wave-numbers q_i are all taken smaller than a cut-off value q_0 . The motivation for this cut-off is that for $|q'_i| > q_0$, we expect the various products (2.62) to be rapidly decaying and of little interest; nevertheless, the introduction of this cut-off is rather artificial, as we shall discuss later on. For example, the two first components of A are:

$$\hat{A}^1_q = \hat{a}_q \quad (2.63a)$$

$$\hat{A}^2_{q+q',-q'} = \hat{a}_{q+q'} \hat{a}_{-q'} - \hat{a}_q \langle \hat{a}_{q-q'} \hat{a}_{q'} \hat{a}_{-q} \rangle / \langle \hat{a}_q \hat{a}_{-q} \rangle \quad (2.63b)$$

(q' arbitrary but smaller than q_0).

We have then indeed

$$\langle \hat{A}^2_{-q+q',-q'} \hat{A}^1_q \rangle = 0. \quad (2.64)$$

Correspondingly, we define also the operator $\hat{A}_q(t) \equiv \exp(iL_N t) \hat{A}_q$.

We now introduce a projection operator $\hat{\mathcal{P}}_q$ by an extension of (2.32):

$$\hat{\mathcal{P}}_q \dots = \hat{A}_q \cdot (\hat{A}_{-q} \hat{A}_q)^{-1} \cdot (\hat{A}_{-q}, \dots). \quad (2.65)$$

With the help of (2.33), we can now write the analog of (2.37):

$$\partial_t \hat{A}_q(t) - i\Omega_q \cdot \hat{A}_q(t) = - \int_0^t \psi_q(t-t') \cdot \hat{A}_q(t') dt' + \hat{\mathcal{F}}_q(t). \quad (2.66)$$

We shall not display here the explicit form of $\hat{\mathcal{F}}_q(t)$ and of the matrices Ω_q and ψ_q ; they extend in an obvious manner (2.38, 40, 41).

A further formal simplification is reached when one realizes that (2.66) is redundant*. For instance, we have from (2.63b):

$$\begin{aligned} \partial_t \hat{A}_q^2(t) &= \partial_t \exp(iL_N t) [\hat{a}_{q-q'} \hat{a}_{q'} - \dots] \\ &= \partial_t [\hat{a}_{q-q'}(t) \hat{a}_{q'}(t) - \dots] \\ &= [\partial_t \hat{a}_{q-q'}(t)] \hat{a}_{q'}(t) + \hat{a}_{q-q'}(t) [\partial_t \hat{a}_{q'}(t)] - \dots \end{aligned} \quad (2.67)$$

*Nevertheless, it is sometimes convenient to consider this whole set of equations [22].

Hence, provided we are ready to face non-linear equations, we may as well consider only the first component (i.e., $\partial_t \hat{a}_q(t)$) of the vector equation (2.67). If we limit ourselves to bilinear terms in \hat{a}_q , which hopefully will already describe the relevant physical properties, we get

$$\begin{aligned} \partial_t \hat{a}_q(t) - i \sum_{q' < q_0} \Omega_q^{q; q', q-q'} \cdot \hat{A}_{q+q', -q'}^{(2)}(t) = \\ = - \int_0^t \psi_q^{q; q}(t') \hat{a}_q(t-t') dt' - \sum_{q' < q_0} \int_0^t \psi_q^{q; q', q-q'} \hat{A}_{q+q', -q'}^2(t-t') dt' + \hat{\mathcal{F}}_q^q(t) \end{aligned} \quad (2.68)$$

together with the definition (2.63b). Here, we have used an obvious superscript notation to characterize given elements of the matrices Ω_q and ψ_q and of the vector $\hat{\mathcal{F}}_q$. For example, we have

$$\Omega_q^{q; q', q-q'} = \frac{1}{2} \langle \hat{a}_q L_N \hat{A}_{q+q', -q'}^2 \rangle / \langle \hat{A}_{-q-q', q'}^2 \hat{A}_{q+q', -q'}^2 \rangle \quad (2.69)$$

(the factor $\frac{1}{2}$ is to avoid overcounting); usually this quantity can be *approximately* evaluated in terms of simple equilibrium properties of the system, like the susceptibility (2.60) etc. ...

Except for its limitation to two mode couplings, eq. (2.68) is still an exact identity, just as hopeless to solve as the starting equation (2.31); in particular, the complicated structure of the projector $\hat{\mathcal{P}}_q$ makes it almost impossible to get even an approximate form for the quantities ψ_q and $\hat{\mathcal{F}}_q$. Yet, we may adopt a more phenomenological attitude and repeat the argument which first led us to (2.44): now that hopefully all slowly varying quantities have been eliminated, we assume again that $\psi_q(t)$ and $\hat{\mathcal{F}}_q(t)$ are rapidly varying. Moreover, we use a set of assumptions which are probably less crucial but which are nevertheless required to bring the theory into a manageable form:

i) The dissipative part, $\psi_q^{q; q', q-q'}$, of the non-linear coupling is neglected, with little more justification than that of simplicity.

ii) One treats situations where:

$$\langle \hat{a}_{-q} \hat{a}_{q+q'} \hat{a}_{-q'} \rangle = 0 \quad (2.70)$$

which is generally valid in the absence of a non-vanishing order parameter.

iii) Although the quantity:

$$\psi_q^{q, q} = \int_0^\infty dt \psi_q^{q, q}(t) \quad (2.71)$$

is in principle well defined in dynamical terms, one cannot evaluate it explicitly. However using (2.35) (for $t = 0$), one easily verifies that $\psi_q^{q, q} \propto q^2$; one writes then:

$$\psi_q^{q, q} \equiv q^2 \mu_0 \quad (2.72)$$

and μ_0 is taken as a phenomenological parameter, often called “bare transport coefficient”.

We arrive then at the following non-linear Langevin equation:

$$\partial_t \hat{a}_q(t) - i \sum_{q' < q_0} \Omega_q^{q; q', q-q'} \hat{a}_{q-q'}(t) \hat{a}_{q'}(t) = -q^2 \mu_0 \hat{a}_q(t) + \hat{\mathcal{F}}_q^q(t). \quad (2.73)$$

As it stands there, this equation is not yet of any direct use, because the force $\hat{\mathcal{F}}_q^q(t)$ is not specified, except by a useless formal definition analog to (2.40). Moreover the “random variables” \hat{a}_q and $\hat{\mathcal{F}}_q^q$ are still defined with phase space as sample space. To overcome these difficulties, more phenomenological assumptions are needed:

i) One approximates the probability distribution for the initial value $\hat{a}_q(0) \equiv \hat{a}_q$ by a Gaussian (see (2.23), (2.24))

$$P_N(\hat{a}_q) \propto \exp(-\hat{a}_q \hat{a}_{-q} / 2\langle \hat{a}_q \hat{a}_{-q} \rangle). \quad (2.74)$$

ii) One assumes that the random force $\hat{\mathcal{F}}_q^q(t)$ is a stationary Gaussian random process, independent of $\hat{a}_q(0)$, and with second moment characterized by the fluctuation dissipation theorem:

$$\langle \hat{\mathcal{F}}_{-q}^{-q}(t) \hat{\mathcal{F}}_q^q(t) \rangle = 2q^2 \mu_0 \delta(t). \quad (2.75)$$

Although the coherent nature of this latter assumption is supported by the fact that it maintains the stationary nature of the correlation function $\langle \hat{a}_{-q}(t + \tau) \hat{a}_q(\tau) \rangle$, we know of no deep justification for its use. Once again simplicity is the guiding principle*.

Eqs. (2.73–75) completely define the stochastic process $\hat{a}_q(t)$, although the task of explicitly solving the non-linear Langevin equation is not an easy one. Yet, in principle, we can calculate from it the correlation function $\langle \hat{a}_{-q}(t) \hat{a}_q(0) \rangle$ and we can then investigate the “true” wave number and frequency dependent transport coefficient $\mu_{q,\omega}$, which is now *defined* with the help of (2.53, 64). This method will be illustrated in later sections but, presently, let us limit ourselves to a few general remarks:

i) As is well known [47], when we have a Langevin equation for a stochastic process, we can equivalently write down a Fokker–Planck equation for the time dependent probability distribution; this has indeed been developed, in particular in the elegant paper of Zwanzig [19]. To save space, we shall however not discuss this viewpoint here.

ii) A comment is in place about the cut-off dependence of the Langevin equation (2.73): of course, from the way this cut-off has been introduced, it is clear that the solution $\hat{a}_q(t)$ of the exact equation (2.68) is independent of q_0 for all times: this is simply because there is no such parameter at the starting point, eq. (2.31). Yet this exact equation had to be mutilated in order to bring it into the manageable form (2.73) and, in this procedure, the cut-off independence of the theory has been lost. The best one can do is either not to bother about the cut-off dependence of the final results (because one is only interested in model calculation) or to force a cut-off dependence on μ_0 (notice that the exact $\psi_q^{q,q}$ is cut-off dependent) in such a way that the true zero frequency transport coefficient $\mu_{0,0}$ (provided it exists!) is cut-off independent; but even if this point of view is adopted, one cannot force the solution $\hat{a}_q(t)$ to be q_0 independent for all times; a third attitude would be to take $q_0 = \infty$ but then, for large q , one cannot take μ_0 to be ω and q -independent, which introduces extra complications in the theory. These remarks clearly show that the definition of μ_0 is rather arbitrary and that one cannot give a deep physical meaning to this “bare” transport coefficient: it has no unique purely mechanical definition as we have found one (eq. (2.61)) for the transport coefficient. Of course we see formally on eq. (2.73) that μ_0

*Of course an exact result, analogous to (2.37) holds here, namely: $\langle \hat{\mathcal{F}}_{-q}^{-q}(t) \hat{\mathcal{F}}_q^q(t) \rangle = \psi_q^{q,q}(t)$ and, in the Markoffian limit, this reduces to (2.75). However we have no reason to expect that the exact force $\hat{\mathcal{F}}_q^q(t)$ is a Gaussian process and thus the correlation function of $\hat{\mathcal{F}}_q^q(t)$ only gives us a very limited information.

is the transport coefficient which would be measured in a fictitious fluid where all fluctuations would vanish. While this definition is perfectly meaningful in the frame of a stochastic theory, it does not help us in giving any microscopic meaning to it: from this point of view, the analogy of this bare transport coefficient with the bare charge in quantum electrodynamics – where this latter can at least be formally defined in terms of a well defined Lagrangian – remains very vague. Kinetic theory suggests [31–34] that this bare transport coefficient can be conceived as describing the short range and short time phenomena; yet, no precise identification has been made until now.

2.3. *The kinetic approach*

Though we shall see later that the methods developed in the two preceding subsections are very powerful to deal with the asymptotic behavior of the Green–Kubo integrands – and with a variety of connected problems – their common feature is that they avoid to attack directly the detailed microscopic dynamics; this is achieved at the price of reasonable but not completely justified assumptions.

To get a deeper understanding of these assumptions, one needs the detailed many-body analysis which is provided by kinetic theory. Unfortunately, such an analysis becomes rapidly technically very involved and, not to burden the reader with very awkward mathematics, we shall remain rather sketchy: we shall try to pick up the relevant ideas of this kinetic theory approach and to illustrate them on rather simple examples. We refer the reader to the original literature for the details.

A first point we want to illustrate is how the evaluation of the Green–Kubo integrands can be reduced to a typical problem of kinetic theory. In this aim, let us consider again the example of the velocity autocorrelation function

$$D(t) = \langle v_{1x}(t) v_{1x}(0) \rangle. \quad (2.76)$$

Using the definitions (1.8) and (1.12), we may write this explicitly as:

$$D(t) = \lim_{\Omega} \int d\mathbf{r}^N d\mathbf{p}^N v_{1x} \exp[-iL_N t] v_{1x} \rho_N^{\text{eq}}. \quad (2.77)$$

Noticing that v_{1x} only occurs on the left of the operator of motion, we may rewrite (2.77) as:

$$D(t) = \int d^3 p_1 v_{1x} \delta\varphi_1(p_1; t) \quad (2.78)$$

with the following definitions:

$$\delta\varphi_1(p_1; t) = \lim_{\Omega} \int d\mathbf{p}^{N-1} d\mathbf{r}^N \delta\rho_N(\mathbf{r}^N, \mathbf{p}^N; t) \quad (2.79)$$

$$\delta\rho_N(\mathbf{r}^N, \mathbf{p}^N; t) = \exp[-iL_N t] \delta\rho_N(\mathbf{r}^N, \mathbf{p}^N; 0) \quad (2.80)$$

$$\delta\rho_N(\mathbf{r}^N, \mathbf{p}^N; 0) = v_{1x} \rho_N^{\text{eq}}. \quad (2.81)$$

We now remark that $\delta\rho_N(\mathbf{r}^N, \mathbf{p}^N; t)$ satisfies the Liouville equation:

$$i\partial_t \delta\rho_N = L_N \delta\rho_N \quad (2.82)$$

and, except that it has phase space integral which is zero, it can be interpreted as a time dependent N -particle distribution function. Then $\delta\varphi_1(p_1; t)$ analogously represents a non equilibrium one particle velocity distribution function. Obtaining a closed equation for this reduced d.f. from the exact solution of the Liouville equation is precisely the central problem of kinetic theory and there exists a variety of methods to solve this question (see, for example [49–53]).

Moreover, the simplicity of the initial conditions (2.81) makes the velocity correlation function a particularly simple example to treat, for which an extensive literature exists (see for example [54–56]). A suitable formalism is provided by Zwanzig's projection operator method. Define the operator \hat{P}_N :

$$\hat{P}_N \dots = \frac{\rho_N^{\text{eq}}}{\varphi^{\text{eq}}(p_1)} \int dr^N dp^{N-1} \dots \quad (2.83)$$

where $\varphi^{\text{eq}}(p_1)$ denotes the Maxwellian:

$$\varphi^{\text{eq}}(p_1) = \frac{1}{(2\pi mk_B T)^{3/2}} \exp(-p_1^2/2mk_B T). \quad (2.84)$$

It is easily established that this operator is a projector ($\hat{P}_N^2 = \hat{P}_N$), moreover, we see that:

$$\delta\varphi_1(p_1; t) = \lim_{\Omega} \frac{\varphi^{\text{eq}}(p_1)}{\rho_N^{\text{eq}}} \hat{P}_N \delta\rho_N(r^N, p^N; t). \quad (2.85)$$

It is then a matter of straightforward calculation to prove from (2.79–85) that $\delta\varphi_1(p_1; t)$ obeys the following non-Markoffian linear kinetic equation:

$$\partial_t \delta\varphi_1(p_1; t) = \int_0^t d\tau \tilde{G}_0(p_1; \tau) \delta\varphi_1(p_1; t-\tau) \quad (2.86)$$

where the one-body collision operator is defined by

$$\tilde{G}_0(p_1; \tau) = - \lim_{\Omega} \int dr^N dp^{N-1} [L_N \exp\{-i(1 - \hat{P}_N)L_N\tau\} (1 - \hat{P}_N)L_N \rho_N^{\text{eq}}/\varphi^{\text{eq}}(p_1)]. \quad (2.87)$$

This equation has to be supplemented by the initial condition:

$$\delta\varphi_1(p_1; 0) = v_{1x} \varphi_1^{\text{eq}}(p_1). \quad (2.88)$$

We defer a proof of eq. (2.87) to Appendix A and we rather limit ourselves here to a few general remarks:

i) It is obvious from the definition (2.83) that the projection operator \hat{P}_N is a very complicated object and, for this reason, no mathematically rigorous properties of $G_0(p_1; \tau)$ are known. In particular there is no general proof that the thermodynamic limit involved in (2.87) exists.

ii) Because of this complication, one is always led to some kind of perturbative analysis of (2.87) when explicit results are needed. We shall illustrate this point for the low density case in Appendix B and also in section 3. It is comforting that these perturbation calculations always indicate that, term by term at least, $\tilde{G}_0(p_1, \tau)$ is well defined in this thermodynamic limit.

iii) A third point which is worth mentioning is the linear character of the kinetic equation (2.86). This result is a rigorous consequence of the particular nature of the initial condition (2.81)*; as is clear from the calculation of Appendix A, it is completely independent of any molecular chaos assumption, which is not invoked at any stage. This point is often misunderstood in the literature.

iv) As a last remark, let us stress the big difference between the projector \hat{P}_q , eq. (2.32) and the present operator \hat{P}_N , eq. (2.83). In the former case, we have projected over the conserved variable \hat{a}_q , which depends on the whole set of dynamical variables $r_1 \dots r_N, p_1 \dots p_N$ and, consequently, we have lost track of the detailed motion of the particles in the system. Here, on the contrary, we study the velocity distribution of the tagged particle 1 which was put out of equilibrium at $t = 0$, keeping thus a detailed information on the dynamics of this particle; of course, by the same token, we have lost the dynamical information on the other particles: this dynamics is implicitly kept in $\tilde{G}_0(p_1; \tau)$.

Let us now see what the consequences of eq. (2.86) are for the velocity autocorrelation function. To this end, we define the Laplace transforms

$$\tilde{C}_0(p_1, z) = \int_0^{\infty} dt \exp[izt] \tilde{G}_0(p_1; t) \quad (2.89)$$

$$D_z = \int_0^{\infty} dt \exp[izt] D(t). \quad (2.90)$$

Straightforward algebra leads then to:

$$D_z = \int d^3p_1 v_{1x} \frac{1}{-iz - \tilde{C}_0(p_1; z)} v_{1x} \varphi^{\text{eq}}(p_1). \quad (2.91)$$

This important formula shows that the frequency behavior of D_z can be traced back in the frequency dependence of the collision operator $\tilde{C}_0(p_1; z)$. From the inverse Laplace transform:

$$D(t) = -\frac{1}{2\pi} \oint \exp(-izt) D_z dz \quad (2.92)$$

classical theorems of analysis [57] tell us that the long time behavior of $D(t)$ will be governed by $\tilde{C}_0(p_1, z)$ for small z : this is how the asymptotic behavior of Green–Kubo integrands is related to the collision operator, which is the central object of kinetic theory.

In order to prepare the analysis of section 3, we still need to introduce some more concepts of kinetic theory. Yet, in order to remain as simple as possible, we shall illustrate these ideas for the dilute gas, indicating only very schematically how they can be generalized. This attitude is largely justified by the key role of the Boltzmann equation in our understanding of the dynamics of many particle systems, even for problems which require to go much beyond this low density limit.

*This essential feature remains preserved even if the initial condition is of the form: $\delta \rho_N(r^N, p^N, 0) = [\sum_{i=1}^N a_1(r_i, p_i) + \sum_{i>j}^N a_2(r_i, r_j; p_i, p_j)] \rho_N^{\text{eq}}$ as is the case for the other Green–Kubo integrands (for the viscosity for example). The important point is that the deviations from equilibrium can be represented as a *sum* of n -body (n finite!) terms, multiplied by ρ_N^{eq} .

To make the link with our previous discussion, let us mention that one can indeed show (see [54–56]) that, at low density, the non-Markoffian equation (2.86) reduces to the Markoffian equation:

$$\partial_t \delta\varphi_1(p_1; t) = n \tilde{C}(p_1) \delta\varphi_1(p_1; t) \quad (2.93)$$

where \tilde{C} is the linearized Boltzmann–Lorentz collision operator, appropriate to describe self-motion:

$$\tilde{C}(p_1) \delta\varphi_1(p_1, t) = \int d^3p_2 \int d\Omega |v_1 - v_2| \sigma(\Omega, |v_1 - v_2|) [\delta\varphi_1(p'_1, t) \varphi^{eq}(p'_2) - \delta\varphi_1(p_1, t) \varphi^{eq}(p_2)]. \quad (2.94)$$

Here $\sigma(\Omega, |v_1 - v_2|)$ is the two-body scattering cross section with deflection into the solid angle $d\Omega$ and p'_1, p'_2 denote the momenta after the collision process. Moreover, one shows that this operator \tilde{C} is related in the following way to the *formal* density expansion of $\tilde{C}_0(p_1; z)$ (see also Appendix B):

$$\tilde{C}_0(p_1, 0) = n \tilde{C}(p_1) + O(n^2). \quad (2.95)$$

An important property of the operator $\tilde{C}(p_1)$ is its semi-negative character. More precisely, let us use an abstract vector space notation in which any function $f(p_1)$ is considered as the momentum space representation of the vector $|f\rangle$:

$$f(p_1) \equiv \langle p_1 | f \rangle. \quad (2.96)$$

In this abstract space, we define the scalar product between two functions $f(p_1)$ and $g(p_1)$ by:

$$\langle f | g \rangle = \int d^3p_1 (\varphi^{eq}(p_1))^{-1} f(p_1) g(p_1). \quad (2.97)$$

It is easy to prove from the definition that:

$$\langle f | \tilde{C} | f \rangle \leq 0 \quad (2.98)$$

and the equality sign only obtains when $f = \varphi^{eq}$. Hence if we define the eigenvalue problem:

$$\tilde{C} | \tilde{\Phi}_j^0 \rangle = \tilde{\lambda}_j^0 | \tilde{\Phi}_j^0 \rangle \quad (2.99)$$

we see that all eigenvalues will be negative, except the one, denoted $\tilde{\lambda}_1^0$ corresponding to the equilibrium eigenfunction:

$$| \tilde{\Phi}_1^0 \rangle = | \varphi^{eq} \rangle. \quad (2.100)$$

More precisely, for the so-called “hard potentials”, increasing faster than r^{-4} at short intermolecular distances, this zero eigenvalue is isolated from all the others but for “soft potentials” (slower than r^{-4}) there is a continuum of eigenvalues which go up to zero [58]. To simplify, we shall always assume in the following that we have hard potentials. Moreover, even in this case, the eigenvalue problem (2.99) has both a discrete and a continuous spectrum. However, we shall formally only consider the discrete part of this spectrum labelled by the index $j = 1, \dots$.

This property of course ensures that the diffusion coefficient $D = D_{z=0}$ is positive (see (1.5), (2.76, 91)).

Let us also point out that, long before the correlation function formalism was developed to

describe transport coefficients, the calculation of these coefficients was based on the solution of the *inhomogeneous* Boltzmann equation. For self-diffusion, one started from:

$$\partial_t f_1(\mathbf{r}_1, \mathbf{p}_1; t) + v_1 \frac{\partial f_1(\mathbf{r}_1, \mathbf{p}_1; t)}{\partial r_1} = n\tilde{C} f_1(\mathbf{r}_1, \mathbf{p}_1; t) \quad (2.101)$$

and looked for the solution in the long term for slowly varying spatial dependence of f_1 . In modern language, one considers the Fourier transform of (2.101):

$$\partial_t f_q(\mathbf{p}_1; t) + iqv_{1x} f_q(\mathbf{p}_1; t) = n\tilde{C} f_q(\mathbf{p}_1; t) \quad (2.102)$$

where:

$$f_q(\mathbf{p}_1; t) = \int d^3r_1 \exp(-iqr_{1x}) f_1(\mathbf{r}_1, \mathbf{p}_1; t) \quad (2.103)$$

(to simplify, we have oriented q along the x -axis), and, in order to solve this equation in the limit of small q and large t , one studies the associated eigenvalue problem:

$$(-iqv_x + n\tilde{C}) |\tilde{\Phi}_1^q\rangle = \tilde{\lambda}_1^q |\tilde{\Phi}_1^q\rangle. \quad (2.104)$$

Notice that the operator on the left-hand side is not Hermitian but this implies only small technical difficulties (one has also to consider left-eigenfunction of this problem) which we shall ignore.

One then remarks that, for $t \rightarrow \infty$ and $q \rightarrow 0$, the only eigenvalues of (2.104) which will contribute to the solution of (2.102) have to go to zero when $q \rightarrow 0$; all the other eigenvalues lead to asymptotically negligible contributions. We also notice that, at $q = 0$, (2.104) becomes identical to (2.99) and we conclude therefrom that there is only one eigenvalue, denoted $\tilde{\lambda}_1^q$, which has the property of going to zero with q . For small q , we may expand it:

$$\tilde{\lambda}_1^q = \tilde{\lambda}_1^0 + q\tilde{\lambda}_1^{(1)} + q^2\tilde{\lambda}_1^{(2)} \dots \quad (2.105)$$

and we write similarly:

$$|\tilde{\Phi}_1^q\rangle = |\tilde{\Phi}_1^0\rangle + q|\tilde{\Phi}_1^{(1)}\rangle + \dots$$

with $\tilde{\lambda}_1^0 = 0$, $|\tilde{\Phi}_1^0\rangle = |\varphi^{e_q}\rangle$. A straightforward perturbation calculus leads then to:

$$\lambda_1^q = -q^2 D^B + O(q^3) \quad (2.106)$$

$$D^B = \left\langle \varphi^{e_q} | v_{1x} \frac{1}{n\tilde{C}} v_{1x} | \varphi^{e_q} \right\rangle. \quad (2.107)$$

Clearly, this slowly decaying mode should be identified with the self-diffusion for the dilute gas, and, indeed, we may easily check that D^B is identical to $D_{z=0}$ in the dilute gas limit (use (1.5) and (2.76, 80, 95, 97)).

