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KINETIC EQUATIONS AND BROWNIAN MOTION

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Introduction.

In this series of lectures, we shall deal mainly with the microscopic theory of brownian motion.

Brownian motion owes its name to an English botanist, Robert Brown, who noticed in 1827 the fact that small particles suspended in fluids perform peculiarly erratic movements. The origin of this phenomenon is of course quite simple: we are dealing with a manifestation of the molecular motion.

The first satisfactory theory of brownian motion was produced by Einstein in 1905 who derived the diffusion equation. This result has been particularly important because the expression he obtained for the diffusion coefficient D allowed a determination of Avogadro's number N by Perrin.

Thereafter, the phenomenological theory has been widely developed. A very good presentation of the ideas used can be found in a review paper by Chandrasekhar [1]. We shall give a brief summary of these ideas in chapter I. The starting point is the Langevin equation which introduces as basic assumption the fact that the interactions of the particle with the medium have a twofold effect; first, an overall dynamical friction, then a fluctuating force. Intuitive assumptions about the statistical properties of this fluctuating force lead to the Fokker-Planck equation for the time evolution of the probability distribution of finding the particle at a given point in space with a given velocity. One of the most interesting features of the Fokker-Planck equation is that it is an irreversible equation; it predicts an irreversible evolution towards an equilibrium distribution.

The stochastic theory has been widely used and proved successful in the study of a great variety of phenomena. Neverthele , it requires a good deal of intuition to reach a phenomenological description of the

effect of the medium on the particle. However, intuition can sometimes be misleading ; therefore, there has been much effort to understand this phenomenon on a microscopic level. Such an effort can be rewarding in several ways ; it will clarify the conditions under which the phenomenological theory will be valid, it will give us the phenomenological constants in terms of molecular parameters and finally, it may be hoped that it will show us the path to follow when the conditions for the validity of the phenomenological theory are not fulfilled.

An understanding of the brownian motion on a microscopic level necessarily requires the consideration of an N-body system. It is quite obvious that the detailed description provided by the laws of mechanics cannot be used directly and that one must resort to the methods of statistical mechanics. A most useful concept is the idea of an ensemble introduced by Gibbs. In classical statistical mechanics , such an ensemble is characterized by the N-particle distribution function which obeys the Liouville equation.

The Liouville equation has been the starting point for the study of non equilibrium many-body systems by Prigogine and his coworkers. An extensive presentation of the basic ideas can be found in the monographs by Prigogine [2] , Balescu [3] and Résibois [4] . This method emphasizes strongly the role played by the correlations in the evolution of the distribution function. We really deal with a "dynamics of correlations". This formalism is particularly well suited to take account of the characteristic features of macroscopic systems : large number of degrees of freedom N, large volume Ω , finite concentration ; these features allow the consideration of the asymptotic case :

$$N \longrightarrow \infty;\ \Omega \longrightarrow \infty,\ N/\Omega = C \quad \text{finite} \tag{1}$$

which brings in several important simplifications.

Moreover, in general, we are interested in the asymptotic behavior in time of the system. Then , it can be shown that in many cases, the behavior of the system can be correctly described by the so called kinetic equations. (A simple example of kinetic equation is the Boltzmann equation for dilute gases) . The derivation of the kinetic equation for the velocity distribution function will be discussed in chaper II.

The kinetic equation is an irreversible equation : systems for which such an equation holds tend asymptotically to an equilibrium distribution , which is a function of the hamiltonian only.

Once we have equations for the description of the asymptotic behavior of the N-body system, we can introduce the special features of the brownian motion problem. There, we are interested in the motion of a single particle in a surrounding fluid. The simplest case will of course be that of a particle moving in a fluid at equilibrium . This is in fact the problem which , in microscopic theories, is often referred to as the brownian motion or test particle problem. The assumption that the fluid is at equilibrium introduces an enormous simplification in the kinetic equation: all the particles no longer play the same role. All of them, but one, are in the equilibrium state (strictly speaking, the fact that one particle is out of equilibrium prevents the others to stay in the equilibrium state; however, this departure from the equilibrium state is of order N^{-1} and can be neglected) .