Besides providing a link between the Green–Kubo method and the traditional kinetic theory description of transport coefficients, this simple calculation also has a deep interest because it shows that, although the general solution of the linearized Boltzmann equation is very complicated, its long time behavior is governed by the familiar transport coefficients. To illustrate this point, suppose that, in some problem, we need an explicit representation of the following Green's

function:

$$\tilde{X}_q(z) = \frac{1}{iz + iqv_{1x} - n\tilde{C}(p_1)}. \quad (2.108)$$

Formally, this can be written with the help of (2.104)

$$\tilde{X}_q(z) = \sum_j |\tilde{\Phi}_j^q\rangle \frac{1}{iz - \tilde{\lambda}_j^q} \langle \tilde{\Phi}_j^q|, \quad (2.109)$$

but, generally, this formula is of no much use because we do not know the eigenvalues $\tilde{\lambda}_j^q$ and the eigenfunctions $|\tilde{\Phi}_j^q\rangle$. If, however, we only need the low wavenumber, low frequency behavior of $\tilde{X}_q(z)$, then to leading order in q , we may use (2.100) and (2.106) to get the asymptotic result:

$$\tilde{X}_q(z) \underset{q, z \rightarrow 0}{\simeq} |\varphi^{eq}\rangle \frac{1}{-iz + Dq^2} \langle \varphi^{eq}| \quad (2.110)$$

which is a very convenient formula. Expressions like (2.110) will play a crucial role in the kinetic analysis of the long time behavior of the Green-Kubo integrands.

The case of self diffusion, treated here in some detail, is particularly simple because the Boltzmann Lorentz collision operator has one simple zero eigenvalue, corresponding to particle conservation. Yet, a very similar analysis can be developed for the full linearized Boltzmann equation [59-61].

The starting point here is:

$$\partial_t \delta f_q(p_1; t) + iqv_{1x} \delta f_q(p_1; t) = C(p_1) \delta f_q(p_1; t) \quad (2.111)$$

with

$$C(p_1) \delta f(p_1) = n \int d^3 p_2 \int d\Omega |v_1 - v_2| \sigma(\Omega, |v_1 - v_2|) \\ \times [\delta f(p'_1) \varphi^{eq}(p'_2) + \delta f(p'_2) \varphi^{eq}(p'_1) - \delta f(p_1) \varphi^{eq}(p_2) - \delta f(p_2) \varphi^{eq}(p_1)]. \quad (2.112)$$

The analog of (2.92) holds here also, although the eigenvalue problem

$$C|\Phi_j\rangle = \lambda_j^0 |\Phi_j\rangle \quad (2.113)$$

now has five (instead of one) eigenvalues, denoted λ_α^0 [$\alpha \in (\alpha)$; $(\alpha) = (1, 2, 3, 4, 5)$]. Physically this degeneracy corresponds to conservation of the number of particles, of their total momentum and of their kinetic energy in a collision process. This is confirmed by the explicit form of the corresponding eigenfunctions:

$$\begin{aligned} \lambda_1^0 &= 0 & \langle p_1 | \Phi_1 \rangle &= \varphi^{eq}(p_1) \\ \lambda_{2,3,4}^0 &= 0 & \langle p_1 | \Phi_{2,3,4} \rangle &= p_{1,i} (mk_B T)^{-1/2} \varphi^{eq}(p_1), \quad i = 2, 3, 4, \equiv x, y, z \\ \lambda_5^0 &= 0 & \langle p_1 | \Phi_5 \rangle &= \sqrt{\frac{2}{3}} \left(\frac{p_1^2}{2m\kappa_B T} - \frac{3}{2} \right) \varphi^{eq}(p_1). \end{aligned} \quad (2.114)$$

Here again, the long time behavior of the solution of (2.111) will be determined by those eigenvalues λ_α^0 of the problem:

$$(-iqv_{1x} + C)|\Phi_j^q\rangle = \lambda_j^q |\Phi_j^q\rangle \quad (2.115)$$

which tend to zero when $q = 0$. From (2.114), we see that there are five such eigenvalues and, except for minor extra difficulties connected with the degeneracy of the unperturbed zero eigenvalue, the perturbation calculus sketched for the case of self-diffusion can be reproduced here. One finds

$$\lambda_{1,2}^q = \pm ic^B q - \Gamma^B q^2 + O(q^3) \quad (2.116a)$$

$$\lambda_{3,4}^q = -\nu^B q^2 + O(q^4) \quad (2.116b)$$

$$\lambda_5^q = -\kappa^B q^2 / n C_p^B + O(q^4) \quad (2.116c)$$

where the only difference with (2.12) is in the superscript B: this indicates that the dilute gas limit for the transport coefficients and for the thermodynamic quantities should be taken. The eigenfunctions can similarly be calculated and, to lowest order in q , we get the following eigenfunctions:

$$\begin{aligned} |\Phi_{1,2}^0\rangle &= \frac{1}{\sqrt{2}} [\sqrt{\frac{3}{5}} |\Phi_1\rangle \pm |\Phi_2\rangle + \sqrt{\frac{2}{5}} |\Phi_5\rangle] \\ |\Phi_{3,4}^0\rangle &= |\Phi_3, \Phi_4\rangle \\ |\Phi_5^0\rangle &= \sqrt{\frac{2}{5}} [-|\Phi_1\rangle + \sqrt{\frac{3}{2}} |\Phi_5\rangle] \end{aligned} \quad (2.117)$$

which obey:

$$\langle \Phi_\alpha^0 | \Phi_\beta^0 \rangle = \delta_{\alpha,\beta}^{Kr} \quad (\alpha, \beta \in (1, \dots, 5)). \quad (2.118)$$

Finally, we gain also the analog of (2.110):

$$X_q(z) \equiv \frac{1}{-iz + iqv_{1x} - C(p_1)} = \sum_{\alpha=1}^5 |\Phi_\alpha^0\rangle \frac{1}{-iz - \lambda_\alpha^q} \langle \Phi_\alpha^0 |. \quad (2.119)$$

$\begin{matrix} q \rightarrow 0 \\ z \rightarrow 0 \end{matrix}$

The interest of this eigenvalue method is that it can be formally extended to fluids at an arbitrary density; the idea, which we now sketch, is very simple [60–62].

We have already seen that, for spatially homogeneous systems, the Boltzmann Lorentz collision operator is the low density limit of the homogeneous frequency dependent operator $\tilde{C}_0(p_1; z)$; conversely one can show that, for an inhomogeneous system, the kinetic equation which generalizes (2.102) is of the form (compare with (2.86)):

$$\partial_t f_q(p_1; t) + iqv_{1x} f_q(p_1; t) = \int_0^t \tilde{G}_q(p_1; \tau) f_q(p_1; t-\tau) d\tau. \quad (2.120)$$

The explicit form of the q -dependent non Markoffian operator \tilde{G}_q will not be needed here (it is quite close to (2.87)). Accordingly, the study of this equation is related to the *non-linear* eigenvalue problem:

$$[-iqv_{1x} + \tilde{C}_q(p_1; i\tilde{\lambda}_j^q)] |\tilde{\Phi}_j^q\rangle = \tilde{\lambda}_j^q |\tilde{\Phi}_j^q\rangle \quad (2.121)$$

where \tilde{C}_q extends to non vanishing q the operator \tilde{C}_0 defined by (2.89).

Although very little is known of this sort of problem in general [63], decisive progress can be achieved by looking at the zero wavenumber problem:

$$\tilde{C}_0(p_1; i\tilde{\lambda}_j^0) |\tilde{\Phi}_j\rangle = \tilde{\lambda}_j^0 |\tilde{\Phi}_j\rangle. \quad (2.122)$$

Despite the fact that it does not exist any closed form for $\tilde{C}_0(p_1, z)$, one can show that, exactly as in the dilute gas, the eigenvalue problem (2.122) for a tagged particle possesses one zero eigenvalue (for the same physical reason) and the same eigenfunction (2.100). Hence, the problem (2.121) should again have one eigenvalue $\tilde{\lambda}_1^q$ which tends to zero when $q \rightarrow 0$ and this should be calculable by expanding the operator \tilde{C}_q like:

$$\tilde{C}_q(p_1; z) = \tilde{C}_0(p_1; 0) + q \frac{\partial \tilde{C}_0}{\partial q}(p_1; 0) + z \tilde{C}_0(p_1; 0) + \frac{1}{2} q^2 \frac{\partial^2 \tilde{C}_0}{\partial q^2}(p_1; 0) + qz \frac{\partial \tilde{C}_0}{\partial q}(p_1; 0) + \frac{1}{2} z^2 \tilde{C}_0(p_1; 0) + \dots, \quad (2.123)$$

where the dots denote derivatives with respect to z . Let us stress that we *assume* here that such an expansion has a meaning; this is not obvious in view of the expected non analyticities of the collision operator; yet we shall not justify this procedure here.

One finds then that the eigenvalue $\tilde{\lambda}_1^q$ is precisely given by the diffusive mode $-Dq^2$, where D is the proper diffusion coefficient for the dense fluid.

Similar conclusions are reached when one considers the case where the whole fluid is put slightly out of equilibrium, instead of one single tagged particle. We now find five hydrodynamical modes λ_α^q which are precisely given by (2.12) where the transport coefficients and the thermodynamic coefficients have their value for a dense fluid. The corresponding eigenfunction $|\Phi_\alpha^q\rangle$ can also be calculated: they are still given, to zeroth order in q , by linear combinations of the states $|\Phi_\alpha\rangle$:

$$|\Phi_\alpha^q\rangle = \sum_{\alpha'=1}^5 C_{\alpha\alpha'} |\Phi_{\alpha'}\rangle + \mathcal{O}(q), \quad (\alpha \in (\alpha)) \quad (2.124)$$

although the coefficients $C_{\alpha\alpha'}$ are complicated functions of the thermodynamic properties of the system, instead of simple numbers as in (2.117).

In this way, we have found a complete microscopic analog to the hydrodynamical modes introduced first at the level of macroscopic physics; this analogy is one of the key steps toward the microscopic analysis of the asymptotic behavior of the Green-Kubo integrands.

Before closing this section, let us make a few more remarks about the so-called potential contributions to the transport coefficients; indeed, the case of self-diffusion which we treated here in some detail is exceptional because the microscopic flow operator $\hat{J}^D \propto v_{1x}$ does not depend on the interactions. For the shear viscosity for example, one has:

$$\hat{j}^n = \sum_{i=1}^N \hat{j}_i^n, \quad \hat{j}_i^n = p_{ix} v_{iy} - \frac{1}{2} \sum_{j \neq i}^N \frac{\partial V}{\partial r_{ij,y}} r_{ij,x} \quad (2.125)$$

and, besides the purely kinetic term $p_{ix} v_{iy}$ – which is very similar to v_{1x} and can be treated by similar methods – we also find two-particle terms which complicate a bit the kinetic description of the Green-Kubo integrands: in particular, an equation for $\delta\varphi(p_1; t)$ (see (2.86)) does not

suffice. Yet the analysis presented above can be generalized (see for example [64]) to this case and, although new operators have to be introduced in the theory, the frequency dependent collision operator $C_0(p_1; z)$ remains the prototype of the quantities which we have to study; hence self-diffusion is indeed a good example to treat. In passing, it is also interesting to point out that if one attacks the microscopic theory of transport coefficients from the point of view of the hydrodynamic modes, the question of a separate treatment of these potential contributions does not occur: we have mentioned already that the correct transport coefficients, including their potential part, appear in the eigenmodes λ_q^a ; however, there is a price to be paid for this apparent simplicity: instead of having only the zero wave number collision operator to consider, as in the Green–Kubo method, we now need the wave number-frequency dependent operator $C_q(p_1; z)$ in the vicinity of $q = 0$ and $z = 0$. The respective virtues of the two methods thus depend both on one's taste and on the problem one has to tackle.

3. Mode–mode coupling illustrated

In this section, we wish to illustrate the methods presented in the previous section by discussing in some detail a particular example: the asymptotic behavior of the velocity autocorrelation function. However, before dealing with this problem in the frame of time dependent statistical mechanics, it is worthwhile to recall a purely stochastic analog as analyzed first by Lorentz [65]: the generalization of Brownian motion theory to include frequency dependent effects; as we shall presently see this generalization already introduces many ingredients present in the recent developments and is not burdened by technical difficulties.

3.1. Generalization of classical Brownian motion theory

As already mentioned, the Langevin equation (1.6) is the starting point of stochastic motion theory. It is complemented by the assumption that the stochastic force $F(\tau)$ is a Gaussian random variable with white spectrum* [2]:

$$\langle F(t) F(0) \rangle = 1 \delta(t-t') 2\xi k_B T \quad (3.1)$$

(1 is the unit tensor), *and* the hypothesis that $F(t)$ is uncorrelated to the velocity $v_1(t')$ of the B-particle at earlier times ($t' < t$). While eq. (3.1) is not required to get the second moment (1.7), this assumption is necessary for getting the more general result:

$$\begin{aligned} \langle \delta(u - v_1(t)) \delta(v - v_1(0)) \rangle &= \left(\frac{m_1}{2\pi k_B T} \right)^3 \{1 - \exp(-2\xi|t|/m_1)\}^{-3/2} \\ &\times \exp\left(-\frac{m_1}{2k_B T} \left[\frac{(u - v \exp(-\xi|t|/m_1))^2}{1 - \exp(-2\xi|t|/m_1)} + v^2 \right]\right). \end{aligned} \quad (3.2)$$

It is important to notice that the viscous force $-\xi v_1$ in the Langevin equation (1.6) is, by defini-

*In this subsection, the bracket $\langle \dots \rangle$ denotes an average over the stochastic variables, and not the canonical average (1.8); no confusion should arise from this notation.

tion, computed as if the particle velocity v_1 was a constant. Lorentz was the first to point out a difficulty with this latter assumption. Indeed, the viscous drag should be proportional to the instantaneous velocity $v_1(t)$ only if the relaxation time for this velocity, i.e. $(\xi/m_1)^{-1}$, is much larger than the characteristic time for the evolution of the viscous flow around the molecule, which is $\rho R^2/\eta$ (R = radius of the molecule). As, from Stokes law $\xi \sim R\eta$, the validity of the Langevin equation requires:

$$m_1/R^3 \gg \rho. \quad (3.3)$$

If the mass density of this particle is not much larger than the one of the surrounding fluid, one should account for the time dependence of v_1 when computing the drag. The Langevin equation (1.6) has then to be generalized into:

$$\frac{dv_1}{dt} = -\frac{1}{m_1} \int_0^t dt' \xi(t-t') v_1(t') + \frac{F(t)}{m_1}, \quad (3.4)$$

where the kernel $\xi(t-t')$ has to be determined from a solution of the linearized Navier-Stokes equation in such a way that the linear functional:

$$\int_{-\infty}^t dt' \xi(t-t') v_1(t') \quad (3.5)$$

represents the viscous force exerted at time t upon the B-particle when it has the non-stationary velocity $v_1(t')$ at earlier times.

The formal solution of (3.4) is:

$$v_1(t) = \int_{-\infty}^t dt' M(t-t') F(t'), \quad (3.6)$$

where $M(t)$ is the solution of:

$$\frac{dM}{dt} = -\frac{1}{m_1} \int_0^t dt' \xi(t-t') M(t'), \quad (3.7)$$

with:

$$M(0) = 1. \quad (3.8)$$

The condition that $v_1(t)$ has a Gaussian distribution with constant width is satisfied by choosing $F(t)$ a Gaussian random variable characterized by:

$$\langle F(t) F(t') \rangle = 1 k_B T \xi'(t-t'). \quad (3.9)$$

Yet, except for the requirement coming from $\langle v_1^2 \rangle = 3k_B T/m_1$:

$$\int_0^{\infty} dt' \int_0^{\infty} dt'' M(t') \xi'(|t'-t''|) M(t'') = 1, \quad (3.10)$$

the function $\xi'(t)$ remains quite undetermined at this stage and so is the velocity correlation function:

$$\langle v_1(0) v_1(t) \rangle = 1 \frac{k_B T}{m} \int_0^\infty \int_0^\infty dt' dt'' M(t') \xi'(|t-t'-t''|) M(t''). \quad (3.11)$$

For a definite characterization of $\xi'(t)$, we need crucially the assumption – already needed in classical B-motion theory, but not always clearly stated in the literature – that the random force $F(t)$ is uncorrelated to $v_1(t')$ at earlier times*:

$$\langle F(t) v_1(0) \rangle = 0, \quad t \geq 0. \quad (3.12)$$

Indeed, only in this case is the formal solution of (3.4):

$$v_1(t) = M(t) v_1(0) + \int_0^t dt' M(t-t') F(t') \quad (3.13)$$

the sum of two independent Gaussian variables; this feature, together with the stationarity of the random process, $d\langle v_1^2(t) \rangle / dt = 0$ yields then readily to the identification:

$$\xi'(t-t') = \xi(t-t'), \quad (3.14)$$

which is nothing else than an elementary version of the so-called “fluctuation–dissipation theorem”.

From (3.13), we also have:

$$\langle v_1(t) v_1(0) \rangle = 1 \frac{k_B T}{m_1} M(t), \quad (3.15)$$

and:

$$\langle \delta(u-v_1(t)) \delta(v-v_1(0)) \rangle = \left(\frac{m_1}{2\pi k_B T} \right)^3 (M_1(t))^{-3/2} \exp \left(-\frac{m_1}{2k_B T} \left[\left(\frac{u-v M(t)}{M_1(t)} \right)^2 + v^2 \right] \right) \quad (3.15)$$

with:

$$M_1(t) = \int_0^t dt' M(t-t') \int_0^t dt'' M(t-t'') \xi(|t'-t''|) = [1 - M^2(t)]^{1/2}. \quad (3.17)$$

Before looking at the explicit form of $\xi(t)$ and $M(t)$, let us stress that, although the detail of the velocity correlation function is of course modified by the non-local time dependence of the viscous drag, the diffusion coefficient itself only depends on the time independent drag. Indeed, we have:

*If $F(t)$ was a physical force, time reversal invariance would imply: $\langle v_1(0) F(t) \rangle = -\langle v_1(0) F(-t) \rangle$ and $\langle v_1(0) F(t) \rangle$ would thus vanish at any time. This argument does not hold for the Langevin force which is only part of the physical force: to deduce the former from the latter, one would need the instantaneous value of the viscous drag, which itself depends on the past history of the B-particle.

$$D = \frac{1}{3} \int_0^{\infty} dt \langle v_1(t) \cdot v_1(0) \rangle = \frac{k_B T}{m_1} \int_0^{\infty} dt M(t), \quad (3.18)$$

and from (3.7, 8):

$$1 = \left[\int_0^{\infty} dt M(t) \right] / \left[\int_0^{\infty} dt \xi(t) \right]. \quad (3.19)$$

Hence:

$$D = k_B T / \int_0^{\infty} \xi(t) dt \quad (3.20)$$

which would follow from the usual Langevin equation (1.6) as $\int_0^{\infty} \xi(t) dt$ is precisely the friction coefficient ξ for a stationary motion.

For the calculation of $\xi(t)$ and $M(t)$, we may use the result of Stokes' investigations on the viscous damping of the oscillations of a ball pendulum [66]; he showed that the complex drag coefficient of a sphere of radius R is:

$$\xi_{\omega} = \frac{4}{3} \pi \rho R^3 \left(\frac{1}{2} + \frac{9}{4\beta_1 R} \right) i\omega + \frac{3\omega \rho R^2}{\beta_1} \left(1 + \frac{1}{\beta_1 R} \right) \quad (3.21)$$

(we use the same notation as in (2.9)), where:

$$\beta_1 = (\omega/2\nu)^{1/2}. \quad (3.22)$$

Inverting the Laplace transform (3.21), we can in principle deduce $\xi(t)$; as pointed out by Landau and Lifshitz [37], this latter function is singular at $t = 0$ and yields a finite difference between $v_1(0)$ and $v_1(0_+)$ in the case of an impulsive motion. This unphysical result is a consequence of the assumed incompressibility of the fluid and disappears when proper account is taken of the propagation of sound waves in the medium.

Widom [67] was the first to point out the connection between the present theory and the slow decay of the velocity correlation function found by Alder and Wainwright. His argument goes as follows: near $\omega = 0$, ξ_{ω} expands like

$$\xi_{\omega} = 6\pi\eta R + \sqrt{2\nu\omega}(1+i)\rho R^2 + O(\omega). \quad (3.23)$$

Because the Fourier-Laplace transform of $M(t)$ is:

$$\frac{M_{\omega}}{i\omega + \xi_{\omega}} = \frac{1}{i\omega + \xi_{\omega}}, \quad (3.24)$$

it expands near $\omega = 0$ as:

$$M_{\omega} = \frac{1}{6\pi\eta R} \left[1 - \frac{\rho R \sqrt{2\nu\omega}}{6\pi\eta} (1+i) + O(\omega) \right], \quad (3.25)$$

and, from well-known Tauberian theorems [57], one can show that $M(t)$ decreases like $t^{-3/2}$ at infinity, owing to the term of order $\sqrt{\omega}$ in (3.25). From (3.15), one finds the explicit result:

$$\langle v_1(0) v_1(t) \rangle \underset{t \rightarrow \infty}{\simeq} 1 \frac{2k_B T}{3\rho} \frac{1}{(4\pi\nu t)^{3/2}} \quad (3.26)$$

which indeed agrees with (1.22).

Once suitably modified to account for the finite compressibility effects, the present generalized B-motion theory properly describes the velocity correlation function of a large spherical particle of arbitrary mass; without doubt, it is the simplest example of the slow asymptotic decay of the Green–Kubo integrands.

In passing, it is worthwhile to point out that the generalized B-motion equation (3.4), which is here the starting point of the theory, can itself be derived from the fluctuating hydrodynamics of Landau and Lifshitz [37], taken as the starting point to describe the (stochastic) behavior of the fluid. This fluctuating hydrodynamics is obtained by simply adding random terms to the equations of linearized hydrodynamics. For example, we add to the stress tensor (2.4) a “stochastic” Gaussian stress tensor τ_{ij} with zero average such that, in the incompressible approximation:

$$\langle \tau_{ij}(r, t) \tau_{kl}(r', t') \rangle = 2k_B T \eta \delta(t-t') \delta(r-r') [\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}]. \quad (3.27)$$

Then, of course the hydrodynamic variables themselves become random variables and if we calculate the motion of the B-particle through:

$$dv_1/dt = F_1/m_1,$$

where F_1 is the total force exerted by the fluid on the B-particle:

$$F_1 = \oint dS n \{ p 1 - \eta(\nabla \cdot v - (\nabla \cdot v)^T) \}$$

(n is the unit vector orthogonal to the surface element dS of the B-particle and $(\partial_i v_j)^T = (\partial_j v_i)$), it is obvious that this force F_1 can be split into a systematic and a fluctuating part corresponding to the similar decomposition of the fluid velocity field. This program was explicitly fulfilled by Hauge and coworkers [68, 69] and leads indeed to the generalized Langevin equation (3.4), with the proper properties of $\xi(t)$ and $F(t)$. We shall not dwell any further on this interesting viewpoint; we shall however derive in section 3.3 the $t^{-3/2}$ behavior of the velocity correlation function from fluctuating hydrodynamics, following the elegant method of Bedeaux and Mazur [21]. Recently, much work has been done along the line sketched here [70–75].

We should realize that the present B-motion theory, though very illuminating, is not general enough to tackle the various physical problems involving collective effects at a microscopic scale. Indeed, at least at two stages, the large size of the B-particle was used in a crucial manner; hence, we do not know yet anything about the motion of a particle mechanically identical to the rest of the fluid, as in Alder and Wainwright’s experiment and in many other problems of physical interest. To convince ourselves that this point is not as academic as it may appear first, let us reconsider with some detail the points of the above theory where the large size of the B-particle is important:

i) Lorentz’s argument neglects the diffusion of the Brownian particle in the velocity field created by its own motion; in particular, the calculation of the drag coefficient ξ_ω (3.21) is

purely linear. For a large particle, this assumption becomes rigorous because the diffusion coefficient for the velocity field, measured by the kinematic viscosity ν , is much larger than the self-diffusion coefficient:

$$\nu/D \sim Rm_1.$$

However, when the B-particle becomes similar to the fluid particle, this is generally no more true. Then the calculation of the complex drag coefficient ξ_ω becomes enormously more difficult because we have to jump from the linear problem of calculating the response of the fluid to a prescribed velocity $v_{1\omega}$ of the B-particle, to a problem involving the non-linear coupling between the fluid and the B-particle motion: one of the important merits of the mode–mode coupling theories is precisely to allow for the treatment of such non-linearities. Notice moreover that even if the ratio ν/D is large when the B-particle and the fluid molecules become alike (as appears – empirically – to be often the case), similar problems occur when dealing with other Green–Kubo integrands which cannot be simply disposed of by invoking such numerical accidents.

ii) The drag coefficient (3.21) has been calculated with the help of hydrodynamics (in particular, with a proper choice of the boundary condition on the B-particle) and, for small R , this procedure obviously becomes doubtful. Yet, the independence of the final asymptotic result (3.26) on the explicit value of R suggests that this difficulty can be overcome: this is a second merit of the various mode–mode coupling theories which we now discuss.

3.2. The phenomenological (or Landau–Placzek) method

A slight generalization of the Landau–Placzek method explained in section 2.1 offers a very direct procedure to analyze the asymptotic behavior of the Green–Kubo integrand for self-diffusion [11, 17, 18], as well as for the other correlation functions.

Let us however immediately stress that this method will not settle the problem because the assumption involved should be clarified from a more fundamental viewpoint.

An apparently innocuous “trick” allows the method to work: it amounts in formally replacing the spatially homogeneous function:

$$D(t) = \frac{1}{3} \langle v_1(t) \cdot v_1(0) \rangle \quad (3.28)$$

by an integral over a spatially inhomogeneous quantity:

$$D(t) = \frac{1}{3} \int d^3r \int d^3r' \langle v_1(t) \delta(r - r_1(t)) \cdot v_1(0) \delta(r' - r_1(0)) \rangle \quad (3.29)$$

which introduces the current density operator of the tagged particle $j_1(r) = v_1 \delta(r - r_1)$.

We now remark that two conserved quantities are relevant in the dynamics of the tagged particle:

i) its local density:

$$\hat{n}_1(r) = \delta(r - r_1); \quad (3.30)$$

ii) the momentum density (2.27) of the *whole* fluid: indeed, only the momentum of the total system (tagged particle + fluid) is conserved. Equivalently, we may take the local fluid velocity which, in a linear approximation, is given by:

$$\hat{v}(r) = \frac{1}{n} \sum_{i=1}^N v_i \delta(r-r_i). \quad (3.31)^*$$

In the spirit of the Landau-Placzek method, we write then the canonical average in (3.29) by performing first a partial average in which the local density of the tagged particle and the velocity field (or their Fourier transforms $\{n_{1,q}, v_q\}$) are fixed. Moreover, in order to avoid delicate but irrelevant mathematical problems, we work in a finite, albeit large, volume Ω ; we have then discrete Fourier components. In analogy with (2.18), we obtain:**

$$D(t) = \int \prod_{q < q_0} dn_{1,q} dv_q \left\{ \left(\prod_{q' < q_0} P(n_{1,q'}) P(v_{q'}) \right) \left(\int d^3r \int d^3r' \int d^N r \right. \right. \\ \left. \left. \times \int dp^N j_1^D(r) \exp(-iL_N t) j_1^D(r') \rho_N^l(\{n_{1,q}\}, \{v_q\}) \right) \right\} \quad (3.32)$$

where we have only taken wave number smaller than a small cut-off value q_0 , in order to insure that our local equilibrium state is slowly varying (over distances $R > q_0^{-1}$). Here $\rho_N^l(\{n_{1,q}\}, \{v_q\})$ is a self-evident generalization of (2.19): it describes a local equilibrium with fixed density for the tagged particle and fixed velocity field for the whole fluid. Similarly, the probability $P_N(v_q)$ is given by (2.24) while $P_{1,N}(n_{1,q})$ is defined by:

$$P_{1,N}(n_{1,q}) = \int d^N r dp^N \delta(\hat{n}_{1,q} - n_{1,q}) \frac{\exp(-\beta H_N)}{Z_N}. \quad (3.33)$$

Noticing that $\hat{n}_{1,q} = \exp(iq \cdot r_1)$ only depends on the location of particle 1, translation invariance of H_N leads to the equivalent formula:

$$P_{1,N}(n_{1,q}) = \frac{1}{\Omega} \int d^3r_1 \delta(\hat{n}_{1,q} - n_{1,q}); \quad (3.33')$$

there is no need to evaluate this latter integral.

Consider now the average current density in the local equilibrium state; we have:

$$j_1^l(r) \equiv \int d^N r dp^N j_1(r) \rho_N^l(\{n_{1,q}\}, \{v_q\}) = n_1(r) v(r), \quad (3.34)$$

where $n_1(r)$ and $v(r)$ are respectively the inverse Fourier transforms of the given $\{n_{1,q}\}$ and $\{v_q\}$. Though this property is physically obvious, its formal proof is not immediate and, to simplify, we shall merely *assume* its validity here. Thus we also have:

$$\int dr j_1^l(r) = \frac{1}{\Omega} \sum_{q_1} n_{1,q_1} v_{-q_1}. \quad (3.35)$$

*Delicate mathematical problems always occur in connection with the use of microscopic operators, which are singular functions of position. This is particularly obvious with the velocity field which is formally defined by: $\hat{n}(r) v(r) = \hat{g}(r)/m$, where $\hat{g}(r)$ is defined by (2.27) and $\hat{n}(r)$ is the total density $\sum_i \delta(r-r_i)$; of course it makes no sense to divide both sides of this equation by $\hat{n}(r)$! Yet, suppose that we average this equation over any *smooth* distribution function $\rho_N(t)$ (this average is denoted by $\langle \dots \rangle_{\rho_N}$), we get: $\langle \hat{n}(r) \hat{v}(r) \rangle_{\rho_N} = \langle \hat{g}(r) \rangle_{\rho_N}/m$. Suppose moreover that the fluctuation of the density from its average value n is small; there we may replace this latter formula by the approximation: $\langle \hat{v}(r) \rangle_{\rho_N} \simeq \langle \hat{g}(r) \rangle_{\rho_N}/nm$. Our formal definition (3.31) precisely leads to this result.

**We assume from the very beginning that the probabilities of fluctuations of the $\{n_{1,q}\}$ and $\{v_q\}$ are independent, a result which is only legitimate in the long wavelength limit $q < q_0$.

Let us now consider the following decomposition:

$$\hat{j}_1(r) \rho_N^l = j_1^l(r) \rho_N^l + (\hat{j}_1(r) - j_1^l(r)) \rho_N^l \quad (3.36)$$

and let us examine the action of the operator of motion $\exp(-iL_N t)$ on this quantity; we make here the assumption, which was not necessary in the original Landau–Placzek problem treated in section 2, that this operator will rapidly bring the second term of (3.36) to zero, for times $t \gg \tau_r$ where τ_r is some finite relaxation time; this hypothesis, which is crucial for the further development of the theory, is based on the idea that any non-equilibrium state rapidly relaxes toward local equilibrium.

With the help of (3.35, 36), we can now cast (3.32) in the following form:

$$D(t) \underset{t \gg \tau_r}{=} \frac{1}{\Omega} \sum_{q_2 < q_0} \int \left(\prod_{q' < q_0} dn_{1,q} dv_q \right) \left\{ \left(\prod_{q' < q_0} P_{1,N}(n_{1,q'}) P_N(v_{q'}) \right) n_{1,q_2} v_{-q_2} \right. \\ \left. \times \left[\int d^3r \int dr^N dp^N j_1^D(r) \exp(-iL_N t) \rho_N^l(\{n_{1,q}\}, \{v_q\}) \right] \right\}. \quad (3.37)$$

The remaining part of the calculation is straightforward; we use formula (2.21) to describe the evolution of the local distribution function ρ_N^l ; as discussed previously, this formula, which is the key assumption of the Landau–Placzek method, is only reasonable for small wave numbers; we shall thus have to a posteriori verify that indeed the small wave number contributions govern the long time behavior of $D(t)$. Taking again (3.34) into account, we get:

$$D(t) = \frac{1}{3\Omega^2} \sum_{q_1 < q_0} \sum_{q_2 < q_0} \int \prod_{q < q_0} (dn_{1,q} dv_q) \prod_{q' < q_0} P_{1,N}(n_{1,q'}) P_N(v_{q'}) n_{1,q_1}(t) v_{-q_1}(t) \cdot n_{1,q_2}(0) v_{-q_2}(0). \quad (3.38)$$

Retaining only the terms $q_1 = -q_2$ in the sums (because different wave numbers are uncoupled), we arrive at the following result:

$$D(t) = \frac{1}{3\Omega} \sum_{q_1 < q_0} \int dn_{1,q_1} \int dv_{q_1} P_{1,N}(n_{1,q_1}) \frac{P_N(v_{q_1})}{\Omega} n_{1,q_1}(t) v_{-q_1}(t) \cdot n_{1,-q_1}(0) v_{q_1}(0). \quad (3.39)$$

The time evolution of the “macroscopic” density $n_{1,q}(t)$ was given in (3.26):

$$n_{1,q}(t) = \exp(-Dq^2 t) n_{1,q}(0). \quad (3.40)$$

Moreover, although we have in principle a “mixture” made of the tagged particle 1 and of all the other molecules in the system, this mixture is infinitely dilute; the hydrodynamical velocity $v_q(t)$ can thus be calculated as for a pure fluid:

$$v_q(t) = v_{q\parallel}(t) + v_{q\perp}(t), \quad (3.41)$$

where the longitudinal and transverse parts of the velocity field are given by (2.15a) and (2.15b) respectively.

With the help of these results, and of:

$$\sum_q \xrightarrow{\Omega \rightarrow \infty} \frac{\Omega}{(8\pi)^3} \int d^3q, \quad (3.42)$$

the calculation of $D(t)$ reduces to trivial quadratures which we shall not reproduce in detail here; the final result is:

$$D(t) \underset{t \rightarrow \infty}{\simeq} \frac{2k_B T}{3\rho} \frac{1}{[4\pi(\nu + D)t]^{3/2}}, \quad (3.43)$$

in agreement with (1.21). Notice that, in (3.39), only the transverse velocity field contributes to the long time result (3.43); the oscillating character of the longitudinal field leads to a rapid exponential decay in the long term. Moreover, it is easily checked that the contribution (3.43) entirely comes from wave numbers which are arbitrarily small for sufficiently large times: this justifies the assumption made above.

This asymptotic result is slightly more general than (3.26) as it is valid independent on the size of the tagged particle; if this latter is large, $\nu \gg D$ and we recover our previous formula; moreover, it clearly shows the connection between the $t^{-3/2}$ decay and the vorticity diffusion process. Finally, it is easily extended to other Green–Kubo integrands [17, 18].

Although, as already pointed out in the introduction, it is rather arbitrary to classify the various methods which have been used in mode–mode coupling theory, we feel it is a good place here to mention the theory of Kadanoff and Swift [16]: although this theory has more of a microscopic flavor than the present Landau–Placzek method, it is also based on the central role of local equilibrium; however here, linearized local equilibrium is introduced by the formal eigenstates $|\alpha, q\rangle$ of the Liouville operator:

$$L_N |\alpha, q\rangle = z_\alpha(q) |\alpha, q\rangle, \quad (3.44)$$

($\alpha \in 1, 2, 3, 4, 5$ labels the five conserved quantities in a system of identical particles, q is the wave number characterizing the state), such that the corresponding eigenvalues $z_\alpha(q)$ go to zero when $q \rightarrow 0$ (remember also the kinetic approach of section 2.3). Kadanoff and Swift then remark that products of such states are also slowly varying:

$$L_N |\alpha, q'; \beta, q - q'\rangle = [z_\alpha(q') + z_\beta(q - q')] |\alpha, q'; \beta, q - q'\rangle \quad (3.45)$$

with

$$\langle r^N, p^N | \alpha, q'; \beta, q - q'\rangle \equiv \langle r^N, p^N | \alpha, q'\rangle \langle r^N, p^N | \beta, q - q'\rangle.$$

Retaining these product states to get an approximate representation of the Liouville operator:

$$\begin{aligned} \exp(iL_N t) = \sum_\alpha |\alpha, q\rangle \exp\{z_\alpha(q)t\} \langle q, \alpha | + \frac{1}{2} \sum_{q'} \sum_{\alpha, \beta} |\alpha, q'; \beta, q - q'\rangle \exp\{[z_\alpha(q') \\ + z_\beta(q - q')]t\} \langle \alpha, q'; \beta, q - q' | + \dots \end{aligned} \quad (3.46)$$

and inserting this representation into the Green–Kubo integrand (2.15)* leads to results which are entirely equivalent to those of the Landau–Placzek method. In particular, one exactly recovers (3.43).

*Eq. (1.15) is spatially homogeneous and thus correspond to $q = 0$; in this case, the first term of (3.46) does not contribute and we are again left with “mode–mode coupling terms”.

Although the present very sketchy presentation may not give full justice to the importance of this theory of Kadanoff and Swift, which is particularly well adapted to and has been very successful in the difficult problem of critical dynamics, we shall not discuss it any further here, to keep this report within reasonable length. A more complete review – and a comparison with other mode–mode coupling theories – has been given elsewhere [48].

3.3. *The method of fluctuating hydrodynamics*

In this subsection, we shall illustrate the use of fluctuating hydrodynamics by outlining the derivation of the $t^{-3/2}$ law for self-diffusion as presented by Bedeaux and Mazur [21].

Their model takes, as a starting point, an explicit realization of the non-linear Langevin equation (2.73) and is thus, implicitly, based on the assumptions explained in section 2.2. However, it is simple enough so that its solution can be obtained explicitly in a quite convincing manner. Moreover this model deals exclusively with stochastic processes and not with microscopically defined operators (no Hamiltonian needs to be specified); in particular, the Green–Kubo formula for the correlation functions is not assumed at the beginning, a point which is of some interest.

The starting point is the continuity equation for the number density $n_1(r, t)$ of tagged particles in a fluid:

$$\frac{\partial}{\partial t} n_1(r, t) = -\nabla \cdot J(r, t). \quad (3.47)$$

The current is the sum of a diffusion current $-D_0 \nabla n_1$, plus a convective current $v(r, t) n_1(r, t)$, plus a fluctuating current J_R :

$$J(r, t) = -D_0 \nabla n_1(r, t) + v(r, t) n_1(r, t) + J_R. \quad (3.48)$$

The term J_R is the source of the thermal fluctuations of n_1 ; yet, it will be neglected in the forthcoming calculation; moreover D_0 is a “bare diffusion coefficient”, as was introduced in section 2.2: we have already discussed above how little precise is the physical meaning which can be given to this quantity.

Of course, precisely as in the general case sketched in section 2.2, the important term in (3.48) is the convective term which involves a coupling between n_1 and the fluid velocity $v(r, t)$; however the simplicity of the present model stems from the fact that the fluid is discernable from the tagged particles; the velocity field $v(r, t)$ can thus consistently be taken as known: we take it as a Gaussian stationary random function obeying the usual linearized fluctuating hydrodynamics. Hence the mode–mode coupling which appears here is “pseudo”-linear, in contrast with the truly non-linear equation (2.73) which is the starting point of many other works on the subject [19, 21–26]. This simplicity of the model leads to a particularly simple and elegant solution.

If we take the Fourier–Laplace transform of (3.47, 48), neglecting J_R , we get:

$$(i\omega + D_0 q^2) n_{1;q,\omega} = iq \cdot A n_{1;q,\omega} + n_{1;q}(t=0), \quad (3.49)$$

where A is a vector operator which depends linearly on $v_{q,\omega}$ and acts on any function $\varphi_{q,\omega}$ as:

$$A \varphi_{q,\omega} \equiv \frac{1}{(2\pi)^4} \int d^3 q' d\omega' v_{q-q',\omega'} \varphi_{q',\omega}. \quad (3.50)$$

Setting:

$$G_0 = -(i\omega + D_0 q^2)^{-1} \quad (3.51)$$

and:

$$n_{1;q,\omega}^0 = i G_0 n_{1,q}(t=0), \quad (3.52)$$

we get from (3.49):

$$n_{1;q,\omega} = (1 + i G_0 q \cdot A)^{-1} n_{1;q,\omega}^0 \quad (3.53)$$

and:

$$J_{q,\omega} = (A + iqD_0)(1 + iG_0q \cdot A) n_{q,\omega}^0. \quad (3.54)$$

We now have to relate the mean values of $J_{q,\omega}$ and $n_{1;q,\omega}$ for a given $n_{1;q,\omega}^0$, the fluctuating quantity being A . This will provide us with a linear relation between $\langle J_{q,\omega} \rangle$ and $\langle n_{1;q,\omega} \rangle$ and hence with a value of the macroscopic, or “dressed”, diffusion coefficient which will account for the fluctuations of the fluid velocity. Simple algebra leads to:

$$D = D_0 + q^{-2} \frac{\langle iq \cdot A (1 + iG_0q \cdot A)^{-1} \rangle}{\langle (1 + iG_0q \cdot A)^{-1} \rangle}. \quad (3.55)$$

Notice that, in this way, we are led quite naturally to a q, ω -dependent diffusion coefficient, without recourse to any Green–Kubo formula.

To make the $\omega^{1/2}$ dependence of D apparent, let us formally expand the right-hand side of (3.55) in increasing powers of A :

$$D = D_0 + q^{-2} \langle q \cdot A G_0 q \cdot A \rangle + \text{higher order terms.} \quad (3.56)$$

The average involved in this expression is very close to a mode–mode contribution, since A is proportional to the fluctuating velocity field. From (3.50):

$$\langle q \cdot A G_0 q \cdot A \rangle = \frac{1}{(2\pi)^4} \int d^3q' \int d\omega' \langle q \cdot v_{q-q', \omega-\omega'} G_0(\omega', q')(q-q') \cdot v_{q-q', \omega-\omega'} \rangle. \quad (3.57)$$

From space–time translation invariance:

$$\langle v_{q-q', \omega-\omega'} v_{q'-q'', \omega'-\omega''} \rangle = (2\pi)^4 \delta(\omega-\omega'') \delta(q-q'') S_v(q-q', \omega-\omega') \quad (3.58)$$

where, from the Wiener–Khinchin theorem [41], $S_{v;q,\omega}$ is the Fourier–Laplace transform of the space–time correlation of the velocity field fluctuations. From the usual linearized hydrodynamics, we know that these fluctuations decay according to sound modes and to a vorticity mode. Retaining this latter only, we have:

$$S_{v;q,\omega} = \left(1 - \frac{qq}{q^2}\right) \frac{kT}{\rho} \frac{1}{i\omega + \nu q^2}. \quad (3.59)$$

Inserting this expression into (3.58), one readily gets a contribution to D which has the familiar mode–mode form. Expanding around $\omega = 0$, one finds at once a $\omega^{1/2}$ term in the frequency expansion of D : it exactly agrees with the previous results except that the bare self-diffusion coefficient D_0 appears instead of the physical (or dressed, or renormalized) transport coefficient D , which appears in other theories. However, this difference is actually due to the neglecting of the “higher order” terms in (3.56): when these are properly taken into account, one recovers the physical diffusion in the final result. Due to the simplicity of their model, Bedeaux and Mazur were also able to obtain many results at small but finite q but we shall not discuss them here.

3.4. Kinetic theory method

Let us now indicate how the asymptotic behavior of the velocity autocorrelation function can be studied by the methods of kinetic theory, sketched in section 2.3. As already mentioned, such calculations are always based on expansion in some smallness parameter, like the density or the strength of the potential, although such expansions can sometimes be formally pushed to infinite order and thus allow for the treatment of arbitrary dense fluids.

To simplify, we shall explain with some detail how to recover the $t^{-3/2}$ behavior of the Green–Kubo integrands from the beginning of a density expansion only [29, 30]; the extension to arbitrary densities has been done but is involved [31–34] and we shall merely sketch the main ideas of this general proof.

We have seen (eq. (2.91)) that the exact evolution of the time correlation function can be reduced to the study of the frequency dependent linearized collision operator $\tilde{C}_0(p_1; z)$. As indicated in Appendix B, the first few terms of the density expansion of this operator are:

$$\tilde{C}_0(p_1; z) = n \tilde{C}_0^{(0)}(p_1; z) + n^2 \tilde{C}_0^{(1)}(p_1; z) + n^3 \tilde{C}_0^{(2)}(p_1; z) + \dots \quad (3.60)$$

The leading term of this expansion, $\tilde{C}_0^{(0)}(p_1; z)$, is the finite frequency generalization of the Boltzmann–Lorentz collision operator (2.94); whenever the two-body interaction has a finite duration, it is explicitly frequency dependent [76]; however, to simplify, we shall completely neglect this type of frequency dependence because we are interested in phenomena varying over a relaxation time, much longer than the duration of a collision; hence, we shall put:

$$\tilde{C}_0^{(0)}(p_1; z) = \tilde{C}(p_1), \quad (3.61)$$

where the right-hand side is defined in (2.94); note that (3.61) is rigorous for hard spheres, a feature which makes this latter model very attractive in many calculations. From (3.60), (2.91) and (2.99), we readily see that, in the dilute gas limit, the velocity correlation function $D(t)$ decreases at least like $\exp(-\mu_r t)$, where μ_r is some finite relaxation frequency (approximately the collision frequency $\sim n$), in the case of hard potentials which we consider here*.

This simple exponential bound is lost when the higher terms in the density expansion (3.60) are considered. Consider first the correction $\tilde{C}_0^{(1)}(p_1; z)$; it describes two types of effects:

- i) modifications of the two-body dynamics by the equilibrium static correlation,

*To our knowledge, no general result of that kind is known for soft potentials. In particular, an interesting limiting case would be the one of Coulomb potentials where, in the case of a hot plasma, the Balescu–Guernsey–Lenard kinetic equation may be applied [50], especially in connection with the recent computer results by Hansen et al. [77].

ii) genuine three-body dynamical effects.

It can be shown that the short range equilibrium correlations do not play any important role in the long term (this point is discussed, for instance, in Appendix A of ref. [78]), and we shall thus limit ourselves to the three-body collisions, which are described by the finite frequency generalization of the so-called Choh–Uhlenbeck [79] collision operator; we shall not display this operator here (see Appendix B) but we shall rather discuss its main features in purely qualitative terms, keeping in mind that it describes the dynamical correlations created by the collisions between three particles. From our viewpoint, the most important characteristic of this generalized Choh–Uhlenbeck operator is its non analyticity with respect to z near $z = 0$. In 2d, we shall see presently that:

$$\tilde{C}_0^{(1)}(p_1; z) \underset{z \rightarrow 0}{\simeq} \ln z \quad (3.62)$$

and, similarly, in 3d, one finds:

$$\tilde{C}_0^{(1)}(p_1; z) \simeq \tilde{C}_0^{(1)}(p_1; 0) + \mathcal{O}(z \ln z) \quad (3.63)$$

which suggests the following extension at arbitrary dimensionality:

$$\tilde{C}_0^{(1)}(p_1; z) = \tilde{C}_0^{(1)}(p_1; 0) + \mathcal{O}(z) + \dots + \mathcal{O}(z^{d-3}) + \mathcal{O}(z^{d-2} \ln z) + \dots \quad (3.64)$$

From the theory of Laplace transform, these results correspond to an asymptotic time behavior like $t^{-(d-1)}$; such a slow decay of three-body processes can be understood as follows: consider the probability for particle 3 colliding particle 2 in the time interval $(t, t + dt)$ after a first collision (12); we want this collision (23) to be such that 1 and 2 will collide again in the future, leading to a correlated sequence of dynamical events. As usual in this sort of problem, we work in the frame where 1 is at rest after the first collision (12). The probability of an arbitrary collision (23) in dt is of course given by $na^{d-1}v dt$ (a is the interaction range; v the average thermal velocity); if we furthermore impose that this collision throws 2 back onto 1, the velocity of 2 after (23) has to point into the solid angle under which 1 is seen from the location of this collision (23): this leads to a supplementary factor $a^{d-1}/(vt)^{d-1}$ for t large. Hence the collision events happening in the time interval $(t, t + dt)$ contribute a factor

$$dt/t^{d-1} \quad (3.65)$$

to the Choh–Uhlenbeck collision operator.