There are two cases where the kinetic equation, particularized to the brownian motion problem, can be shown to lead to a Fokker-Planck equation. The simplest case is that of weakly interacting systems which will be discussed in chapter III. There, a Fokker-Planck equation

is obtained whatever the mass of the brownian particle. The other case is that of brownian motion in systems interacting through short range forces where the brownian particle is much heavier that the particles of the fluid. This problem, in the absence of any external force, will be studied in chapter IV . In chapter V , we shall generalize it to the case where the brownian particle is charged and acted upon by a constant external electrical field . The interest of all these problems not only lie in the fact that they allow us to state the conditions of validity of the Fokker-Planck equation. They also enable us to obtain expressions of the diffusion coefficient which enters into the Fokker-Planck equation in therms of microscopic quantities. Moreover, they show us the way to obtain corrections to the Fokker-Planck equation when required . This will be briefly discussed in Chapter V.

So far, we have only considered classical systems. The same ideas can be extended to quantum mechanics, as we shall show in chapter VI . Here contact can be made with the results of recent experiments on the mobility of heavy ions in liquid He^4 and He^3 .

All the work which will be described in chapters III to VI concerns one special class of brownian motion: that of a particle moving in a fluid at thermal equilibrium (in chapters IV to VI , the brownian particle is supposed to be much heavier than the particles of the fluid) . Less specialized situations could of course be considered. We could for instance consider the motion of a test particle in a medium which is not at equilibrium . In this case, the problem is much less simple; we can no longer obtain a single closed equation for the distribution function of the test particle . However, in all systems

where the kinetic equation is asymptotically valid, the basic features are preserved. The distribution function of the particle will obey an irreversible equation. Whenever, in the brownian motion in a fluid at equilibrium, we can derive a Fokker-Planck equation, the same kind of equation can be obtained if the fluid is out of equilibrium but the coefficients appearing in the equation will be functionals of the state of the system. A simple example of this is given in chapter III for the case of weakly coupled systems. More details can be found in a paper by Balescu and Soulet [5].

However, there are systems where the kinetic equation is not valid, even asymptotically. An important case is that of systems interacting through gravitational forces. For such systems, an entirely new approach seems necessary. We first have to derive an equation which will, in this case, play the same role as the kinetic equation for systems with short range interactions. In the last chapter (VII) we shall briefly describe a recent attempt by Prigogine and Severne [6] to obtain such an equation. This equation predicts a behavior which differs in many important aspects from the behavior predicted by the kinetic

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I

I. STOCHASTIC THEORY

I.I. Introduction

The stochastic theory does not make any attempt to describe in detail the interactions between the brownian particle and the particles of the fluid. Rather, it describes the effect of the medium on the heavy particle in a phenomenological way. From the beginning, one assumes that the influence of the medium on the particle can be split into two parts.

First, we have a systematic friction effect. Secondly, we have to account for the random motion. This is done by assuming that the medium exerts a fluctuating force on the particle. It is obvious that this force is not known exactly and that the best thing we can do is to make guesses about its statistical properties. The main question will then be: given the statistical properties of the fluctuating force, what is the probability that, if the brownian particle at $t = 0$ is at the point $\underset{\sim}{r}_0$ with velocity $\underset{\sim}{u}_0$, it will be at time t at the point $\underset{\sim}{r}$ with velocity $\underset{\sim}{u}$? The assumptions of the stochastic theory lead to the Fokker-Planck equation for this probability distribution.

We shall first discuss the assumptions which lead to the Langevin's equation of motion for the heavy particle (§ 2). Then we shall make some further assumptions about the statistical properties of the fluctuating force (§ 3) which will enable us to write down the probability distribution in velocity space (§ 4).

We shall then show how the problem of finding this distribution function can be reduced to the solution of a differential equation (§ 5), the Fokker-Planck equation in velocity space. The Fokker-Planck equation for the complete distribution function in phase space, with or without an

external field acting on the particle , will then be obtained by means of an easy generalization of the previous problem (§ 6) . Finally, we shall consider the case of an inhomogeneous system where the density gradient is small over distances of the order of the mean free path. Then, we shall see that for times much longer than the relaxation time, the spatial distribution obeys a diffusion equation.

All this discussion will follow quite closely the excellent review paper by Chandrasekhar [1] . An extensive bibliography can be found there.