What is the asymptotic behavior of the time correlation function at this order of approximation? To get a hint to this problem, we suppose that we may merely replace the velocity operators $\tilde{C}_0^{(0)}$ and $\tilde{C}_0^{(1)}$ by c -numbers. From (2.90), (3.61) and (3.63), we get in 3d:

$$D(z) = v^2[-iz + \mu_r + i(na^3)^2 z \ln z]^{-1} \quad (3.66)$$

(we have formally included $\tilde{C}_0^{(1)}(p_1; 0) \sim n^2$ in μ_r).

By inverting this transform, we find two contributions: a pole term, behaving like $v^2 \exp(-\mu_r t)$ at large t , and a cut term of order $[(na^3)^2/(\mu_r t)^2]v^2$ in the same limit. These asymptotic values are both reached for times of order μ_r^{-1} ; thus, for times $\mu_r^{-1} \lesssim t \lesssim \mu_r^{-1} \ln(1/na^3)$, the relaxation remains essentially exponential but, for much larger times, it behaves like t^{-2} . Let us stress however that these results only obtain in the very formal limit where all post Choh–Uhlenbeck terms in

the density expansion (3.60) are neglected. Notice also that this t^{-2} decay is fast enough so that the Green–Kubo integral (1.5) still exists in this approximation for $d = 3$. However, in the next order, involving $\tilde{C}_0^{(2)}(p_1; z)$, and denoted super Choh–Uhlenbeck (S.C.U.) this Green–Kubo integral no more exists; indeed, reproducing the dimensional argument which led us to (3.63), we find:

$$\tilde{C}_0^{(2)}(p_1; z) \sim \ln z \quad (d = 3), \tag{3.67}$$

due to long living dynamical events between four molecules. At this order, we would then find, instead of (3.66):

$$D(z) \underset{z \rightarrow 0}{\sim} v^2[-iz + \mu_r + i(na^3)^2 \mu_r \ln z]^{-1} \tag{3.68}$$

and the diffusion coefficient $D \equiv D(0)$ vanishes!

This paradoxical result is of course quite formal because the density expansion (3.60) is meaningful iff:

$$\ln |\tilde{C}_0^{(0)}(p_1; z)| \gg \ln^2 |\tilde{C}_0^{(1)}(p_1; z)| \gg \ln^3 |\tilde{C}_0^{(2)}(p_1; z)| \dots \tag{3.69}$$

when $n \rightarrow 0$, whatever z is. Clearly this ordering is violated near $z = 0$: a straightforward density expansion is thus meaningless.

As is immediate to see from (3.62), the same difficulty already occurs at the Choh–Uhlenbeck level at $d = 2$; as we shall see later, it is generally believed that here the difficulty is of a deep nature and not simply due to an illegitimate density expansion.

Keeping in mind the formal character of the results based on (3.68), let us nevertheless analyze the time correlation function at S.C.U. order; we now find that, for $\mu_r^{-1} < t < \mu_r^{-1} \ln(1/na^3)$, the time correlation function is dominated by $v^2 \exp(-\mu_r t)$, coming from the pole near $z = i\mu_r$; for $\mu_r^{-1} \ln(1/na^3) < t < (a/v) \exp(-1/na^3)$, the S.C.U. contribution already dominates the C.U. one and leads to a decay like $((na^3)^2/(\mu_r t))v^2$. Finally, for $t > (a/v) \exp(-1/na^3)$, the dominant contributions arise from values of z so close to zero that the logarithmic term dominates the Boltzmann contribution in the denominator of (3.68); the result is a decay like $v^2[(na^3)^2(\mu_r t) \ln(tv/a)]^{-1}$. This discussion is summarized in the following diagram:

$$\begin{array}{ccccccc}
 t : & 0 & \mu_r^{-1} & & \mu_r^{-1} \ln(1/a^3 n) & & (a/v) \exp(-1/a^3 n) \\
 \hline
 D(t) : & 1 & \exp(-\mu_r t) & & (na^3)^2 / \mu_r t & & [(na^3)^2(\mu_r t) \ln(tv/a)]^{-1}
 \end{array}
 \xrightarrow{t}$$

Note that nothing remains from the C.U. decay t^{-2} ; it is always dominated by the S.C.U. terms.

Coming back to the vanishing of the diffusion coefficient in this S.C.U. approximation, we remark – as indicated by (3.65) – that this property is a consequence of the unbounded duration of the collision processes involving four isolated particles. Yet, if some collision event exceeds substantially a mean free flight time, the chance will increase for a collision of anyone of the four given particles with a fifth, sixth, ... one. Such a collision will destroy the dynamical correlation existing between these four particles and will hopefully eliminate the divergence of the collision operator. This qualitative point may be embedded into a systematic “renormalization program” and it will turn out that the diverging S.C.U. collision operator will be replaced by a new operator, the so-called “ring collision operator” [80], which is free of divergence at zero frequency for 3d

fluids; nevertheless this new ring operator will still be non analytic at small frequency z and this non-analyticity will precisely give rise to the $t^{-3/2}$ asymptotic behavior for the Green–Kubo integrand; hence there is a strong connection between the difficulties involved in straightforward density expansions and the problem of the long time tails.

It is unfortunate that, even in the moderately dense gas considered here, the explicit realization of this renormalization program requires a non trivial formalism. In order not to burden the reader with too much technicality, we prefer to report the general principles underlying this renormalization in Appendix C. Here, we limit ourselves in presenting the result of this renormalization applied to the particular case of the C.U. and S.C.U. (to dominant order, these are both renormalized together) and we then interpret this result in intuitive terms. Moreover, we limit ourselves to the simple case of hard spheres. As indicated in Appendix B, these are conveniently described with the help of the binary collision operator t_{ij} , which is an operator depending on r_i, v_i, r_j, v_j . Its Fourier transform which remains a velocity operator is defined by:

$$\langle\langle k+q; k'-q | t_{ij} | k, -k' \rangle\rangle = \frac{1}{\Omega^2} \int d^3 r_i \int d^3 r_j \exp\{-i[(k+q) \cdot r_i - (k'-q) \cdot r_j]\} t_{ij} \exp\{i(k \cdot r_i - k' \cdot r_j)\} \quad (3.70)$$

and has the following representation:

$$\langle\langle k+q; k'-q | t_{ij} | k, -k' \rangle\rangle \varphi(v_i, v_j) = a^2 \int d^2 \kappa \kappa \cdot v_{ij} \Theta(\kappa \cdot v_{ij}) [\exp(-iq \cdot \kappa a) \varphi(v'_i, v'_j) - \exp(iq \cdot \kappa a) \varphi(v_i, v_j)], \quad (3.71)$$

where $\varphi(v_i, v_j)$ denotes an arbitrary function of the velocities v_i and v_j , and where $v_{ij} = v_i - v_j$. Moreover κ is a unit vector, $\Theta(x)$ is the Heaviside function and v'_i, v'_j denote the velocities after the collision process which are given by

$$v'_i = v_i - \kappa(\kappa \cdot v_{ij}), \quad v'_j = v_j + \kappa(\kappa \cdot v_{ij}); \quad (3.72)$$

finally a is the diameter of the hard spheres.

The Boltzmann–Lorentz operator \tilde{C} (see (2.94)) and the linearized Boltzmann operator C (see (2.112)) are simply related to this binary collision operator; for hard spheres again, we have:

$$\tilde{C}(p_1) \delta\varphi(p_1) = \int d^3 p_2 \langle\langle q, 0 | t_{12} | q, 0 \rangle\rangle \delta\varphi(p_1) \varphi^{eq}(p_2), \quad (3.73)$$

and:

$$C(p_1) \delta\varphi(p_1) = \int d^3 p_i [\langle\langle q, 0 | t_{1i} | q, 0 \rangle\rangle \delta\varphi(p_1) \varphi^{eq}(p_i) + \langle\langle q, 0 | t_{1i} | 0, q \rangle\rangle \varphi^{eq}(p_i) \delta\varphi(p_i)]. \quad (3.74)$$

In terms of this binary collision operator, the so-called “ring collision operator” which renormalizes both C.U. and S.C.U. to dominant order is* ($d = 3$):

$$\begin{aligned} \tilde{C}^R(p_1; z) \delta\varphi(p_1) &= n \int \frac{d^3 q}{(2\pi)^3} \int d^3 p_2 \langle\langle 0, 0 | t_{12} | q, -q \rangle\rangle \\ &\times \{ [iz + iq \cdot v_{12} + n \tilde{C}(p_1) + n C(p_2)]^{-1} - [iz + iq \cdot v_{12}]^{-1} \} \langle\langle q, -q | t_{12} | 0, 0 \rangle\rangle \delta\varphi(p_1) \varphi^{eq}(p_2). \end{aligned} \quad (3.75)$$

*The free particle contribution $[iz + iq \cdot v_{12}]^{-1}$ is subtracted to avoid an unphysical term where particles 1 and 2 collide twice successively with each other; see also (B.15) and footnote thereafter.

The reason for the terminology “ring collision operator” is rather clear from the above expression: \tilde{C}^R corresponds to any “cycle” of collisions starting with a collision (12) (the t_{12} operator at the extreme right); then, the motion of particle 1 and 2 instead of being a free motion, is described by a “Boltzmann propagation”: one considers that they collide an arbitrary number of times with other gas molecules. Hence, the usual free motion propagator $[iz + iq \cdot v_{12}]^{-1}$ is replaced by $[iz + iq \cdot v_{12} + n\tilde{C} + nC]^{-1}$; finally, the tagged particle 1 collides again with a particle connected to the particle entering the first collision (i.e., 2) through a set of binary collisions; that this particle is generally different from 2 itself comes from the fact that the Boltzmann operator (3.74) involves one contribution in which the non-equilibrium distribution function is the one of the dummy particle i , not of 1.

For example the sequence:

$$\tilde{C}(p_2) \tilde{C}(p_2) \delta\varphi(p_2) \quad (3.76)$$

does not imply that particle 2 is the non equilibrium particle; indeed, it corresponds to four terms, which we write schematically as:

$$\int d^3p_3 d^3p_4 [t_{23} t_{24} \delta\varphi(p_2) \varphi^{eq}(p_3) \varphi^{eq}(p_4) + t_{23} t_{24} \delta\varphi(p_4) \varphi^{eq}(p_2) \varphi^{eq}(p_3) + t_{23} t_{34} \varphi^{eq}(p_2) \delta\varphi(p_3) \varphi^{eq}(p_4) + t_{23} t_{34} \varphi^{eq}(p_2) \delta\varphi(p_4) \varphi^{eq}(p_3)] \quad (3.77)$$

and only in the first term is particle 2 out of equilibrium*.

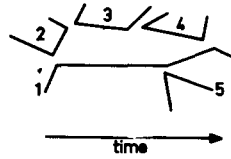


Fig. 3.1. A ring collision.

Figure 3.1 illustrates, in a self-explanatory manner, this ring structure.

It is difficult to extract general analytical results from (3.75), as the operator $[iz + iq \cdot v_{12} + n\tilde{C}(p_1) + nC(p_2)]^{-1}$ involves at least the explicit solution of the linearized Boltzmann operator, a very complicated problem indeed! However, it is possible to extract the first term in the expansion of $C^R(p_1; z)$ near $z = 0$ – and the corresponding contribution to the asymptotic time correlation – with the hydrodynamical eigenmodes introduced in section 2.

Indeed, with the help of (2.104) and (2.115), we gain the formal representation:

$$[iz + iq \cdot v_{12} + n\tilde{C}(p_1) + nC(p_2)]^{-1} = \sum_{j, l} |\tilde{\Phi}_j^q, \Phi_l^{-q}\rangle \frac{1}{[iz + \tilde{\lambda}_j^q + \lambda_l^{-q}]} \langle \tilde{\Phi}_j^q, \Phi_l^{-q} | \quad (3.78)$$

where

$$\langle v_1, v_2 | \tilde{\Phi}_j^q, \Phi_l^{-q} \rangle \equiv \tilde{\Phi}_j^q(v_1) \Phi_l^{-q}(v_2). \quad (3.79)$$

The connection with the previous theories – which all rely upon the hydrodynamic behavior of the time correlation functions – is now made by noticing that only a finite number of eigenvalues

*In this respect, there is an abuse of language in speaking of the linearized Boltzmann operator as being a one-particle operator. This terminology is used because of the symmetrical role played by all the particles in the system.

$\tilde{\lambda}_j^q$ and λ_l^q go to zero with q . More precisely, we have found the self-diffusion mode (2.106) for the self-motion and $(d + 2)$ hydrodynamical eigenvalues for the Boltzmann case (they are displayed in (2.116) for $d = 3$). In particular, symmetry arguments show that, in the present problem, the interesting eigenvalue is the mode (2.116b) of vorticity diffusion.

Let us assume that, in the small z limit, the dominant contribution to (3.75) comes from small wave numbers q ; * we limit then the domain of integration over q to a small sphere of radius q_0 , much smaller than any inverse molecular length; in the region $q < q_0$, the existence of hydrodynamic modes can be ascertained. Moreover, as all non-hydrodynamical eigenvalues ($j \notin (1)$, $l \notin (\alpha)$) tend to a finite limit when $q \rightarrow 0$, it is readily verified that their contribution to the q integral in (3.75) is analytic in z ; schematically we have:

$$(\tilde{C}^R(p_1; z) - \tilde{C}^R(p_1; 0))|_{\text{non hyd.}} \underset{z \rightarrow 0}{\sim} z, \quad (3.80)$$

where the subscript "non hyd." indicates that we retain all terms in (3.78) with at least one of the two eigenvalues $\tilde{\lambda}_j^q$ or λ_l^{-q} taken as non hydrodynamic.

Hence, as far as asymptotic behavior is concerned, we are left with:

$$\begin{aligned} \tilde{C}^R(p_1; z)|_{\text{hyd.}} &= n \sum_{\alpha=1}^5 \int_{q < q_0} \frac{d^3 q}{(2\pi)^3} \int d^3 p_2 \langle\langle 0, 0 | t_{12} | q, -q \rangle\rangle \langle v_1, v_2 | \tilde{\Phi}_1^q \Phi_\alpha^{-q} \rangle \\ &\times \frac{1}{iz + \tilde{\lambda}_1^q + \lambda_\alpha^{-q}} \langle \tilde{\Phi}_1^q \Phi_\alpha^{-q} | v_1, v_2 \rangle \langle\langle q, -q | t_{12} | 0, 0 \rangle\rangle. \end{aligned} \quad (3.81)$$

It is very easy to show on (3.81) that:

i) $\tilde{C}^R(p_1, 0)$ is finite in 3d; hence the divergences associated with the S.C.U. operator have been removed by the ring collision operator.

ii) $\tilde{C}^R(p_1, z)$ expands near $z = 0$ like:

$$\tilde{C}^R(p_1; z) - \tilde{C}^R(p_1; 0)|_{\text{hyd.}} \sim z^{1/2}. \quad (3.82)$$

In order to do this, we neglect the q -dependence of the matrix elements of t_{12} ; moreover, we only retain in (3.81) the vorticity mode $\alpha = 3$ which, because of the symmetry of the eigenfunctions (2.117), turns out to be the only term which can contribute to the velocity correlation function**.

Thus, we immediately get for $\tilde{C}^R(p_1; 0)$:

$$\tilde{C}^R(p_1; 0)|_{\text{hyd.}} \sim \int_{q < q_0} \frac{d^3 q}{q^2}, \quad (3.83)$$

a finite integral. Moreover, we have:

*It is a trivial matter to check that the region of integration $q > q_0$, while generally giving the main contribution to the full \tilde{C}^R , and thus to transport coefficients, is both non diverging at $z = 0$ and analytic in z for small z : it is thus irrelevant in the present discussion.

**In order to make the explicit calculation, one needs to generalize the eigenfunctions (2.117) for arbitrary direction of q . This elementary problem is solved for example in ref. [81].

$$\begin{aligned} \tilde{C}^R(p_1; z) - \tilde{C}^R(p_1; 0)|_{\text{hyd.}} &\simeq n \int \frac{d^3 q}{(2\pi)^3} \int d^3 p_2 \langle\langle 0, 0 | t_{12} | 0, 0 \rangle\rangle \langle v_1, v_2 | \tilde{\Phi}_1^0 \Phi_3^0 \rangle \\ &\times \frac{iz}{[iz + \tilde{\lambda}_1^q + \lambda_3^{-q}] [\tilde{\lambda}_1^q + \lambda_3^{-q}]} \langle \tilde{\Phi}_1^0 \Phi_3^0 | v_1, v_2 \rangle \langle\langle 0, 0 | t_{12} | 0, 0 \rangle\rangle. \end{aligned} \quad (3.84)$$

Setting $q z^{-1/2}$ as integration variable, one readily obtains for (3.84) the estimate:

$$(\tilde{C}^R(p_1; z) - \tilde{C}^R(p_1; 0))|_{\text{hyd.}} \underset{z \rightarrow 0}{\simeq} (z/\mu_r)^{1/2} (a^3 n)^2. \quad (3.85)$$

Inserting this into the general formula (2.91), one gets:

$$D_z - D_0 \underset{z \rightarrow 0}{\simeq} v^2 (z/\mu_r)^{1/2} (na^3)^2 / \mu_r \quad (3.86)$$

and this leads in turn to an asymptotic behavior:

$$D(t) \underset{t \rightarrow \infty}{\simeq} v^2 (na^3)^2 / (\mu_r t)^{3/2} \quad (3.87)$$

for the time correlation function. This behavior dominates the Boltzmann exponential behavior for $t \gg \mu_r^{-1} \ln(1/na^3)$ and it replaces for any time $t > \mu_r^{-1}$ the cut contribution from the S.C.U. term.

A more careful calculation allows one to take into account the operator character of t_{12} and to get the explicit form of this $z^{1/2}$, or $t^{-3/2}$ contribution. One recovers then, with the same coefficients, the result found by the other methods provided that one considers the dilute gas regime where the present theory is applicable.

Of course the question remains as to whether the asymptotics deduced from the ring collision term is the right one. This question is particularly pertinent if we remember that by adding more and more terms in the virial expansion for $\tilde{C}_0(p_1; z)$, we have found qualitatively different results. Perhaps, by adding more terms, could a new behavior appear? Although the question is still quite open in 2d, this conjecture is very unlikely in 3d. Indeed, although this calculation offers no guarantee as far as mathematical rigor is concerned, it is possible to analyze the complete collision operator \tilde{C}_0 , to infinite order in any perturbative parameter, and one recovers the $t^{-3/2}$ behavior with the correct thermohydrodynamical coefficients at finite density [31–34]. We cannot give here a detailed account of this work, as it involves a number of non-trivial technical points. The starting point is a “renormalized” expression for the collision operator, as is briefly discussed in Appendix C. By establishing bounds to the various contributions of this renormalized operator, it is then shown that to dominant order at low frequency*, the generalized collision operator can be written in a form quite analogous to (3.81) with the substitutions:

$$\langle\langle 0, 0 | t_{12} | q, -q \rangle\rangle \rightarrow \langle\langle 0, 0 | C(p_1, p_2; z) | q, -q \rangle\rangle, \quad (3.88)$$

involving a frequency dependent operator C which, roughly speaking, represents the most general short range collision process involving particles 1 and 2, and:

$$\lambda_1^q \rightarrow \lambda_1^{q, \text{full}}, \quad \lambda_\alpha^{-q} \rightarrow \lambda_\alpha^{-q, \text{full}}, \quad (3.89)$$

*In the same sense that (3.81) is dominant at low frequency in the ring approximation.

where the superscript “full” indicates that we now have the correct transport modes at finite densities. A careful study indicates that, to order $t^{-(2+\epsilon)}$, the wave-number and frequency dependence of C can be neglected. Obviously, these substitutions leave the estimate (3.83, 85) unchanged except for the constant coefficients, which now refer to the dense system, as obtained previously by the Landau–Placzek method for example. A remarkable feature of the theory is that the operator C , although unknown in explicit form, entirely disappears from the final result, which only involves thermodynamical coefficients.

Though the difficulties involved in this type of N body analysis are quite considerable, as compared to the other methods developed above, we nevertheless believe that such calculations are of interest because they show that, beyond the ring contributions, the asymptotic decay of the Green–Kubo integrand becomes “stable” and its qualitative form is not affected by higher density effects; more precisely, the only modification to the $t^{-3/2}$ law is in giving the thermodynamical coefficients their correct value for a dense system. Moreover, this theory shows that all “multiple mode couplings”, involving the simultaneous excitation of an arbitrary number p of modes ($p > 2$) lead to terms at least of order $t^{-(2+\epsilon)}$. As, at the same order, contributions appear which depend on the detailed dynamics of the system, we are then left with a hopeless problem.

However, below this order, the asymptotic contributions have all the same structure as already encountered with the “ring term”; in particular the details of the dynamics are irrelevant and only macroscopic properties play a role; this point is of course assumed in the more phenomenological approaches.

4. The applications

Up to now, we have considered mainly the velocity time correlation function; this problem is of particular interest because, as already stressed in the introduction, it goes back to the foundations of non-equilibrium statistical mechanics; moreover this quantity is the most accurately known from molecular dynamics computer simulation experiments, because an independent calculation may be performed for each of the N particles in the system.

Here, we consider a variety of other problems, where the same methods can be applied: all are characterized by some parameter, related to time, which becomes large. The first case which comes to mind is a discussion of the asymptotic behavior ($t \rightarrow \infty$) of the Green–Kubo integrands corresponding to the other transport coefficients: shear and bulk viscosity and thermal conductivity as well as diffusion and thermal diffusion in mixtures without chemical reactions. Second we shall consider the still conjectural problem of 2d systems as well as a brief discussion of the higher order corrections ($\ll t^{-3/2}$) to these Green–Kubo integrands and to the hydrodynamical normal modes (here the wave number $q \sim t^{-1/2}$ is the smallness parameter).

A third non-trivial application of mode–mode coupling theory is furnished by the transport properties of the Van der Waals fluid: here, one supposes that the two-body interaction can be split into a short range part and a long range part with the inverse range γ . In the limit $\gamma \rightarrow 0$, we expect that the effects of this long range potential will be fully felt by the system only for long times, of the order $\gamma^{-1/2}$, and thus hydrodynamical considerations should again be applicable.

Finally, we briefly explore a field where mode–mode coupling theory led to the most spectacular successes, namely critical dynamics: here the equilibrium correlation length ξ becomes large when T approaches the critical temperature T_c and again we can expect important hydrodynamical

cal effects in the time regime $t \sim \xi^2 \rightarrow \infty$. As however this problem is rather far from our general plan and has moreover been reviewed recently from different points of view [46, 82, 83], we shall remain rather brief, indicating simply how it can be related to the general ideas discussed here. This should however not be considered as a prejudice against this type of application of mode–mode coupling: as mentioned in the introduction, the modern aspects of mode–mode coupling have emerged from this field; moreover, the present understanding of critical dynamics is without doubt one of the great achievements of modern statistical mechanics.

As we have indicated in detail in previous sections for self-diffusion a series of different methods can be applied to deal with these problems. The only formalism which works for self-diffusion (at least for a large particle) and not for the other cases is the generalized Brownian motion theory of section 3.1, as there is no smallness parameter analogous to R^{-1} (inverse of the Brownian particle radius) in a fluid of identical molecules*. Otherwise, the Landau–Placzek method, the fluctuating hydrodynamics approach and the kinetic theory approach can be equally well applied to these other problems, with their merits and defects, and lead to equivalent results. Hence, to remain as concise as possible, we shall generally limit ourselves to the Landau–Placzek method, pointing out merely the main differences with self-diffusion.

4.1. Asymptotic behavior of the Green–Kubo integrands

As an example of the general Green–Kubo integrand (1.15), consider the thermal conductivity κ ; define:

$$\kappa(\tau) = \lim_{\Omega} \frac{1}{\Omega k_B T} \langle \hat{J}^\kappa(\tau) \hat{J}^\kappa(0) \rangle, \quad (4.1)$$

where

$$\hat{J}^\kappa(\tau) = \hat{J}'^\kappa(\tau) - \hat{J}''^\kappa(\tau), \quad (4.2)$$

$\hat{J}'^\kappa(\tau)$ being the x -component of the microscopic energy flow:

$$\hat{J}'^\kappa(\tau) = \sum_{i=1}^N v_{ix}(\tau) \left(\frac{mv_i^2(\tau)}{2} + \frac{1}{2} \sum_{j \neq i} V(r_{ij}(\tau)) \right) - \frac{1}{2} \sum_{i \neq j \neq 1} v_i(\tau) \frac{\partial V(r_{ij}(\tau))}{\partial r_{ij}} r_{ij,x}(\tau) \quad (4.3)$$

while $\hat{J}''^\kappa(\tau)$ is the “counterterm”**:

$$\hat{J}''^\kappa = \sum_{i=1}^N \frac{h}{n} v_{ix}(t), \quad (4.4)$$

which guarantees that J^κ is orthogonal to the invariants of L_N . With the exception of the trivial factor T^{-1} , the thermal conductivity κ is then given by the analog of (1.11), namely:

$$\kappa = \frac{1}{T} \int_0^\infty \kappa(t) dt. \quad (4.5)$$

*Let us recall here that the virtues of the generalized Langevin equation of Mori–Zwanzig (section 2.2) have been exploited in justifying the stochastic theory of section 3.2; yet, this formalism is quite different and more elaborate than the simple Brownian motion approach developed for self-diffusion.

**Here we consider canonical averages only; it is well-known that the explicit form of this counterterm depends on the ensemble chosen [84].

The main differences between the flow J^κ and the self-diffusion flow v_1 , is the appearance of potential terms. However, as in the latter case, the local equilibrium value $J^{\kappa, l}$ of J^κ is easily obtained as:

$$J^{\kappa, l}(t) = \sum_{q < q_0} n h_q(t) v_{-q, x}(t), \quad (4.6)$$

where h_q is the Fourier transform of the local enthalpy density; it is of course a function of n_q and T_q :

$$h_q(t) = \frac{\partial h}{\partial n} \Big|_T n_q + \frac{\partial h}{\partial T} \Big|_n T_q + \mathcal{O}(n_q^2, T_q^2, n_q T_q). \quad (4.7)$$

Notice that, in writing (4.6), we have retained only quadratic terms in the fluctuations; the cubic terms (i.e. $\propto n_q h_q v_{-q-q', x}$, $q' \neq 0$) lead to negligible contributions to the asymptotic behavior of $\kappa(t)$.

We now write, in analogy with (3.32):

$$\begin{aligned} \kappa(t) = \lim_{\Omega} \frac{1}{\Omega k_B T} & \left\{ \int \prod_{q < q_0} (dn_q dv_q dT_q) \prod_{q' < q_0} P_N(n_{q'}) P_N(v_{q'}) P_N(T_{q'}) \right. \\ & \times \left. \left[\int dr^N dp^N J^\kappa(0) \exp(-iL_N t) \cdot J^\kappa(0) \rho_N^l(\{n_q\}, \{v_q\}, \{T_q\}) \right] \right\}, \end{aligned} \quad (4.8)$$

with obvious definitions for $\rho_N^l(\{n_q\}, \{v_q\}, \{T_q\})$ and $P_N(T_q)$.

Here again the major step is the replacement, for $t \gg \tau_r$ (where τ_r is some finite relaxation time):

$$\exp(-iL_N t) \hat{J}^\kappa(0) \rho_N^l \xrightarrow[t \gg \tau_r]{} \exp(-iL_N t) J^{\kappa, l}(0) \rho_N^l.$$

Taking into account that $J^{\kappa, l}$ only depends on $\{n_q\}$, $\{v_q\}$, $\{T_q\}$ and may be pulled out of the phase space integral, we get:

$$\begin{aligned} \kappa(t) \simeq \lim_{t \gg \tau_r} \frac{1}{\Omega} \frac{1}{\Omega k_B T} & \left\{ \int \prod_{q < q_0} (dn_q dv_q dT_q P_N(n_q) P_N(v_q) P_N(T_q)) J^{\kappa, l}(\{n_q, v_q, T_q\}) \right. \\ & \times \left. \left[\int dr^N dp^N J^\kappa(0) \exp(-iL_N t) \rho_N^l(\{n_q, v_q, T_q\}) \right] \right\}. \end{aligned} \quad (4.9)$$

Using now the approximation (2.21), we immediately get:

$$\begin{aligned} \kappa(t) \simeq \lim_{t \gg \tau_r} \frac{1}{\Omega} \frac{1}{\Omega k_B T} & \left\{ \int \prod_{q < q_0} (dn_q dv_q dT_q P(n_q) P(v_q) P(T_q)) J^{\kappa, l}(\{n_q, v_q, T_q\}) \right. \\ & \times \left. J^{\kappa, l}(\{n_q(t), v_q(t), T_q(t)\}) \right\}, \end{aligned} \quad (4.10)$$

which is completely analogous to (3.39) despite the difference in nature of J^κ and v_1 . The rest of the calculation is mere computation and follows closely the self-diffusion case. Let us repeat the main steps:

i) the conserved variables $n_q(t)$, $v_q(t)$, $T_q(t)$ are evaluated with the help of the linearized hydrodynamic equations (2.8), with the hope – verified a posteriori – that only small wave numbers contribute to the sum (4.6);

ii) the static fluctuations are averaged with the help of standard formulas (see (2.23, 24)), keeping in mind that the fluctuations at different wave numbers are decoupled;

iii) one performs asymptotically the q -integral, taking into account the symmetry of the various modes when performing the angular part.

The result of these straightforward manipulations is:

$$\kappa(t) \underset{t \rightarrow \infty}{\simeq} \frac{(k_B T)}{3} \left(\frac{1}{4\pi t} \right)^{3/2} \left[\frac{2C_p T}{(\nu + \kappa/nC_p)^{3/2}} + \frac{mc^2}{(2\Gamma)^{3/2}} \right]. \quad (4.11a)$$

Similarly, one finds for the shear viscosity Green–Kubo integrand:

$$\eta(t) \underset{t \rightarrow \infty}{\simeq} \frac{(k_B T)}{15} \left(\frac{1}{8\pi t} \right)^{3/2} \left(\frac{7}{\nu^{3/2}} + \frac{1}{\Gamma^{3/2}} \right). \quad (4.11b)$$

One sees on these two examples that the $t^{-3/2}$ behavior is recovered; the only differences with the self-diffusion case are:

i) more complicated mode couplings, because of the different symmetry properties of the flows;

ii) the occurrence of non trivial thermodynamical quantities, like the specific heat at constant pressure C_p and sound velocity c . These are consequences of the thermodynamic derivatives which appear in the expansions of the type (4.7). Notice however that no such thermodynamic derivatives appear in (4.11b), which is particularly simple. On the contrary, the formula for bulk viscosity, which also has been obtained, involves higher order derivatives because, in the analog of (4.7), we now have to expand to second order in the conserved variables n_q and T_q . The result is [17, 18]:

$$\zeta(t) \underset{t \rightarrow \infty}{\simeq} \zeta^v(t) + \zeta^\theta(t) + \zeta^s(t), \quad (4.11c)$$

with

$$\zeta^v(t) \simeq 4(k_B T)^2 \left(\frac{1}{8\pi t} \right)^{3/2} \left[\frac{1}{3\nu^{3/2}} + \frac{\alpha}{2} \left(\frac{C_p}{C_v} - 1 \right) \right],$$

$$\zeta^\theta(t) \simeq \frac{\alpha^2}{2} \left(\frac{C_p}{C_v} - 1 \right)^2 (k_B T)^2 \left(\frac{nC_p}{8\pi t \kappa} \right)^{3/2} \left[\left. \frac{T}{C_p} \frac{\partial C_p}{\partial T} \right|_p - n\alpha T \left. \frac{\partial C_p}{\partial p} \right|_T \right]^2,$$

and

$$\zeta^s(t) = \frac{(k_B T)^2}{2} \left(\frac{1}{8\pi \Gamma t} \right)^{3/2} \left[\frac{1}{3} - \left. \frac{\partial p}{\partial \epsilon} \right|_n - \frac{n}{c} \left. \frac{\partial c}{\partial n} \right|_s \right],$$

where

$$\alpha = \frac{n}{T} \frac{\partial T}{\partial n} \Big|_p.$$

Similar formulae have also been obtained for binary non-reacting mixtures. For concentration diffusion in a mixture of particles of species 1 and 2 one finds [89] :

$$\begin{aligned} D(t) &= \frac{1}{3} \langle \hat{J}_\gamma(\mathbf{r}, 0) \cdot \hat{J}_\gamma(t) \rangle \\ &\simeq \frac{3}{\mu_\gamma} (k_B T)^2 \left(\frac{\rho}{4\pi t} \right)^{3/2} (\eta_+ - \eta_-)^{-1} \sum_{a=\pm} a (\eta + \eta_a)^{-3/2} \left[\frac{\kappa + DT^2 \mu_T^2 + 2D_1 T \mu_T}{TC_p} - \eta_a \right] \end{aligned} \quad (4.12)$$

where

$$\mathbf{J}_\gamma(\mathbf{r}_1, \tau_1) = \sum_i^1 m_i v_i \delta(\mathbf{r} - \mathbf{r}_i) - \gamma_1 \sum_j m_j v_j \delta(\mathbf{r} - \mathbf{r}_j)$$

is the flux of concentration of particles of species (1), as the sum Σ_i^1 runs over the whole set of particles of species 1, while Σ_j runs of all particles, either of species 1 or of species 2. Furthermore γ_1 is the mass concentration of particles of species 1 and

$$\mathbf{J}_\gamma(t) = \int d\mathbf{r} \mathbf{J}_\gamma(\mathbf{r}, t)$$

is the local concentration flux integrated over the whole system.

In the asymptotic formula for $D(t)$, a number of thermodynamical parameters appear, which need to be defined. Let $\mu = \mu_1 - \mu_2$ be the difference between the dynamical potential per unit mass of species 1 and 2, then $\mu_\gamma = \partial\mu/\partial\gamma_1|_{T, p}$ and $\mu_T = \partial\mu/\partial T|_{p, \gamma_1}$; furthermore D_1 is the thermodiffusion coefficient which is defined in such a way that the linearized hydrodynamic equation for γ_1 is

$$\frac{\partial \gamma_1}{\partial t} = D \Delta \mu + \frac{D_1}{T} \Delta T.$$

The quantities η_\pm are the roots of the equation

$$\eta_\alpha^2 + \eta_\alpha \left[\left(\frac{\kappa}{T} + 2D_1 \mu_T + DT \mu_T^2 \right) / C_p + D \mu_\gamma \right] + \frac{\mu_\gamma}{TC_p} (\kappa D - D_1^2) = 0$$

and C_p is the heat capacity per unit mass (contrary to the convention used throughout the whole paper, where C_p is the heat capacity per particle, which is obviously meaningless in a mixture). Let us only point out that one may recover from (4.12) the asymptotic formula given in (3.43), as in the limit of a low concentration $DT^2 \mu_T^2 \simeq D_1 T \mu_T \simeq 0$, $\eta_\pm = \kappa / TC_p$ and $\mu_\gamma D$ becomes the self diffusion coefficient defined from the Einstein formula.

4.2. Higher order terms in the Enskog expansion and in the asymptotics of time correlation functions

Up to now, we have focused our attention on the dominant part of the long time behavior of

the Green–Kubo integrands. Here we discuss the higher order corrections. As usual in any search for such terms, one has to consider a number of possible sources of corrections, each of them arising from improving one of the assumptions made in deriving the main contribution. Corrections to the $t^{-3/2}$ behavior of the Green–Kubo integrands may be computed up to order $t^{-2+\epsilon}$, i.e. by keeping terms of order $t^{-\alpha}$ with $\frac{3}{2} < \alpha < 2$, and these corrections are intimately connected with the so-called Enskog expansion of the hydrodynamical frequencies. More precisely, the usual frequency of a diffusive mode, say

$$\lambda^q = \mu q^2 \quad (4.13)$$

is the beginning of an infinite expansion (the Enskog expansion) of λ^q near $q = 0$.

Our starting point will be the definition of frequency-wavelength dependent transport coefficients given in (2.55). In this formula, the projector \hat{P}_q appears, which can be set equal to zero when $q = 0$ with a proper choice of the fluctuating current. However, in the two-mode coupling theory at the approximation considered here, it plays no role even for $q \neq 0$ and we shall completely neglect it from now on.

We have seen that, in the low frequency limit, the transport coefficients expand like (in this section, we write $\mu(q, \omega) \equiv \mu_{q, \omega}$):

$$\mu(q = 0, \omega) - \mu(0, 0) \simeq (i\omega)^{1/2}, \quad (4.14)$$

due to mode–mode contributions. A straightforward extension of any one of the methods leading to (4.14) provides the more general expansion of $\mu(q, \omega)$ near ω and $q = 0$; this leads to a sum of well defined integrals over the wave numbers of two interacting modes. These integrals can be performed analytically without restriction on the respective value of ω and q near 0; however, this general result is complicated [85, 87]. The most interesting limit corresponds to the case of hydrodynamics, where the frequency and wave number are related to each other by:

- i) $\omega \simeq \mu q^2$ for diffusive processes
- ii) $\omega \simeq icq + \Gamma q^2$ for the sound modes.

In both cases, accounting for the mode–mode contribution leads to:

$$\mu(q, \omega) - \mu(0, 0) \simeq q^{1/2} \begin{matrix} \omega \sim q^2 \\ \text{or } \omega \sim \pm icq \end{matrix} \quad (4.15)$$

The coefficients in front of the $q^{1/2}$ factor in (4.15) are given in refs. [86, 87].

Now, we may expect that this wave number frequency dependence of transport coefficients will modify the hydrodynamical frequencies themselves. The definition of these frequencies requires some care; indeed, the very notion of hydrodynamical modes is intimately connected with the exponential time behavior of long wave length perturbations. In the usual case, this is obtained by taking the Laplace inverse of $(i\omega + \mu q^2)^{-1}$; with frequency-wave number dependent transport coefficients, we now have to consider the Laplace inverse of:

$$[i\omega + \mu(q, \omega)q^2]^{-1}, \quad (4.16)$$

which is a very difficult problem because $\mu(q, \omega)$ remains largely unknown. Yet, as indicated by

(4.14), its expansion near ω and q equal 0 begins with a $\omega^{1/2}$ term: this manifests the existence of a cut in the ω -plane near $\omega = 0$ (this cut is exactly at $\omega = 0$ for $q = 0$, but, in the simplest two modes approximation, it is slightly shifted below $\omega = 0$ if $q \neq 0$).

To be more precise, consider again a model with a single diffusive mode and let us suppose that the mode–mode contribution to this diffusion coefficient $\mu(q, \omega)$ is built of two such modes; we have:

$$\mu(q, \omega) |_{\text{mode-mode}} \propto \int_{q' < q_0} \frac{d^3 q'}{(2\pi)^3} \left[i\omega + \left(\frac{q}{2} + q' \right)^2 \mu + \left(\frac{q}{2} - q' \right)^2 \mu \right]^{-1}, \quad (4.17)$$

where, as in (2.57), $\mu \equiv \mu(0, 0)$. As usual the quantity $\mu(q, \omega) |_{\text{mm}} - \mu(0, 0) |_{\text{mm}}$ can be made cut-off independent:

$$\begin{aligned} \delta\mu(q, \omega) &\equiv \mu(q, \omega) |_{\text{mm}} - \mu(0, 0) |_{\text{mm}} \\ &\propto \int_{\omega, q \rightarrow 0} \frac{d^3 q'}{(2\pi)^3} \left[\left(i\omega + \frac{\mu q^2}{2} + 2\mu q'^2 \right)^{-1} - (2\mu q'^2)^{-1} \right] \propto \left(\omega + \frac{\mu q^2}{2} \right)^{1/2} \Gamma_1, \end{aligned} \quad (4.18)$$

where Γ_1 is some constant.

The time dependence of the amplitude of the hydrodynamical mode is given by the Laplace inverse of:

$$\left[i\omega + \mu q^2 + \Gamma_1 q^2 \left(i\omega + \frac{\mu q^2}{2} \right)^{1/2} \right]^{-1}. \quad (4.19)$$

This function has a pole at:

$$\omega = i[\mu q^2 \pm i\Gamma_1 q^3 (\mu/2)^{1/2} + \dots], \quad (4.20)$$

but, owing to the square root, it also has a cut at $\omega = -\frac{1}{2} i\mu q^2$ which is closer to the origin than the pole. Hence, at fixed q , the cut contributions dominate the pole, being of order $q^{-2} t^{-3/2} \exp[-q^2 \mu t/2]$ compared to $\exp(-q^2 \mu t)$. Yet, the pole still dominates in the hydrodynamical limit:

$$q^2 \rightarrow 0 \quad t \rightarrow \infty \quad (q^2 t) \text{ finite.} \quad (4.21)$$

Albeit this non-uniform behavior of the hydrodynamical amplitude is rather unexpected and quite interesting [30, 34], we shall not discuss it anymore here because, when evaluating the mode–mode contributions to time correlation functions, we are precisely working in the limit (4.21). We are thus left with the calculation of the generalized hydrodynamic frequencies λ^q which are solutions of the dispersion equation:

$$\lambda^q = q^2 \mu(q, -i\lambda^q) \quad (4.22)$$

or

$$\lambda^q - q^2 \mu = [\mu(q, -i\lambda^q) - \mu(0, 0)] q^2 \propto q^{5/2} \quad (4.23)$$

from (4.15).

This result of course suggests an iteration procedure: starting from the usual Navier–Stokes value for the hydrodynamical frequency and from the mode–mode contribution to the Green–Kubo integrands, one is able to get the next order term in the Enskog expansion for λ^q . Inserting back this last value in the mode–mode contribution to λ^q , we now generate a $q^{7/4}$ term for λ^q , and so on. In this way, one gets from (4.22) an infinite series:

$$\lambda^q \simeq \mu q^2 + \mu_1 q^{5/2} + \dots + \mu_k q^{3-2^{-k}} + \dots \quad (4.24)$$

The three sets of coefficients μ_k (one set for each of the three distinct hydrodynamic modes) are given by means of coupled linear recurrence relations. The infinite series (4.24) are given by the solution of coupled linear integral equations, which have not been solved in full generality, although some progress has been made toward their solution [89, 90]. Let us still add that our derivation of (4.24) has been very sketchy; in particular, we have tactily neglected any correction arising from:

- i) the wavelength dependence of the equilibrium fluctuations,
- ii) the three- and more mode couplings,
- iii) microscopic processes which cannot be described in terms of hydrodynamical modes.

The discussion of these points is given in refs. [31–34] where it is shown that, to the order considered here, the present simplified treatment is legitimate.

The existence of these infinite expansions has various consequences. The most direct one is a similar expansion near $\omega = 0$ for the Laplace transform of the Green–Kubo integrands; from the so-called Tauberian theorems [57] one deduces that for long times these correlation functions behave like:

$$X(t) \sim \sum_{j=1}^{\infty} X^{(j)} t^{2-j-2} \quad (4.25)$$

This property holds, in particular, for the velocity correlation function of a tagged particle in an equilibrium fluid. By time integration, we obtain a generalization of the Einstein formula (1.1):

$$\langle \Delta r_1^2(t) \rangle = 6Dt + \sum_{j=1}^{\infty} O(t^{2-j}). \quad (4.26)$$

These expansions also provide a natural framework for extending the results of the Navier–Stokes equations to smaller distances and shorter times. In any problem of hydrodynamics, a large length or a small frequency does appear; for example, in a stationary drag problem, one must assume, usually implicitly, that the characteristic size of the drifting body, say R , is much larger than any molecular length. Roughly speaking R^{-1} plays a role similar to the wave number q in expansion like (4.24). Hence, we expect that the drag coefficient C of an object of size R should expand like:

$$C \propto R \left[1 + \sum_{n=1}^{\infty} O(R^{-2-n}) \right]. \quad (4.27)$$

This could be relevant, for example, in computing the diffusion coefficient of a Brownian particle in a critical fluid, wherein the correlation length can be made very large.

More phenomenological approaches to the calculation of the corrections discussed in this section have also been proposed [91].

4.3. Mode–mode coupling in 2d fluids

As explained at the beginning of this review, the velocity time correlation of a particle seems to decrease like $t^{-d/2}$ at large times. Hence, in 2d fluids, the self diffusion coefficient, which is the integral of this time correlation, should diverge logarithmically; this is one more of the many peculiarities of 2d many-body systems. This same divergence should hold for any other transport coefficients in a 2d fluid, for example the shear viscosity. Yet, this shows that the “proof” of this divergence is just invalid, because it needs as a basic ingredient the very existence of transport coefficients and the conclusion is precisely that these coefficients do not exist!

This strange behavior of 2d fluid was first discovered by two different approaches: Alder and Wainwright [9–11] deduced it from computer experiments on hard discs; they presented at the same time an explanation of this phenomenon which is essentially the one we have given in the introduction. Approximately at the same time, one of the authors of this review (Y.P.) studied [92] the renormalization of the virial expansion of the collision operator, as proposed by Kawazaki and Oppenheim [80]; he concluded that this renormalization fails for a 2d gas of identical particles, due to hydrodynamical modes; he also pointed out that this new divergence was non renormalizable, due to the absence of any low frequency–low wave number cut-off for hydrodynamical phenomena.

However, a striking difference appears between the two approaches: the Landau–Placzek analysis leads to a divergence of the transport coefficients themselves, while kinetic theory shows a divergence of the collision operator (see (3.62)) so that the transport coefficient which is, roughly speaking, the inverse collision operator (see (2.91)) should vanish! In fact, there is no real contradiction, as both methods are inconsistent: the Landau–Placzek theory assumes from the beginning the existence of transport coefficients and concludes that they do not exist; the kinetic theory assumes that the ring collision term is small compared to the Boltzmann collision operator and concludes that it is infinite! Thus, one is left with the qualitative properties of 2d fluid: transport coefficients in 2d fluid cannot be both finite and non vanishing. Yet important questions remain to be answered:

i) What is the long time behavior of the Green–Kubo integrands? and are the corresponding transport coefficients zero or infinite?

ii) What does replace the usual linear and local (in space and time) relations between fluxes and thermodynamical forces, as the Fourier law for the heat flux?

Attempts to answer these questions have been made by Kawazaki [25] and Alder and co-workers [11]. Their analysis goes as follows: in the Landau–Placzek approach the mode–mode contribution to a transport coefficient is:

$$\mu(\omega, 0)|_{mm} = M \int_{q \leq q_0} \frac{d^d q}{(2\pi)^d} \frac{1}{i\omega + 2\mu q^2}, \quad (4.28)$$

where we consider again a hypothetical fluid with a single diffusive mode μq^2 ; M is some parameter which depends on static fluctuations only. For $d = 2$, the right-hand side of (4.28) logarithmically diverges at $\omega = 0$ but, at the same time one is no longer allowed to take μ as a

constant, since it diverges at $\omega = 0$. Accounting for this dependence, we should obtain instead of (4.28):

$$\mu(q, \omega)|_{\text{mm}} = M \int_{q < q_0} \frac{d^2 q'}{(2\pi)^2} \frac{1}{i\omega + \lambda(|q/2 + q'|) + \lambda(|q/2 - q'|)} \quad (4.29)$$

where the hydrodynamical frequency $\lambda(q)$ is related to $\mu(q, \omega)$ itself by (4.22). Equation (4.29) is extremely complicated to solve, even if we disregard any non mode–mode contribution to $\mu(q, \omega)$. Hence, Kawasaki and Alder and coworkers have not only neglected such contributions but they also assumed that μ depended on ω only: $\mu(q, \omega) = \mu(\omega)$. This allows one to replace (4.29) and (4.22) by:

$$\mu(\omega) = M \int_{q < q_0} \frac{d^2 q'}{(2\pi)^2} \frac{1}{i\omega + \lambda(q') + \lambda(-q')}, \quad (4.30)$$

with

$$\lambda(q) = q^2 \mu[-i\lambda(q)]. \quad (4.31)$$

A further assumption takes place, which is checked a posteriori: one replaces $\mu[-i\lambda(q)]$ by $\mu(\omega)$ in (4.30); this gives:

$$\mu(\omega) \simeq \frac{M}{2\pi} \int_0^{q_0} \frac{q dq}{i\omega + 2q^2 \mu(\omega)} \simeq \frac{M}{8\pi} \frac{\ln \omega}{\mu(\omega)} \quad (4.32)$$

which leads to the self-consistent solution:

$$\mu(\omega) \underset{\omega \rightarrow 0}{\simeq} \left(\frac{M}{8\pi} \right)^{1/2} (\ln \omega)^{1/2}. \quad (4.33)$$

This corresponds to a long time behavior of the inverse Laplace transform (i.e., of the Green–Kubo integrand) presumably of the type $(\ln t)^{-1/2}/t$; notice that the coefficient in front of this $(\ln t)^{-1/2}/t$ only depends on equilibrium properties. The validity of replacing $\mu[-i\lambda(q)]$ by $\mu(\omega)$ is easily checked; indeed, from the final result (4.33) we have:

$$\lambda(q) \underset{q \rightarrow 0}{\simeq} q^2 \left(\frac{M}{8\pi} \right)^{1/2} \sqrt{\ln q} \quad (4.34)$$

which, once inserted into (4.30), preserves the answer (4.33).