1. 2. Langevin equation

The first step in the stochastic theory is to write down an equation of motion for the heavy particle. From the beginning , one assumes that the influence of the medium leads :

1. to a systematic slowing down effect ; the friction coefficient β is assumed to be independent of the velocity of the heavy particle . Usually, one also assumes that it is given by Stokes' law. For a sperical particle of mass M and radius a, we then have :

$$\beta = \frac{6 \pi a \eta}{M} \qquad \text{(I.2.1)}$$

where η is the viscosity of the fluid.

2. to the random motion of the particle; to account for this, we assume that, besides the dynamical friction, the medium exerts a a fluctuating force $\underset{\sim}{A}(t)$ on the particle. This fluctuating force is assumed to depend only on the time t. It is of course not known but

plausible assumtions can be made about its statistical properties Comparison with experiment will have to decide a posteriori of the validity of these assumptions.

If we now suppose that these two effects are additive, the motion of a brownian particle in the absence of an external field of force is given by the Langevin equation :

$$\frac{d\underset{\sim}{u}}{dt} = -\beta \underset{\sim}{u} + \underset{\sim}{A}(t) \tag{I.2.2}$$

where $\underset{\sim}{u}$ is the velocity of the particle :

$$\underset{\sim}{u} = \frac{d\underset{\sim}{r}}{dt} \tag{I.2.3}$$

$\underset{\sim}{r}$ being its position.

If an external field of force $\underset{\sim}{K}(\underset{\sim}{r}, t)$ acts on the particle, its effect has to be included in the equation of motion. This means that (I.2.1) has to be replaced by :

$$\frac{d\underset{\sim}{u}}{dt} = -\beta \underset{\sim}{u} + \underset{\sim}{K}(\underset{\sim}{r}, t) + \underset{\sim}{A}(t) \tag{I.2.4}$$

We may notice an important feature of the Langevin equation . The motion of the particle at time t is entirely independent of its motion at previous times. Whatever happened to the particle in the past does not matter to determine its future behavior at t+dt. This clearly corresponds to the assumption that the collisions between the brownian particle and the particles of the fluid are instantaneous.

I. 3. Statistical properties of the fluctuating force

Our next problem is now to specify the statistical properties of the fluctuating force $\underset{\sim}{A}(t)$. Of course, in the framework of a phenomenological theory, this amounts to the introduction of a certain number of a priori assumptions. These assumptions will be based on a very intuitive feeling of the phenomenon of brownian motion. Their justification and limitations certainly require a description on a microscopic level of the whole system.

First of all, we know empirically that the characteristic time for the variation of the macroscopic quantities (i.e. the quantities which we measure, as for instance the mean velocity) is much longer than the time interval between two successive collisions of the Brownian particle with particles of the fluid (which is of the order of 10^{-21} sec. in a normal liquid). Therefore, we shall assume that we can always find time intervals Δt such that during Δt macroscopic quantities change by a negligible amount :

$$\frac{\langle \underset{\sim}{u}(t+\Delta t)\rangle - \langle \underset{\sim}{u}(t)\rangle}{\langle \underset{\sim}{u}(t)\rangle} \ll\ll 1 \qquad (I.3.1)$$

while $\underset{\sim}{A}(t)$ undergoes a large number of fluctuations, such that $\underset{\sim}{A}(t+\Delta t)$ and $\underset{\sim}{A}(t)$ are completely uncorrelated. This assumption is quite reasonable if we take into account the fact that the brownian particle is much heavier than the particles of the surrounding fluid. Then, during the collisions with the fluid particles, the velocity of the brownian particle changes by a very small amount. During Δt, the net acceleration suffered by the brownian particle because of the action of the fluctuating force will be :

$$\underset{\sim}{B}(\Delta t) = \int_{t}^{t+\Delta t} d\xi\, \underset{\sim}{A}(\xi) \qquad (I.3.2)$$

We assume that this net acceleration depends only on the time interval Δt and not on the time t at which we start to compute it, i.e. we again neglect memory effects.