Alder et al. have tried to check this behavior on computer experiments but this turned out to be too difficult in view of the very weak logarithmic dependence which was looked at.

The assumption leading to (4.33) could be checked more easily in a one-dimensional fluid. Supposing that generalized hydrodynamic modes still exist, the divergence of $\mu(\omega)$ is expected to be stronger than at $d = 2$, since (4.30) is now replaced by:

$$\mu(\omega) = \frac{M}{2\pi} \int_{q < q_0} \frac{dq}{i\omega + \lambda(q) + \lambda(-q)}. \quad (4.35)$$

Supposing:

$$\lambda(q) \underset{q \rightarrow 0}{\propto} q^{\alpha+2} \quad (4.36)$$

where α is to be determined self-consistently, we get:

$$\mu(\omega) \underset{\omega \rightarrow 0}{\propto} \omega^{-(\alpha+1)/(\alpha+2)} \quad (4.37)$$

and from the dispersion relation (4.31)

$$\alpha = -\frac{1}{2} \quad (4.38)$$

and hence:

$$\mu(\omega) \propto \omega^{-1/3}; \quad (4.39)$$

this corresponds to an asymptotic behavior like $t^{-2/3}$, instead of the $t^{-1/2}$ decay obtained when taking $\lambda(q) \propto q^2$.

Recently a model of lattice fluid has been proposed [93] where the vorticity diffusion is essentially a one-dimensional process: the result of computer experiments agrees fairly well with the $t^{-2/3}$ asymptotic law. However this one-dimensional result is certainly not universal, as shown by the exact calculation of Lebowitz et al. [94] for the hard rod fluid: they find a t^{-3} law for the decay of the velocity correlation function; the discrepancy of this result with (4.39) is obviously due to the absence of fluid hydrodynamic modes in this model.

The study of the asymptotic decay of the Green–Kubo integrands does not suffice to settle all questions in 2d transport theory. Of course, this allows one to find, in the linear approximation, the behavior of a thermodynamical flux, say $Y(t)$, due to a time varying force, say $F(t)$; Y being for example the heat current and F the temperature gradient, we have, in this linear approximation:

$$Y(t) = \int_{-t}^t dt' \kappa(t-t') F(t'), \quad (4.40)$$

with, presumably, $\kappa(t) \propto_{t \rightarrow \infty} (\ln t)^{-1/2}/t$. Hence, if $F(t)$ starts at $t = 0$ and remains constant at any positive time, the flux $Y(t)$ grows indefinitely like $(\ln t)^{1/2}$ for large times. Of course, the linear approximation cannot be maintained indefinitely. If a steady stage is reached in the long term, then we must admit that Y , in this stationary state, is a function of F which cannot be proportional to F near $F = 0$ (otherwise, the constant of proportionality would be a well defined transport coefficient) and could behave like $F(\ln F)^{1/2}$ near $F = 0$, or something like that [86, 95]. But it is also possible that no stationary relation between F and Y exists. Perhaps size effects should also be taken into account; for instance, it is known that in a one-dimensional harmonic chain the heat flux does not depend on the temperature gradient but on the temperature difference between the ends [95].

To conclude, we see that the transport properties for 2d and even 1d fluids are far from settled; in particular, as long as the phenomenological and stochastic approaches have not been shown to be consistent with the kinetic theory results, some doubt remains as to the validity of the results derived above. For example, it is not excluded that in the very long time limit, the $1/t$ behavior

in 2d (or the “self-consistent” $(\ln t)^{-1/2}/t$) ceases to be valid. This last remark is born out by the fact that, if we take as a *model* the 2d Choh–Uhlenbeck result for self-diffusion (see (2.91), (3.62)):

$$D_z|_{\text{c.u.}} = 1/(-iz + \mu_r + i\mu_r(a^2n) \ln(za/v)), \quad (4.41)$$

we find indeed an asymptotic behavior $\propto 1/t$ for the inverse Laplace transform in the “intermediate” time regime $\mu_r^{-1} \ln(1/a^2n) < t < (a/v)\exp(-1/a^2n)$ because, for such times, it is legitimate to use the expansion:

$$D_z|_{\text{c.u.}} = \frac{1}{-iz + \mu_r} - \frac{i(a^2n)\mu_r \ln(za/v)}{(-iz + \mu_r)^2} + \dots \quad (4.42)$$

Yet, in the very long term, the logarithmic factor dominates in the denominator of (4.41) and leads to a different behavior, of the type $[t(\ln t)]^{-1}$; moreover the whole time integral of this Green–Kubo integrand is such that the transport coefficient D_0 vanishes! We shall not dwell on this example any further, in particular because the logarithmic term in (4.41) should more realistically be replaced by a much more complicated self-consistent expression; we nevertheless feel that this model illustrates nicely the type of difficulties and the kind of surprise which may very well emerge from a more careful analysis of 2d and 1d system.

4.4. Transport properties of the Van der Waals fluid

The Van der Waals theory for the equilibrium properties of classical fluids is based on the idea of separating the pair interaction between the particles into a short range repulsive part V^R and a long range small attractive part V^L . In modern language, one writes:

$$V = V^R(r) + \gamma^3 V^L(\gamma r) \quad (4.43)$$

where the parameter γ measures the inverse range of V^L and is such that the average attractive energy:

$$\gamma^3 \int d^3r V^L(\gamma r) \quad (4.44)$$

remains finite in the limit $\gamma \rightarrow 0$; γ plays the role of a smallness parameter and can be used to develop various perturbation methods for the thermodynamical properties and the correlation functions of the system. In these calculations, the properties of the short range reference system are assumed to be known [98–100].

In particular, it has been rigorously proved, under very general conditions, that the $\gamma \rightarrow 0$ limit leads to the Van der Waals type equation of state combined with the Maxwell equal area construction [101].

It is of course of much interest to get analogous results for the transport properties of the Van der Waals fluid; because the parameter γ introduces a small wave number, we may expect a priori that long wavelength contributions, described in terms of hydrodynamical modes, will play an important role in the dynamics of this Van der Waals system. This conjecture has been verified by the kinetic theory method briefly sketched in section 3.3: using the renormalized form of the collision operator, it was shown that the dominant correction to transport coeffi-

cients due to V^L is of order γ , and arises from a coupling between two modes quite analogous to the one leading to the $t^{-3/2}$ decay for the Green–Kubo integrands [62, 81, 102]. However as already stressed, the kinetic approach involves an enormous amount of technicality and we shall limit ourselves here in sketching how the results can be recovered by using the much simpler phenomenological Landau–Placzek approach.

Consider again the example of the Green–Kubo formula (4.1, 5) for thermal conductivity. Of course the flow J^k , eqs. (4.2, 3, 4), now depends on the long range potential V^L .

To dominant order in γ , we assume that the correction to κ due to this long range potential arises from slowly decaying long wavelength phenomena for which the Landau–Placzek method of section 3.2 may be applied. Three modifications occur as compared to the short range reference system:

- i) the long range potential explicitly occurs in the flows (4.3, 4);
- ii) the long wavelength static correlations are still of the Gaussian type but their explicit form has to be slightly modified. Consider for example the density fluctuations probability (2.23). This formula is valid only if q is smaller than any molecular inverse length, including γ ; however, it was shown by Van Kampen [98] that Gaussian fluctuations persist in the range $q \sim \gamma$ provided that χ_T is replaced in (2.23) by the wave number dependent susceptibility*:

$$\chi_T \rightarrow \chi_T(q\gamma^{-1}) = \left[\frac{\partial p}{\partial n} \Big|_T^R + n V_{q\gamma^{-1}}^L \right] \quad (4.45)$$

where the superscript R refers to the short range reference system. Due to this difference in the statistical weight, we see that the equilibrium fluctuations of the Van der Waals fluid differ from the reference system for $q\gamma^{-1} \sim 1$. A similar modification occurs for the energy fluctuations while, of course, the velocity fluctuations are unaffected (see (2.24));

iii) similarly, we have to modify the equations of linearized hydrodynamics obeyed by the fluid conserved variables. For doing this, we simply assume that the presence of the long range potential induces an average field term in the Navier–Stokes equation [103–105]; although a detailed justification of this procedure is quite delicate [62], it can be understood by analogy with another long range force problem – namely the Coulomb potential – where it is known that the dominant dynamical effect of these forces is precisely to introduce such a mean field (or Vlasov) term [50].

In the Navier–Stokes equation (2.86), we substitute therefore:

$$\frac{1}{\rho} \frac{\partial p}{\partial n} \Big|_T \rightarrow \frac{1}{\rho} \frac{\partial p}{\partial n} \Big|_T^R + \frac{1}{m} V_{q\gamma^{-1}}^L. \quad (4.46)$$

We now write the long wavelength part of the local equilibrium form of the flow (4.3) as (compare with (4.6))

$$J^k(t) = \sum_{q < q_0} \left[n h_q^R(t) v_{-q,x}(t) + \frac{1}{2} V_{q\gamma^{-1}}^L n_q(t) v_{-q,x}(t) + \frac{1}{2} n_q(t) v_{-q}(t) \frac{\partial}{\partial q_x} (q V_{q\gamma^{-1}}^L) \right], \quad (4.47)$$

where we have introduced a small cut-off wave number q_0 such that $q_0 \gg \gamma$. Indeed, we expect

*We use the convenient definition $V_y^L = \int d^3r V^L(r) \exp(iy \cdot r)$, for the Fourier transform of the long range potential.

that for $q \gtrsim q_0$ the reference system and the Van der Waals fluid behave exactly in the same way and the region $q > q_0$ should therefore not contribute to the correction due to V^L . Moreover, the first two terms represent the approximate enthalpy flow where only quadratic deviations from equilibrium are retained; it can be shown again that cubic deviations (as $n_q h_q v_{-q-q'}$, $q, q' \neq 0$) lead to negligible contributions for $\gamma \rightarrow 0$.

Expressing h_q^R in terms of n_q and T_q in (4.47), we are now in a situation allowing us to apply the Landau-Placzek machinery in a straightforward manner; we merely have to account for the above remarks ii) and iii). We shall not reproduce here the details of these calculations. Subtracting the corresponding contributions from the reference system, we obtain:

$$\kappa - \kappa^R = \frac{\gamma k_B}{6\pi^2 m} \int_0^\infty dy \left\{ \left[1 + \frac{n}{2c^2(y)m} y \frac{\partial V_y^L}{\partial y} \right]^2 \frac{mc^2(y)}{2F(y)} - \frac{m(c^R)^2}{2\Gamma^R} + 2T \left[\frac{C_p(y)}{\nu^{R+\kappa^R}/nC_p(y)} - \frac{C_p^R}{\nu^{R+\kappa^R}/nC_p^R} \right] \right\}, \quad (4.48)$$

where the cut-off has been pushed to infinity.

Similarly one finds for the shear viscosity:

$$\eta - \eta^R = \frac{\gamma k_B T}{60\pi^2} \int_0^\infty dy \left\{ n^2 \chi_T^2(y) \left[\frac{\gamma(y)-1}{\gamma(y)} \right]^2 \left(ny \frac{\partial V_y^L}{\partial y} \right)^2 \frac{nC_p(y)}{2\kappa^R} + \left(1 + \frac{ny}{2c^2(y)} \frac{\partial V_y^L}{\partial y} \right)^2 \frac{1}{\Gamma(y)} - \frac{1}{\Gamma^R} \right\}; \quad (4.49)$$

the corresponding formula for the bulk viscosity is too long to be displayed here (see [81]). In these equations, we have introduced the dimensionless variable y for the quantity $q\gamma^{-1}$; all y dependent quantities in (4.49) then represent finite y generalization of the corresponding thermodynamical coefficient of the Van der Waals fluid; on the other hand, the Onsager transport coefficient themselves remain the ones of the reference system to this order of approximation. For example, the sound velocity:

$$c^2 = \left(\frac{C_p}{C_v} \frac{1}{n\chi_T} \right)_{\text{Van der Waals}} \equiv \frac{C_p^R}{mC_v^R} \frac{\partial p}{\partial n} \Big|_T^R + \frac{n^2}{m} V_0^L \quad (4.50)$$

is generalized into:

$$c^2(y) = \frac{C_p^R}{mC_v^R} \frac{\partial p}{\partial n} \Big|_T^R + \frac{n^2}{m} V_y^L. \quad (4.51)$$

Similarly:

$$C_p(y) = C_p^R + \frac{T}{n} \left[\left(\frac{\partial p}{\partial T} \right)_n^R \right]^2 [\chi_T(y) - \chi_T^R] \quad (4.52)$$

$$C_v(y) = C_v^R \quad (4.53)$$

$$\gamma(y) = C_p(y)/C_v(y) \quad (4.54)$$

$$\Gamma(y) = \frac{1}{2} \left[\frac{(4\eta^R/3 + \zeta^R)}{\rho} + \left(\frac{1}{C_v(y)} - \frac{1}{C_p(y)} \right) \frac{\kappa^R}{n} \right] \quad (4.55)$$

with

$$\chi_T(\gamma) = \frac{n^{-1}}{\partial p / \partial n|_T^R + n V_y^L}. \quad (4.56)$$

Of course, the remarkable feature of this result is that it only requires the knowledge of the equilibrium and transport properties of the reference system (and of course of V_y^L) but is totally independent of the detailed properties of the short range dynamics; this is a feature which is common to all mode–mode coupling calculations.

Results similar to (4.48, 49) were obtained previously by Zwanzig and al. and by Kawasaki [103–105]; their method was very similar to the one displayed here but they assumed moreover that the short range part of the flow \hat{J}^x was rapidly decaying and did not contribute to the corrections studied. With our present understanding of the Green–Kubo integrands, we know that this assumption is in error: the purely short range part decays slowly for long times, due to coupled hydrodynamical mode propagation. As this propagation is different in the reference fluid and in the Van der Waals fluid, we get thus an extra-contribution. As a matter of fact, the reader can easily check that eqs. (4.48, 49) are nothing else than the time integral of the difference between the asymptotic behavior of the corresponding Green–Kubo integral for respectively the reference and the Van der Waals fluid; yet, in this latter case, no $t^{-3/2}$ behavior is recovered (except for times $t \gg \gamma^{-2}$) because of the complicated wave number dependence of V_y^L .

Let us point out that, to the order of approximation considered here, the first correction to the self-diffusion coefficient vanishes identically:

$$\lim_{\gamma \rightarrow 0} \frac{D - D^R}{\gamma} = 0. \quad (4.57)$$

The reason for this is apparent in (3.43): the dominant mode–mode coupling involves the combination of ν^R and D^R :

$$\nu^R + D^R \quad (4.58)$$

which both are γ -independent; hence, their contribution is the same in the presence or in the absence of V^L . The first non trivial correction appears to be of order γ^2 ; as it is of little more than academic character, we shall not reproduce it here [107, 108].

This theory has also been extended to binary mixtures [106].

4.5. Critical dynamics

As already stressed, critical dynamics is a vast subject and it is out of question to review it here in detail (see [46, 82, 83]); we shall limit ourselves in indicating how mode–mode coupling plays a prominent role in this theory.

To illustrate this point, consider again the correction to the viscosity of the Van der Waals fluid due to the coupling between two heat modes; we denote it $\delta\eta_{ss}$; from eq. (4.49), we have:

$$\delta\eta_{ss} \propto \gamma \int_0^\infty dy [n\chi_T(\gamma)]^2 \left(\frac{\gamma(\gamma) - 1}{\gamma(\gamma)} \right)^2 \left(n\gamma \frac{\partial V_y^L}{\partial y} \right)^2 \frac{C_p(\gamma)}{\kappa^R}. \quad (4.59)$$

It is easily seen that, when the temperature is decreased, we finally reach a temperature T_c , such that, for a well defined density n_c , the zero wave number compressibility $\chi_T(0)$, eq. (4.45), becomes singular; we then have:

$$-n_c V_0^L = \left. \frac{\partial p}{\partial n_c} \right|_{T_c}^R, \quad (4.60)$$

which defines the critical point of our model.

Of course, it is known that the equilibrium γ -expansion fails to converge close to the critical point [100]; moreover, eq. (4.59) was derived under the assumption that all thermodynamical coefficients were well behaved, and this is also invalid near (n_c, T_c) . Nevertheless, let us provisionally forget about these difficulties and let us investigate, in the most naive way, the consequences of (4.60) on (4.59). We consider a temperature T such that

$$0 < \frac{T - T_c}{T_c} \equiv \epsilon \ll 1 \quad (4.61)$$

and we look, in the integral (4.59), at the region where $y \ll 1$. Expanding the denominator in (4.56) with the help of:

$$\left. \frac{\partial p}{\partial n_c} \right|_T^R \equiv \left. \frac{\partial p}{\partial n_c} \right|_{T_c}^R + \alpha \epsilon + \dots, \quad V_y^L = V_0^L + y^2 \frac{1}{2} \left. \frac{\partial^2 V^L}{\partial y^2} \right|_0 + \dots, \quad (4.62)$$

we get the well known Ornstein-Zernike equation:

$$\chi_T(y) \propto \frac{1}{\xi_\gamma^{-2} + y^2} \quad (4.63)$$

where

$$\xi_\gamma \equiv \left(\frac{\alpha \epsilon}{\frac{1}{2} n \left. \frac{\partial^2 V^L}{\partial y^2} \right|_{y=0}} \right) \propto \sqrt{\epsilon^{-1}}, \quad (4.64)$$

defines the correlation length in units of γ^{-1} ; the usual correlation length is simply $\xi = \xi_\gamma \gamma^{-1}$; ξ and ξ_γ diverge at the critical point.

From (4.13, 15), we have the estimate:

$$\gamma(y) \sim 1 \quad (4.65)$$

and

$$y \left. \frac{\partial V^L}{\partial y} \right|_0 \sim y^2. \quad (4.66)$$

Hence the contribution to (4.59) coming from the region $y \ll 1$ (or $q \ll \gamma$) is of the order:

$$\delta \eta_{ss} \sim \gamma \int_0^\infty \frac{dy y^4}{(y^2 + \xi_\gamma^{-2})^2} \frac{C_p(y)}{\kappa^R} \sim \frac{\gamma \xi_\gamma^{-1} C_p(0)}{\kappa^R}, \quad (4.67)$$

where we have found it convenient not to use the result of (4.52) $C_p(0) \propto \xi^2$. For γ small but finite, this "correction" becomes infinite when T_c is approached and dominates the short range term η^R . Similarly we would find that $\delta \kappa = \kappa - \kappa^R$ is not small when T_c is approached.

Strictly speaking, these results indicate that our simple theory is inadequate close to T_c . However, qualitatively, it is quite easy to “repair” this inadequacy: we have simply to put the full transport coefficients in the mode–mode term, instead of their value in the reference fluid. Then (4.67) becomes a self-consistency condition:

$$\eta|_{s_s} \kappa \sim \xi^{-1} C_p(0), \quad (4.68)$$

where we have dropped the factor γ which is a small but finite constant. If we use $C_p(0) \sim \xi^2$, we get instead of (4.68):

$$\eta|_{s_s} \kappa \sim \xi, \quad (4.69)$$

the indication of a necessary divergence either in κ or in η .

Though the above argument, based on the unjustified use of the Van der Waals model, is admittedly very crude, the final result – in particular in the form (4.68) – is not as bad as it might appear first. As we shall see soon, the more adequate theory of Kadanoff and Swift reproduces similar results [16].

We have already sketched, in section 3.2, how these authors built up a formalism which introduces mode–mode coupling effects at the level of the formal solution of the Liouville equation. A second ingredient of the theory is the model independent definition of wave number dependent thermodynamical coefficients*. This is very simply done when we realize that a formula like the fluctuation theorem [43]:

$$nk_B T \chi_T = \lim_{q \rightarrow 0} \langle \hat{n}_q \hat{n}_{-q} \rangle \quad (4.70)$$

can be extended to define a wave number dependent compressibility:

$$nk_B T \chi_T(q) = \langle \hat{n}_q \hat{n}_{-q} \rangle. \quad (4.71)$$

Of course, in general, such a definition is of no much help because the right-hand side cannot be evaluated explicitly. Yet, close to T_c , when ξ (which can still be defined for realistic systems) \gg any molecular length, we can use the idea of “static scaling” to assume that the generalized compressibility, which generally depends separately on the parameters q and ξ^{-1} , is in fact a homogeneous function:

$$\chi_T(q, \xi) = q^u f(q\xi), \quad (4.72)$$

where $f(X)$ is an unknown but well defined function which tends to a constant for $X \rightarrow 0$. A justification of (4.72) falls out of the scope of the present work (see for example [83]); let us simply stress that, in estimating the divergence of integrals of the type (4.59), the explicit form of the function $f(q\xi)$ is irrelevant. Moreover the exponent u can be determined from purely thermodynamical properties because, for $q \ll \xi^{-1}$:

$$\chi_T(q, \xi) \propto \xi^u \quad (4.73)$$

as an immediate consequence of the homogeneity of the function f .

*An explicit realization of such quantities is of course offered by (4.52, 56) in the Van der Waals limit.

With these ideas, the Kadanoff–Swift theory runs along lines very parallel to all the previous examples. Let us simply mention the few points where differences appear:

i) because the wave number q is not necessarily the smallest parameter of the problem (very close to T_c , we may very well have a regime $q\xi \gg 1$), the transport modes cannot be written in the simple form:

$$\lambda_\alpha^q = q^2 \mu_\alpha(\xi) \quad (4.74)$$

where μ_α solely depends on temperature (see (4.64)) but one should retain the complete wave number and frequency dependence of μ_α (see also (2.55)):

$$\lambda_\alpha(q, \omega) = q^2 \mu_\alpha(\xi, q, \omega); \quad (4.75)$$

ii) because of the absence of a smallness parameter in the problem, one is not allowed to retain only two mode terms; as a matter of fact, there is good indication that many mode terms contribute equally to the diverging transport coefficients. Fortunately, simple dimensional arguments show that this does not affect the nature of the divergence (and, especially the value of the dynamical critical exponents), found by taking only two and three modes couplings.

iii) As already illustrated by (4.68), this divergence is determined by solving self-consistently homogeneous mode–mode coupling equations. Indeed, the regular term (as η^R in the Van der Waals fluid), which describes the short range effects, remains finite at T_c and is thus irrelevant*.

With these remarks in mind, the mode–mode coupling machinery can be applied straightforwardly; the only difficulty is the large number of equations (corresponding to the various transport coefficients and to the various frequency regimes) which have to be solved simultaneously. We shall not display these equations here; let us simply mention that our naive estimate (4.27) turns out to be one of these equations provided that we substitute:

$$\eta|_{ss} \rightarrow \eta(\xi, 0, 0)|_{ss}; \quad \kappa \rightarrow \kappa(\xi, \xi, \xi^2 \kappa). \quad (4.76)$$

Of course, in this model independent calculation, one should take the actual – and not the Van der Waals – critical behavior for the static quantities; roughly speaking, one has:

$$\xi \sim \epsilon^{-2/3}; \quad C_p \sim \epsilon^{-4/3}. \quad (4.77)$$

It would be out of place to present here the detailed results of this theory; let us simply mention that it has been remarkably confirmed by experiments (see [109]) for an exhaustive list of references). Moreover, it has been extended with success to binary mixtures [46, 110]. Finally, similar ideas have also been applied to magnetic systems [14, 15, 46, 111, 112] and to phase transitions in superfluids [46, 113, 114]; we shall not discuss these problems here.

5. Final remarks

Although we have thus far given a fairly complete review of the theoretical aspects of mode–mode coupling problems, very little has been said about the relevance of these calculations to

*This regular term is “theoretically irrelevant” because one looks at the nature of the singularity; yet, it is “experimentally relevant” in governing the regular background to which the singular part is added.

experimental problems. First of all, we should stress that hydrodynamical phenomena are of such a fundamental importance in the understanding of time dependent correlation functions, that the purely theoretical aspects of the problem are of an enormous interest in themselves. Yet, it is also essential to inquire about the experimental relevance of these effects.

The most spectacular success of mode–mode-coupling theory is without doubt the correct prediction of the singularities of some of the transport coefficients close to the critical point (see [109] and references quoted therein, as well as [145–148] for some key experimental papers on simple fluids and binary mixtures). However, a detailed analysis of these results would fall out of the scope of the present paper and it would require by itself a whole review. Thus, we shall limit ourselves here to a discussion of non-critical systems. Two difficulties appear in this case: – for some apparently accidental reason, the numerical coefficients which weight the decay law of the correlation functions for long times are generally quite small and the effects are thus hard to put in evidence; – as is clear from the previous sections, the only thing theory can predict is the asymptotic behavior of these correlation functions in the limit of long time but no estimate exists yet of the time after which this asymptotic stage is reached; in particular, the occurrence of the sequence $t^{-3/2}$, $t^{-7/4}$... for the first few terms does not help in making a clearcut separation between the initial exponential like (or Gaussian like) relaxation and the final asymptotic behavior. This makes that any simple dimensional argument (based on the idea that the $t^{-3/2}$ behavior becomes correct as soon as the contribution to integrals over wave numbers (see (3.42)) come from q values much smaller than inverse molecular dimensions) is very doubtful.

Probably for these reasons, very little has been reported on experiments on realistic systems which would support the slow decay of the Green–Kubo integrands; let us mention a remark by Andriess [115] suggesting that inelastic neutron scattering data on argon are best fitted by a theoretical model including a non-analytic $\omega^{1/2}$ behavior (see (4.14)) for the Fourier transform of the velocity correlation function; the moderate accuracy of the data does not lead however to conclusive evidence. Another, more recent, result concerns the verification of the generalized Brownian motion theory discussed in section 3.1 [116] by observing the motion of latex particles in air and argon after they have been triggered by a shock wave: the relaxation starts to be exponential, with a characteristic time τ_r , but for times $t \gtrsim 2.5 \tau_r$, the decay of the velocity is consistent with a $t^{-3/2}$ law; though, here also, no definite conclusion has been reached. Let us moreover stress that, even if such an experiment would lead to complete agreement with theory, it would still be far from proving the existence of microscopic mode–mode effects between the molecules in a fluid. Finally, we may still point out an interesting suggestion by Harris [117] which indicates the possibility of proving the slow decay of the Green–Kubo integrand for diffusion by electrical conductivity measurements.

As one can see, the balance with theory is quite meager on the “truly” experimental side and to get more results, we have to come back to the “computer experiments” which, as discussed in the introduction, started the whole problem, for non-critical classical fluids at least. As the field has been reviewed quite recently by Wood [118] we shall be rather brief. The most salient results are the following:

i) For hard discs in 2d, the Alder and Wainwright data clearly show a $1/t$ behavior for the velocity correlation function D_t , for times of the order of 10 to 30 collision times [9], up to packing fraction v/v_0 (v is the volume per molecule, v_0 the volume at close packing) of the order 2, for which computer experiments have been carried out. Moreover the value of the coefficient

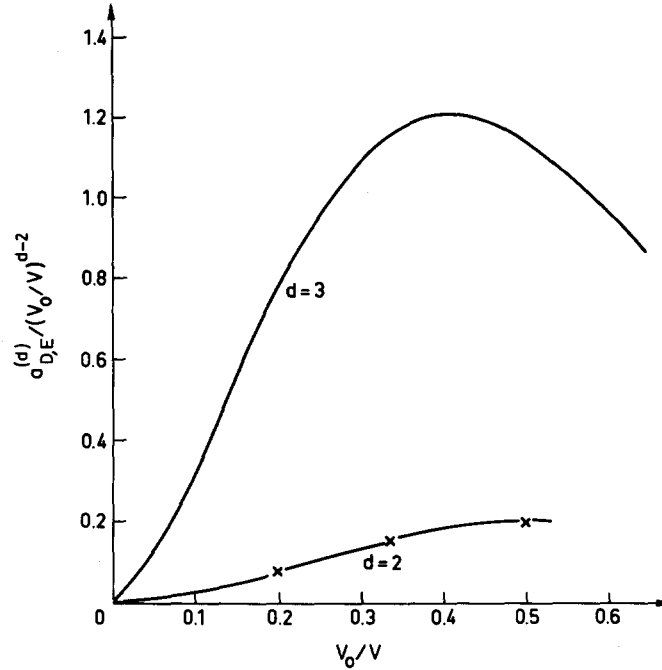


Fig. 5.1. The ratio $\lim_{t \rightarrow \infty} D(t)/t^{-d/2}$ as a function of density (taken from ref. [29]): crosses indicate computer experiment data. (V is the volume per particle and V_0 this same volume at close packing.)

α defined by:

$$D(t) = \alpha/t \quad (5.1)$$

agrees well with the theoretical predictions [29], as is illustrated in fig. 5.1. These results are also confirmed by an interesting calculation of Erpenbeck and Wood [119] who computed the diffusion coefficient, at time t , as the ratio:

$$D(t) = \langle J_x(r, t) \rangle / \langle \nabla_x n_1(r, t) \rangle, \quad (5.2)$$

where $\langle J_x(r, t) \rangle$ denotes the average flow of tagged particles and $\langle \nabla_x n_1(r, t) \rangle$ their average density gradient. Clearly, for a "normal" situation, D_t should tend to a constant for large enough times; however, the experiment is consistent with a growing of D_t like:

$$D(t) \propto \int_0^t \frac{dt}{t} \simeq \ln t. \quad (5.3)$$

Let us stress that the times for which (5.1, 3) have been verified are not very long and these results do not refute the possibility of a more complicated behavior at larger times.

Finally, Carlier and Frisch [120] have performed an interesting calculation for hard squares which displays a similar t^{-1} behavior.

ii) For hard spheres, the situation is less favorable (precise calculations are harder) but, never-

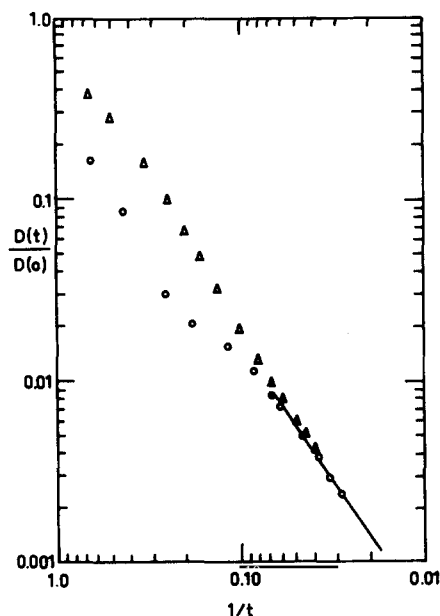


Fig. 5.2. Comparison of the velocity autocorrelation function as a function of time (in terms of mean collision times) between the hydrodynamic model (circles) and a 500-hard-sphere molecular-dynamic calculation (triangles) at a volume relative to close packing of 3 on a log-log plot. The straight line is drawn with a slope corresponding to $t^{-3/2}$. (Taken from ref. [10].)

theless, at not too high densities ($v/v_0 \gtrsim 3$), one can see quite convincingly the $t^{-3/2}$ behavior for the velocity autocorrelation function, as illustrated in fig. 5.2. The line corresponds to hydrodynamical theory, neglecting however the self-diffusive motion of the tagged particle.

Notice moreover that at higher densities ($2 \gtrsim v/v_0 \gtrsim 1.5$), the $t^{-3/2}$ behavior is certainly not yet reached for the largest time considered by Alder and Wainwright ($t/\tau_r \simeq 30$) because $D(t)$ is still negative, while theory predicts it should be asymptotically positive.

Similar, but less precise, data exist for the other transport coefficients.

Recently, very interesting results for Lennard-Jones potentials have been obtained by Levesque and Ashurst [143] which indicate a behavior analogous to that of hard sphere systems.

To end up this very brief review on computer results, let us still mention studies of the Lorentz gas [121], which was unsuccessful in detecting the $t^{-5/2}$ prediction for this model and of Wood and Lado [122] on the wind tree model.

All these results might give the depressing view that mode-mode coupling effects play only a very minor role in the determination of correlation functions and transport coefficients. However, we should stress again that the calculations reviewed here only discussed the asymptotic behavior of these correlation functions. A still unanswered question is whether or not these hydrodynamical effects also play a role in the intermediate region (let us say $t \sim 3-10$ relaxation times); in this case, of course, an asymptotic evaluation based on:

$$\int k^2 dk \exp(-ak^2 t) \propto 1/(at)^{3/2} \quad (5.4)$$

would no more be valid, because the wave numbers which would contribute to the integral would not be small enough (see the approximation leading to (3.87)). Yet, that “precursors” to the long

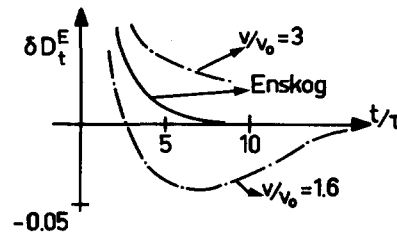


Fig. 5.3. The deviations of the velocity correlation function from Enskog approximation at various densities (taken from ref. [123]). (τ denotes the relaxation time $(4\sqrt{\pi} \rho g_2(a) a^2 \sqrt{k_B T/m})^{-1}$ where $g_2(a)$ is the pair correlation function at the contact distance a .)

time tails do exist at such intermediate times is strongly suggested by Alder et al. [123] in their analysis of the hard sphere fluid in 3d. Considering again the velocity correlation function, we see clearly on fig. 5.3, where the deviations $\delta D_t^E = D_t - D_t^E$ from the Enskog result D_t^E are quite important at these intermediate times: it is hard to understand how such effects could be accounted for by purely “relaxation” processes, which should have a much smaller life time. Similar effects exist for Lenard–Jones fluids [124]. Although a thorough discussion of these questions would be out of place here, it is worthwhile to point out that partially successful attempts in this direction have been made [125–127]: it is our optimistic view that such “extrapolations” of long time tails effects at intermediate time will be an important ingredient of future transport theory.

Finally, let us make three more remarks:

i) little, if any, has been said here about quantum systems. However, there is little doubt that similar effects exist for these systems. Indeed, for wave lengths much longer than the De Broglie wave length there is little difference between a classical and a quantum system (except of course for superfluids) and, precisely as the quantum equivalent of the non-analyticity of the virial expansion for classical gases has been established [128, 129], there should be no basic difficulty in deriving the $t^{-3/2}$ behavior, as well as the related aspects. Moreover, let us repeat that in quantum critical dynamics, mode–mode coupling has already been successfully applied;

ii) even for classical systems, we have limited ourselves here to fluids with no internal degrees of freedom. However, the same type of approach has been developed for internal rotation relaxation [130, 134]; also a series of special models have been analyzed, like the Lorentz gas [35], the wind tree model [135, 136], or magnetic relaxation in solids [137]. For lack of space, we shall not discuss them here; suffice it to say that they clearly show that a slow decay of the Green–Kubo integrands for long times seems quite a universal phenomenon although the $t^{-3/2}$ discussed here is not generally valid, even in 3d;

iii) it is often said that mode–mode coupling theory is a non-linear transport theory. Though this point is of a rather semantic nature, let us stress that such a statement certainly needs some qualification. Indeed, whatever the method we have used, we have only considered correlation functions which are defined within the frame of linear response theory and all deviations of the macroscopic quantities from their equilibrium value are small. Yet, it is true that in describing the time evolution of these macroscopic quantities, we have used formalisms (in particular the phenomenological and the fluctuating hydrodynamical approach) in which non-linear micro-

scopic fluctuations appear. Yet, as should be clear from all this work, the introduction of these non-linear fluctuations simply furnishes a convenient way for describing the microscopic dynamics of the system in an approximate way. If we were clever enough, we could have computed the time dependent correlation functions by solving the exact Hamilton's equation (which of course also are enormously non linear!): yet nobody would speak then about a non-linear transport theory. Moreover, we have seen that, in the kinetic approach, only linear operators appear, although these again involve – in some approximation – products of hydrodynamical modes. Thus this distinction between linear and non-linear effects is rather superficial; what is really important is the final result and, fortunately, we have seen that all the existing methods – whether “linear” or “non-linear” – lead to equivalent results.

Acknowledgments

We thank Prof. B. Alder, Prof. E. Cohen and coworkers for permitting us to use their published data. Similar thanks go to the Editors of Physical Review Letters, Physical Review and Journal of Chemical Physics.

APPENDIX A

Derivation of eq. (2.81)

Acting with \hat{P}_N on both sides of eq. (2.82), we get:

$$i\partial_t \hat{P}_N \delta\rho_N(t) = \hat{P}_N L_N \hat{P}_N \delta\rho_N(t) + \hat{P}_N L_N (1 - \hat{P}_N) \delta\rho_N(t). \quad (\text{A.1})$$

Similarly, acting with $(1 - \hat{P}_N)$ on the same equation leads to:

$$i\partial_t (1 - \hat{P}_N) \delta\rho_N(t) = (1 - \hat{P}_N) L_N (1 - \hat{P}_N) \delta\rho_N(t) + (1 - \hat{P}_N) L_N \hat{P}_N \delta\rho_N(t). \quad (\text{A.2})$$

Formally, the solution of (A.2), considering $\hat{P}_N \delta\rho_N(t)$ as given is:

$$(1 - \hat{P}_N) \delta\rho_N(t) = \exp[-i(1 - \hat{P}_N) L_N t] (1 - \hat{P}_N) \delta\rho_N(0) + \frac{1}{i} \int_0^t \exp[-i(1 - \hat{P}_N) L_N (t - t')] \\ \times (1 - \hat{P}_N) L_N \hat{P}_N \delta\rho_N(t') dt' \quad (\text{A.3})$$

as can be checked by differentiation.

With the help of the initial condition (2.81), we have:

$$(1 - \hat{P}_N) \delta\rho_N(0) = 0. \quad (\text{A.4})$$

Inserting (A.3, 4) into (A.1) and using the readily checked property:

$$\hat{P}_N L_N \hat{P}_N = 0 \quad (\text{A.5})$$

we arrive indeed at (2.86) with the help of (2.85).

This five line derivation of a kinetic equation is of course extremely elegant. Yet, it has obviously told us very little about the extremely complicated dynamics of many particle systems: all the difficulties are still present in the formal expression for the kernel $\tilde{G}_0(p_1; \tau)$ and the real job of the many body physicists starts when unravelling the structure of this kernel, with any method he is able to use, in particular perturbative methods [49, 52, 54, 55]. Refusing to do this amounts to replace an unknown quantity, $\delta\varphi_1(p_1; t)$, by another unknown quantity $\tilde{G}_0(p_1; \tau)$ and then the kinetic equation (2.86) provides us with little more than a definition of the kernel $\tilde{G}_0(p_1; \tau)$, as was stressed by Martin in a different context [6]. Moreover, rough and uncontrolled approximation on this kernel or on the choice of the projector often leads to completely erroneous results (for an example of incorrect use of projection operator techniques, see [138]). These remarks are illustrated in Appendix B and C.

APPENDIX B

Formal density expansion of the collision operator $\tilde{C}_0(p; z)$

It is clear that the definitions (2.87, 89) are very formal and in order to extract any information from them, one needs some kind of expansion method for treating the many body operator $\exp\{-i(1-\hat{P}_N)L_N\tau\}$.

The most straightforward method is based, as usual, on the splitting of the Hamiltonian H_N into two parts:

$$H_N = H_N^0 + \lambda V_N \quad (\text{B.1})$$

where H_N^0 describes the kinetic part of the energy, while V_N describes the interactions:

$$V_N = \sum_{a>b} V(|r_{ab}|). \quad (\text{B.2})$$

This latter term is weighted by a dimensionless parameter λ . Correspondingly

$$L_N = L_N^0 + \lambda\delta L_N \quad (\text{B.3})$$

with:

$$L_N^0 = -i \sum_a v_a \cdot \frac{\partial}{\partial r_a} \quad (\text{B.4})$$

$$\delta L_N = \sum_{a>b} \delta L_{ab} \quad (\text{B.5})$$

$$\delta L_{ab} = i \frac{\partial V}{\partial r_{ab}} \cdot \left(\frac{\partial}{\partial p_a} - \frac{\partial}{\partial p_b} \right). \quad (\text{B.6})$$

Inserting (B.3) into (2.87), we may formally expand the exponential operator in powers of λ according to the well-known formula:

$$\exp[-i(1-\hat{P}_N)L_N\tau] = \exp[-iL_N^0\tau] + \frac{\lambda}{i_0} \int_0^\tau d\tau' \exp[-iL_N^0(\tau-\tau')] (1-\hat{P}_N)\delta L_N \exp[-iL_N^0\tau] + \dots \quad (\text{B.7})$$

where we have used the easily established property:

$$\hat{P}_N L_0 = 0. \quad (\text{B.8})$$

We arrive then at the expansion:

$$\tilde{C}_0(p_1; z) = \sum_{n=2}^{\infty} \lambda^n \tilde{C}_0^{(n)}(p_1; z) \quad (\text{B.9})$$

if we also expand the equilibrium distribution ρ^{eq} in powers of λ (it is easily checked that the contributions of order λ^0 and λ^1 identically vanish). We may now systematically analyze the (infinite) series (B.9); diagram techniques prove very useful in this aim [49–51]. Although this procedure has been successfully applied even in arbitrary dense systems, it is true that the expansion (B.9) is not very convenient for explicit calculations in realistic systems, because the interaction is strong and the simplest limits (for example the Boltzmann limit of the dilute gas) already require infinite partial resummations. This is avoided by an alternative procedure, the so-called *binary collision expansion* [139, 140].

We shall not present this formalism in detail here but the basic idea is easy to grasp by analogy with quantum scattering theory [121]: it is well known indeed that while the potential $V(|r_{ij}|)$ furnishes a valid approximation (Born approximation) to the scattering amplitude when this potential is weak, it has to be replaced by the so-called \mathcal{T}_{ij} matrix for strong potentials:

$$V_{ij} \rightarrow \mathcal{T}_{ij}(z) = V_{ij} + V_{ij} \frac{1}{H_0 - z} \mathcal{T}_{ij}(z); \quad (\text{B.10})$$

this \mathcal{T}_{ij} matrix is generally frequency dependent. The comparison of (B.1) and (B.3) then immediately suggests that the classical collision process between two particles (ij) should be adequately described by the so-called *binary collision operator* $T_{ij}(z)$, solution of an integral equation:

$$\delta L_{ij} \rightarrow T_{ij}(z) = -\delta L_{ij} - \delta L_{ij} \frac{1}{L_0 - z} T_{ij}(z) \quad (\text{B.11})$$

$$= t_{ij}(z) \frac{1}{\Omega}. \quad (\text{B.12})$$

The minus sign in (B.11) have been introduced for convenience; moreover, the definition (B.12) makes the Fourier transform of $t_{ij}(z)$ with respect to the coordinates r_i and r_j volume independent in the large volume limit.

Although the explicit calculation of $t_{ij}(z)$ for arbitrary potential $V(|r_{ij}|)$ is an exceedingly difficult problem, it poses no question of principle (it is a two-body problem); moreover t_{ij} can be evaluated simply in the case of hard spheres where it turns out to be frequency independent (because the hard sphere collision is instantaneous); in this case, a representation of the Fourier transform of t_{ij} is given by eq. (3.70) in the text.

We now have to express the generalized collision operator (2.87, 89) in terms of these t_{ij} , instead of the original δL_{ij} . Here again the formal proof is rather tedious but the final result is transparent, especially for hard spheres [140]. In agreement with the naive picture that hard sphere dynamics can be described as a succession of binary collisions one finds:

$$\tilde{G}_0(p_1; \tau) = -\lim \int d^N r dp^{N-1} [-T_N \delta(t) + T_N \exp\{-i[L_N^0 - (1 - \hat{P}_N)(T_N)]\} [(1 - \hat{P}_N)T_N]] \rho_N^{\text{eq}} / \varphi^{\text{eq}}(p_1). \quad (\text{B.13})$$

Except for the first term, the right-hand side of eq. (B.13) is obtained from (2.87) by replacing everywhere $\delta L_N \rightarrow -T_N$:

$$T_N = \sum_{i > j} T_{ij}. \quad (\text{B.14})$$

The necessity for this first term is easy to understand: indeed, a hard core two-body collision takes essentially no time and an instantaneous contribution ($\propto \delta(t)$) is possible; on the contrary, eq. (A.5) tells us that a soft force cannot give rise to a collision process with zero duration.

By comparing (B.13) and (B.12) with (2.87), the attentive reader will however have noticed an apparent "overcounting" in (B.13): indeed, contributions involving two (or more) successive T_{ij} with the same pair (ij) are allowed in (B.13) and such physical processes are by definition already accounted for by one single T_{ij} ; however there is no contradiction because for hard spheres, one can prove the property*:

$$T_{ij} \frac{1}{L_0 - z} T_{ij} = 0 \quad (\text{B.15})$$

which expresses the geometrical fact that two successive collisions between the two same isolated particles is impossible.

This property (B.15), as well as the z -independence of T_{ij} , are particular features of hard spheres systems which make them particularly convenient to analyze.

With (B.13), we are ready to attack the problem of the formal density expansion of the generalized collision operator. The idea is very simple: we first insert in (B.13) the analog of (B.13) for the exponential factor:

$$\begin{aligned} \tilde{G}_0(p_1; \tau) = & -\lim \int d^N r dp^{N-1} [-T_N \delta(t) + T_N \exp(-iL_N^0 \tau) (1 - \hat{P}_N) T_N \\ & - \frac{1}{i} \int_0^\tau d\tau' T_N \exp[-iL_N^0(\tau - \tau')] (1 - \hat{P}_N) T_N \exp[-iL_N^0 \tau'] (1 - \hat{P}_N) T_N + \dots] \rho_N^{\text{eq}} / \varphi^{\text{eq}}(p_1). \end{aligned} \quad (\text{B.16})$$

In principle, we should also make a cluster expansion for the equilibrium distribution; however, to illustrate the procedure, it is sufficient to approximate ρ_N^{eq} by its perfect gas limit; hence we shall take here:

$$\rho^{\text{eq}} = \frac{1}{\Omega^N} \prod_{i=1}^N \varphi^{\text{eq}}(p_i). \quad (\text{B.17})$$

*We are a little sketchy here. Strictly speaking, one should define T_{ij} by a limiting procedure which is not explicit in eq. (3.11) of the text. As this point plays no important role here (see however (3.75) and the corresponding footnote), we refer the reader to the literature [140] for a careful treatment.

Inserting (B.14) into (B.16), we get an infinite set of contributions which all involve particle 1 at least once (in the extreme left T_N , otherwise the integrals over p^{N-1} lead to zero), but also “dummy particles” ($\neq 1$). In a term involving m dummy particles ($i_1, i_2 \dots i_m$), we can choose these in $(N-1)(N-2) \dots (N-m-1) \sim N^m$ ways; moreover, it is readily verified that such a term is proportional to Ω^{-m} (because the probability of a collision between $(m+1)$ particles randomly distributed in the volume Ω is proportional to Ω^{-m}): hence, we shall obtain all the contributions of order n^m by picking up in (B.16) all the terms involving m dummy particles. In order to do this systematically, it is very convenient to use some kind of diagram technique. For the simple examples we want to treat here, it is however possible to work directly on the analytical formula (B.16).

To first order in n , we need one and only one dummy particle and it is immediate to check that the first term of (B.16) is of that type; moreover, eq. (B.15) guarantees that no other term of order n may appear.

Writing:

$$\tilde{G}_0(p_1; \tau) = n\tilde{G}_0^{(1)}(p_1; \tau) + n^2\tilde{G}_0^{(2)}(p_1; \tau) \dots \quad (\text{B.18})$$

we have thus:

$$\begin{aligned} n\tilde{G}_0^{(1)}(p_1; \tau) &= - \lim_{\Omega} \int d\mathbf{r}^N d\mathbf{p}^{N-1} [-T_N \delta(\tau)] \prod_{i=2}^N \varphi^{eq}(p_i) / \Omega^N \\ &= \lim_{\Omega} \frac{N}{\Omega^2} \int d^3r_1 d^3r_2 d^3p_2 T_{12} \varphi^{eq}(p_2) \delta(\tau) \end{aligned} \quad (\text{B.19})$$

and with the help of (B.12) and (3.70), we get readily:

$$n\tilde{G}_0^{(1)}(p_1; \tau) = n\tilde{C}(p_1)\delta(\tau) \quad (\text{B.20})$$

whose Laplace transform is the frequency independent Boltzmann–Lorentz collision operator for hard spheres.

At the next order, we retain the term involving two dummy particles; the second term in (B.16) vanishes identically in the approximation (B.17) as a consequence of the definition (2.83) for \hat{P}_N and we find the first contribution of order n^2 in the third term of (B.16); we have:

$$\begin{aligned} n^2\tilde{G}_0^{(2)}(p_1; \tau) &= i \lim_{\Omega} \frac{N^2}{\Omega^2} \int d^3r_1 d^3r_2 d^3r_3 d^3p_2 d^3p_3 \\ &\times \{ T_{12} \exp[-iL_3^0(\tau-\tau')] [(1-\hat{P}_N)T_{13} \exp[-iL_3^0\tau'] (1-\hat{P}_N)(T_{13} + T_{23}) \\ &+ (1-\hat{P}_N)T_{23} \exp[-iL_3^0\tau'] (1-\hat{P}_N)(T_{12} + T_{13}) \} \varphi^{eq}(p_2) \varphi^{eq}(p_3) + \dots \end{aligned} \quad (\text{B.21})$$

The dots here correspond to the “higher order” terms in (B.16) which involve similarly two dummy particles; these terms are of no importance for the asymptotic time behavior considered in this work.

The Laplace transform of (B.21) is the frequency-dependent Choh–Uhlenbeck collision operator, $n^2\tilde{C}_0^{(2)}(p_1; z)$ discussed in the text; a tedious calculation based on (B.12) and (3.70) allows to cast (B.21) into a more explicit form; we shall not write it here but it can be easily obtained as the n^2 term of the density expansion of (3.75) in the main text.

We could similarly obtain the super-Choh–Uhlenbeck operator by collecting the terms of (B.16) involving three dummy particles.

APPENDIX C

Structure of the collision operator

Schematically, we may summarize our discussion of Appendix B by saying that the generalized collision operator can be expressed as a functional of the binary collision operator t_{ab} and of the free particle Liouville “streaming” operator $\exp(-iL_0\tau)$.

From the definition (B.4), we can write this latter as:

$$\exp(-iL_N^0\tau) = \prod_{a=1}^N \exp\left(-\tau v_a \cdot \frac{\partial}{\partial r_a}\right). \quad (\text{C.1})$$

If we now introduce the Fourier transform of the free particle “propagator” $\exp(-\tau v_a \cdot \partial/\partial r_a)$:

$$G_k^{(0)}(v_a; \tau) = \frac{1}{\Omega} \int d^3r_a \exp(ik \cdot r_a) \exp\left[-\tau v_a \cdot \frac{\partial}{\partial r_a}\right] \exp(ik' \cdot r_a) = \exp(-ik \cdot v_a \tau) \delta_{k, k'}^{Kr}, \quad (\text{C.2})$$

$\tilde{C}_0(p_1; z)$ appears thus as a functional of t_{ab} and $G_k^0(v_a; \tau)^*$

$$\tilde{C}_0(p_1; z) = \tilde{C}_0(p_1; z | \{t_{ab}\}, \{G_k^0(v_a; \tau)\}). \quad (\text{C.3})$$

Suppose now that, for some reason – examples can be found in the text – low wave numbers k play an important role in the functional dependence of \tilde{C}_0 on G_k^0 ; this means that we describe the motion of the particles in the fluid by free motion over large distances $\sim k^{-1}$. Clearly, such a description makes no physical sense in a dense fluid, and we may expect all kind of difficulties with such an unrealistic (though formally exact!) formalism. What we should rather do is to describe the motion of each particle in terms of a “dressed propagator”, which takes into account the presence of all the particles in the fluid.

The necessity for such a renormalization appears mathematically in the following way: the Fourier Laplace transform of $G_k^0(v_a; t)$ which is:

$$G_k^0(v_a; z) = \frac{1}{k \cdot v_a - z} \quad (\text{C.4})$$

is only very weakly divergent at $k = 0, z = 0$; yet, it is easy to find a whole class of terms which diverge arbitrarily strongly at low k and z : they are obtained by considering, instead of free propagation of particle “a”, the contributions where particle “a” collides an arbitrary number of times with other fluid molecules. This situation is schematically depicted in fig. C.1, where free propagation is represented by a thin line and the dots represent collisions with the fluid mole-

*To simplify, we again neglect the effect of the equilibrium correlations ρ_{ij}^{eq} , which would lead to a further renormalization of the t_{ij} ; this point is of no much conceptual importance here.

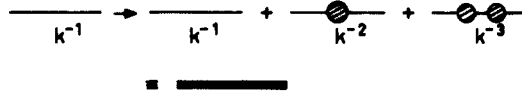


Fig. C.1. Schematic representation of the propagator renormalization.

cles. As is familiar from field theory [142], we can however put together all the contributions depicted in the figure and obtain the dressed propagator $G_k(v_a; t)$ represented by the thick line. We have:

$$G_k(v_a; t) = \frac{1}{2\pi i} \oint_c dz \exp(-izt) X_k(v_a; t) \quad (\text{C.5})$$

where $X_k(v_a; z)$ is given by:

$$X_k(v_a; z) = [k \cdot v_a - z + iC_k(p_a; z)]^{-1}. \quad (\text{C.6})$$

Here $C_k(p_a; z)$ generalizes to non vanishing k the collision operator introduced in section 2. We shall not need its explicit definition here.

It is now possible to write, in an unambiguous way, the collision operator $\tilde{C}_0(p_1; z)$ as a functional of this renormalized propagator*

$$\tilde{C}_0(p_1; z) = \tilde{\tilde{C}}_0(p_1; z | \{t_{ij}\}, \{G_k(v_a; \tau)\}) \quad (\text{C.7})$$

($\tilde{\tilde{C}}_0$ is of course different from \tilde{C}_0). The only difficulty in dealing with (C.7) – as it also is for (C.3) – is to have a proper book keeping of the still infinite number of terms appearing in \tilde{C}_0 ; here again, diagrammatic techniques are very useful.

The main merit of this new expansion (C.7) is that the strong divergences at $k = 0$ indicated in the first line of fig. C.1 are no longer present. Indeed, the analysis sketched in section 3 (see eq. (2.16) and foll.) indicates that, at small k , the divergence of (C.6) is at most of order k^{-2} (in 3d at least) and this is weak enough to make an analysis based on (C.7) meaningful.

This remark is illustrated in the text for the special case of the ring collision operator. Moreover, it is very easy to see that this ring operator emerges as a renormalized form of the Choh–Uhlenbeck operator. Indeed, using (C.1), (C.2) and substituting

$$G_k^0 \rightarrow G_k \quad (\text{C.8})$$

transforms the Choh–Uhlenbeck operator (B.21) into the ring operator (3.15), provided we use the low density approximation $C_k(p_a; z) \simeq nC(p_a; z)$. The proof of this remark is left to the reader.

References

- [1] A. Einstein, Ann. Phys. XVII (1905) 549; Investigations on the theory of Brownian motion, ed. R. Furth (Dover, New York, 1956).

*More precisely, for self-diffusion, we should introduce two propagators: $\tilde{X}_k(v_1; z)$, for the tagged particle, involving a self-collision operator $\tilde{C}_k(p_1; z)$, and $X_k(v_a; z)$, defined here, for $a \neq 1$. We do not dwell here on this technical point.

- [2] P. Langevin, C.R. Acad. Sci. (Paris) 146 (1908) 530; see also:
N. Wax, *Noise and Stochastic Processes* (Dover, New York, 1954).
- [3] M. Green, J. Chem. Phys. 20 (1952) 1281; 22 (1954) 398.
- [4] R. Kubo, J. Phys. Soc. Jap. 12 (1957) 1570.
- [5] R. Zwanzig, Ann. Rev. Phys. Chem. 16 (1965) 67.
- [6] P. Martin, in: *Many Body Physics*, eds. C. de Witt and R. Balian (Gordon and Breach, New York, 1968).
- [7] Although the exponential decay of the correlation functions in the dilute gas is rarely explicitly mentioned in the literature, it is an immediate consequence of the spectral properties of the Boltzmann operator: see section 2.3 and refs. [58], [59].
- [8] J. Dorfman and E. Cohen, Phys. Lett. 16 (1965) 124; see also the review papers on the subject in Th. Bak, *Statistical Mechanics* (Benjamin, New York, 1967).
- [9] B. Alder and T. Wainwright, Phys. Rev. Lett. 18 (1967) 968.
- [10] B. Alder and T. Wainwright, J. Phys. Soc. Jap. 26 (1968) 267; Phys. Rev. A1 (1970) 18.
- [11] B. Alder and T. Wainwright and D. Gass, Phys. Rev. A4 (1971) 233.
- [12] P. Résibois, *Electrolyte Theory* (Harper and Row, New York, 1968);
H. Falkenhagen, *Theorie der Electrolyte* (J. Hirzel Verlag, Leipzig, 1971) and references quoted there.
- [13] M. Fixman, J. Chem. Phys. 36 (1962) 310; 47 (1967) 2808.
- [14] K. Kawasaki, J. Phys. Chem. Sol. 28 (1967) 1277; Phys. Lett. 25A (1967) 448; Prog. Theor. Phys. Jap. 38 (1968) 1052.
- [15] K. Kawasaki, Prog. Theor. Phys. Jap. 39 (1968) 1133; 40 (1968) 11; 40 (1968) 706; 40 (1968) 930.
- [16] L. Kadanoff and J. Swift, Phys. Rev. 166 (1968) 89.
- [17] Y. Pomeau, unpublished report (Rapport LP84, Laboratoire de Physique des Plasmas, Orsay, France); Phys. Rev. A6 (1972) 776.
- [18] M. Ernst, E. Hauge and J. Van Leeuwen, Phys. Rev. Lett. 25 (1970) 1254; Phys. Rev. A4 (1971) 2055.
- [19] R. Zwanzig, in: Proc. I.U.P.A.P. Conf. on Statistical Mechanics, Rice St., eds. K. Freed and J. Light (Chicago Univ. Press, Chicago, 1972) p. 24.
- [20] R. Zwanzig, J. Nordholm and N. Mitchell, Phys. Rev. A5 (1972) 2680.
- [21] R. Bedeaux and P. Mazur, Phys. Lett. 43A (1973) 401; Physica 73 (1974) 431; 76 (1974) 235; 76 (1974) 247 and to appear.
- [22] T. Keyes and I. Oppenheim, Phys. Rev. A7 (1973) 1384; A8 (1973) 437.
- [23] H. Mori and H. Fujisaka, Prog. Theor. Phys. Jap. 49 (1973) 764.
- [24] K. Kawasaki, Phys. Lett. 32A (1970) 379.
- [25] K. Kawasaki, Phys. Lett. 34A (1971) 12.
- [26] R. Kapral and M. Weinberg, Phys. Rev. A8 (1973) 1008; A9 (1974) 1676.
- [27] R. Zwanzig, Phys. Rev. 124 (1961) 983.
- [28] H. Mori, Prog. Theor. Phys. Jap. 33 (1965) 423.
- [29] J. Dorfman and E. Cohen, Phys. Rev. Lett. 25 (1970) 1257; Phys. Rev. A6 (1972) 776.
- [30] J. Dufty, Phys. Rev. A5 (1972) 2247.
- [31] P. Résibois and Y. Pomeau, Phys. Lett. 44A (1973) 97.
- [32] P. Résibois, Physica 70 (1973) 413.
- [33] P. Résibois and Y. Pomeau, Physica 72 (1973) 493.
- [34] M. Theosodopulu and P. Résibois, Physica, to appear.
- [35] M. Ernst and A. Weyland, Phys. Lett. 34A (1971) 34A
- [36] J. Ubbink and E. Hauge, Physica 70 (1973) 297.
- [37] L. Landau and E. Lifshitz, *Fluid Mechanics* (Addison Wesley, Reading, 1959).
- [38] L. Kadanoff and P. Martin, Ann. Phys. 24 (1963) 419.
- [39] L. Landau and G. Placzek, Phys. Z. Sowietunion 5 (1934) 172.
- [40] L. Landau and E. Lifshitz, *Electrodynamics of Continuous Media* (Addison Wesley, Reading, 1959).
- [41] S. De Groot and P. Mazur, *Non-equilibrium Thermodynamics* (North-Holland, Amsterdam, 1963).
- [42] R. Becker, *Theory of Heat* (Springer Verlag, Berlin, 1967).
- [43] L. Landau and E. Lifshitz, *Statistical Mechanics* (Pergamon Press, London, 1958).
- [44] D. Massignon, *Mécanique Statistique des Fluides* (Dunod, Paris, 1957).
- [45] J. Yvon, *Les Corrélations et l'Entropie* (Dunod, Paris, 1966).
- [46] K. Kawasaki, Ann. Phys. 61 (1970) 1.
- [47] See the fundamental paper: G. Uhlenbeck and L. Ornstein, Phys. Rev. 36 (1930) 823, also reprinted in N. Wax, see [2]
- [48] P. Résibois, in: *Irreversibility and the Many-Body Problem*, eds. J. Biel and J. Rae (Plenum, New York, 1972) p. 275.
- [49] I. Prigogine, *Non Equilibrium Statistical Mechanics* (Interscience, New York, 1962).
- [50] R. Balescu, *Statistical Mechanics of Charged Particles* (Interscience, New York, 1964).
- [51] P. Résibois, in: *Physics of Many Particle Systems*, ed. E. Meeron (Gordon and Breach, New York, 1967).
- [52] E. Cohen, in: *Fundamental Problems in Statistical Mechanics*, ed. E. Cohen (North-Holland, Amsterdam, 1962).

- [53] R. Zwanzig, in: Boulder Lectures on Theoretical Physics, ed. W. Brittin (Interscience, New York, 1960); J. Chem. Phys. 33 (1960) 1338.
- [54] R. Zwanzig, Phys. Rev. 129 (1963) 486.
- [55] M. Ernst, L. Haines and J. Dorfman, Rev. Mod. Phys. 41 (1969) 296 and references quoted there.
- [56] G. Mazenko, Phys. Rev. A7 (1973) 209 and references quoted there.
- [57] See for example, G. Doetsch, Handbuch der Laplace Transformation, Vol. I (Birkhauser, Basel, 1950).
- [58] C. Cercignani, Mathematical Methods in Kinetic Theory (Mac Millan and Co. Ltd., New York, 1969).
- [59] G. Uhlenbeck and G. Ford, Lectures on Statistical Mechanics (American Math. Soc., Providence, 1963).
- [60] P. Résibois, J. Stat. Phys. 2 (1970) 21.
- [61] D. Forster and P. Martin, Phys. Rev. A2 (1970) 1575.
- [62] J. Piasecki and P. Résibois, J. Math. Phys. 14 (1973) 1984.
- [63] See for example A. Friedman and M. Shinbrot, Acta Mathematica 121 (1968) 77.
- [64] P. Résibois, J. Chem. Phys. 41 (1964) 2979.
- [65] H. Lorentz, Lessen über Theoretische Naturkunde, Vol. V (E. Brill, ed., Leiden, 1921).
- [66] G. Stokes, Cambridge Trans. T IX (1851) 580;
see also: H. Lamb, Hydrodynamics (Cambridge Univ. Press, 1932).
- [67] A. Widom, Phys. Rev. A3 (1971) 1394.
- [68] E. Hauge and A. Martin-Lof, J. Stat. Phys. 7 (1973) 259.
- [69] M. Velarde and E. Hauge, J. Stat. Phys. 10 (1974) 103.
- [70] R. Zwanzig and M. Bixon, Phys. Rev. A2 (1970) 2005.
- [71] M. Nelkin, Phys. Fluids 15 (1972) 1685.
- [72] R. Mazo, J. Chem. Phys. 54 (1972) 3712.
- [73] T. Choh and J. Hermans, J. Chem. Phys. 56 (1972) 3150.
- [74] J. Dufty and J. Mac Lennan, Phys. Rev. A9 (1974) 1266.
- [75] J. Hynes, J. Chem. Phys. 57 (1972) 5612.
- [76] G. Mazenko, Phys. Rev. A3 (1971) 2121; A5 (1972) 2545.
- [77] J.P. Hansen, E.L. Pollock and I.R. McDonald, Phys. Rev. Lett. 32 (1974) 277.
- [78] M. Ernst, Thesis, University of Amsterdam (1964) (unpublished).
- [79] S. Choh and G. Uhlenbeck, The Kinetic Theory of Phenomena in Dense Gases, University of Michigan, 1958 (unpublished).
- [80] K. Kawasaki and I. Oppenheim, Phys. Rev. 136A (1964) 1519.
- [81] P. Résibois, Y. Pomeau and J. Piasecki, J. Math. Phys. 15 (1974) 1238.
- [82] P. Résibois, in: Advanced Course on Thermodynamics and Statistical Mechanics, ed. B. Schieve (Springer Verlag, Berlin, 1971).
- [83] E. Stanley, Phase Transitions and Critical Phenomena (Clarendon Press, Oxford, 1971).
- [84] M. Green, Phys. Rev. 119 (1960) 829.
- [85] P. Résibois, unpublished calculations.
- [86] Y. Pomeau, Phys. Rev. A7 (1973) 1134.
- [87] M. Ernst and J. Dorfman, Phys. Lett. 38A (1972) 269; Physica 61 (1972) 157.
- [88] I. de Schepper, H. Van Beyeren and M. Ernst, Physica 75 (1974) 1.
- [89] Y. Pomeau, J. Chem. Phys. 57 (1972) 2800.
- [90] A. Gervois and Y. Pomeau, unpublished internal report CEA.
- [91] D. Gass and J. Van Kraendonck, Phys. Rev. Lett. 28 (1972) 1317.
- [92] Y. Pomeau, Ph.D. Thesis, Université d'Orsay, 1969 (unpublished); Phys. Lett. 27A (1968) 601; Phys. Rev. A3 (1971) 1174.
- [93] J. Hardy, O. De Passis and Y. Pomeau, Phys. Rev. Lett. 31 (1973) 276; J. Math. Phys. 14 (1973) 1746; and to be published.
- [94] J. Lebowitz and J. Percus, Phys. Rev. 155 (1967) 122.
- [95] H. Wergeland, in: Fundamental Problems in Statistical Mechanics, ed. E.G.D. Cohen (North-Holland, Amsterdam, 1962).
- [96] A. Erdelyi et al., Tables of Integral Transforms, Vol. I (Mc Graw Hill, New York, 1953).
- [97] M. Kac, G. Uhlenbeck and P. Hemmer, J. Math. Phys. 4 (1963) 216; 4 (1963) 229; 5 (1964) 60.
- [98] N. Van Kampen, Phys. Rev. 135 (1964) 362.
- [99] J. Lebowitz, G. Stell and S. Baer, J. Math. Phys. 6 (1965) 1282.
- [100] P.C. Hemmer, J. Math. Phys. 5 (1964) 75.
- [101] J. Lebowitz and O. Penrose, J. Math. Phys. 7 (1966) 98.
- [102] P. Résibois, J. Piasecki and Y. Pomeau, Phys. Rev. Lett. 38A (1972) 33.
- [103] J. Deutsch and R. Zwanzig, J. Chem. Phys. 46 (1967) 512.
- [104] R. Mountain and R. Zwanzig, J. Chem. Phys. 48 (1968) 1451.
- [105] K. Kawasaki, Prog. Theor. Phys. Jap. 41 (1968) 1190.
- [106] B. Cichocki, Physica 75 (1974) 157.
- [107] Y. Pomeau, Contributed paper at the Van der Waals Centennial Conf. on Statistical Mechanics, Amsterdam (1973).
- [108] M. Seghers, P. Résibois and Y. Pomeau, Phys. Letters A, to be published.

- [109] E. Stanley, *Cooperative Phenomena near Phase Transitions, A Bibliography with Selected Readings* (M.I.T. Press, Cambridge, Mass., 1973).
- [110] J. Swift, *Phys. Rev.* 173 (1968) 257.
- [111] P. Résibois and M. De Leener, *Phys. Lett.* 25A (1967) 65; *Phys. Rev.* 178 (1969) 806; 178 (1969) 819.
- [112] P. Résibois and C. Piette, *Phys. Rev. Lett.* 24 (1970) 514.
- [113] G. Laramore and L. Kadanoff, *Comments on Solid State Phys.* 2 (1969) 105.
- [114] R. Ferrel, *J. Low Temp. Phys.* 1 (1969) 241; 1 (1969) 423.
- [115] C. Andriessse, *Phys. Lett.* 33A (1970) 419.
- [116] Y. Kim and J. Matta, *Phys. Rev. Lett.* 31 (1973) 208.
- [117] S. Harris, *Phys. Lett.* 47A (1974) 77.
- [118] W. Wood, in: *The Boltzmann Equation*, ed. E. Cohen (Springer Verlag, Berlin, 1973).
- [119] J. Erpenbeck and W. Wood, *J. Chem. Phys.* (1974).
- [120] C. Carlier and H. Frisch, *Phys. Rev. A*6 (1972) 1153.
- [121] C. Bruin, *Phys. Rev. Lett.* 29 (1972) 1670; *Physica* 72 (1974) 261.
- [122] W. Wood and F. Lado, *Journal of Computational Physics* 7 (1971) 528.
- [123] B. Alder, D. Gass and T. Wainwright, *J. Chem. Phys.* 53 (1970) 3813.
- [124] D. Levesque and L. Verlet, *Phys. Rev. A*2 (1970) 2514.
- [125] G. Mazenko, *Phys. Rev. A*7 (1973) 222; *A*9 (1974) 360.
- [126] W. Gotze and M. Lucke, to be published.
- [127] P. Résibois and J. Lebowitz, *J. Stat. Phys.*, to appear.
- [128] P. Résibois and M. Velarde, *Physica* 51 (1971) 541.
- [129] J. Weinstock, *Phys. Rev. Lett.* 17 (1966) 130.
- [130] N. Ailawadi and B. Berne, *J. Chem. Phys.* 54 (1970) 3569.
- [131] N. Ailawadi and S. Harris, *J. Chem. Phys.* 56 (1972) 5783.
- [132] B. Berne, *J. Chem. Phys.* 56 (1972) 2164.
- [133] Y. Pomeau and J. Weber, *Phys. Rev. A*8 (1973) 1422.
- [134] F. Garisto and R. Kapral, *Phys. Rev. A*10 (1974) 309.
- [135] E. Hauge and E. Cohen, *Phys. Rev.* 25A (1967) 78; *J. Math. Phys.* 10 (1969) 397.
- [136] H. Van Beyerem and E. Hauge, *Phys. Lett.* 39A (1972) 397.
- [137] M. De Leener and P. Gillis, to be published.
- [138] P. Résibois, J. Brocas and G. Decan, *J. Math. Phys.* 10 (1969) 964.
- [139] The binary collision expansion was first introduced for equilibrium problems by A. Siegert and E. Teramoto, *Phys. Rev.* 110 (1958) 1232. It was adapted to dynamical problems by J. Brocas and P. Résibois, *Bull. Ac. Roy. Belgique, Cl. Sc.* 47 (1961) 226 and by J. Weinstock, *Phys. Rev.* 132 (1963) 454, and then by many other authors.
- [140] The simplicity of the binary collision for hard spheres is stressed for example in: M. Ernst, J. Dorfman, W. Hoegy and J. Van Leeuwen, *Physica* 45 (1969) 127.
- [141] M. Goldberger and K. Watson, *Collision Theory* (J. Wiley and Sons, New York, 1964).
- [142] A. Abrikosov, L. Gorkov and I. Dzyaloshinsky, *Methods of Quantum Field Theory in Statistical Physics* (Prentice Hall, Englewood Cliffs, New Jersey, 1963).
- [143] D. Levesque and W.T. Ashurst, *Phys. Rev. Lett.* 33 (1974) 277.
- [144] E. Hauge, *Phys. Rev. Lett.* 28 (1972) 1501.
- [145] P. Berge, P. Calmettes, C. Laj, M. Tournarie and B. Volochine, *Phys. Rev. Lett.* 24 (1970) 1223.
- [146] C. Garland, D. Eden and L. Mistura, *Phys. Rev. Lett.* 25 (1970) 1161.
- [147] C. Laj and S. Chen, *Phys. Rev. Lett.* 29 (1972) 401.
- [148] P. Mueller, D. Eden, C. Garland and R. Williamson, *Phys. Rev. A*6 (1972) 2272.