We shall now make an assumption about the probability of occurence of different values for $\underset{\sim}{B}(\Delta t)$. The net acceleration in Δt is due to the superposition of a large number of random accelerations. This is very much analogous to the situation one encounters when discussing random flight problems. There, one looks for the distribution function of the increment $\Delta \underset{\sim}{R}$ during Δt in the position of a particle which has performed a large number of random steps. If each displacement is governed by a probability distribution $\tau(|\underset{\sim}{r}|^2)$ which is spherically symmetric, one shows that : (see appendix I)

$$W(\Delta \underset{\sim}{R}; \Delta t) = (4\pi D \Delta t)^{-3/2} \exp\left[-|\Delta \underset{\sim}{R}|^2 / 4 D \Delta t\right] \qquad (I.3.3)$$

where D is the diffusion coefficient which depends on the average length of the step and on the time interval between steps (see A.I.1.17)Using the analogy between these problems, we shall assume that the probability distribution for $\underset{\sim}{B}(\Delta t)$ is given by :

$$W\left[\underset{\sim}{B}(\Delta t)\right] = (4\pi q \Delta t)^{-3/2} \exp\left[-|\underset{\sim}{B}(\Delta t)|^2 / 4q\Delta t\right] \qquad (I.3.4)$$

where q is a constant . The specification of this constant requires some additional assumptions about the equilibrium properties of the velocity distribution function (see § 4)

I.4. - Velocity distribution function.

Before dealing with the general problem of finding the complete probability distribution in phase space $W(\underset{\sim}{r}, \underset{\sim}{u}, t \mid \underset{\sim}{r}_o, \underset{\sim}{u}_o, o)$ to find the particle at $\underset{\sim}{r}$ with velocity $\underset{\sim}{u}$ at time t given the initial condition $\underset{\sim}{r}_o$, $\underset{\sim}{u}_o$, we shall consider a simpler problem . We shall try to find the probability $W(\underset{\sim}{u}, t \mid \underset{\sim}{u}_o)$ that the particle has a velocity $\underset{\sim}{u}$ at time t if its initial velocity is $\underset{\sim}{u}_o$.

The formal solution of the Langevin's equation is :

$$\underset{\sim}{u} - \underset{\sim}{u}_o \, e^{-\beta t} = e^{-\beta t} \int_o^t e^{\beta \xi} \underset{\sim}{A}(\xi) \, d\xi \tag{I.4.1}$$

Both sides of (I.4.1) have the same probability distribution. Now, if

$$\underset{\sim}{\alpha} = e^{-\beta t} \int_o^t e^{\beta \xi} \underset{\sim}{A}(\xi) \, d\xi \tag{I.4.5}$$

we may also write :

$$\underset{\sim}{\alpha} = \sum_{j=1}^{N} \exp\left[-\beta(t - j\,\Delta t)\right] \underset{\sim}{B}(\Delta t) = \sum_{j=1}^{N} \underset{\sim}{\alpha}_j \tag{I.4.3}$$

if we divide the interval $(0, t)$ into N intervals Δt where Δt is of the kind defined above (i.e. such that $\underset{\sim}{A}$ suffers a large number of fluctuations while all other quantities , such as $e^{-\beta t}$, remain practically constant) .

With our assumption (I.3.4) about the probability distribution of $\underset{\sim}{B}(\Delta t)$, i.e. of $\underset{\sim}{\alpha}_j$, we can, using the theory of random flights, obtain the distribution function of $\underset{\sim}{\alpha}$ (see appendix A . I. 2) :

$$W(\underset{\sim}{\alpha}) = \left[4\pi q \int_0^t d\xi \; e^{2\beta(\xi - t)} \right]^{-3/2} \times$$

(I.4.4)

$$\times \exp\left\{ -|\underset{\sim}{\alpha}|^2 \Big/ 4q \int_0^t d\xi \, e^{-2\beta(t-\xi)} \right\}$$

Therefore, the velocity distribution function is :

$$W(\underset{\sim}{u}, t ; \underset{\sim}{u}_o) = \left[2\pi \frac{q}{\beta} (1 - e^{-2\beta t}) \right]^{-3/2} \times$$

(I.4.5)

$$\times \exp\left\{ - \frac{\beta}{2q} \frac{|\underset{\sim}{u} - \underset{\sim}{u}_o e^{-\beta t}|^2}{1 - e^{-2\beta t}} \right\}$$

For long times ($\beta t \gg 1$), we obtain asymptotically :

(I.4.6) $$W(\underset{\sim}{u}, t \to \infty ; \underset{\sim}{u}_o) = (2\pi q/\beta)^{-3/2} \exp(-\beta u^2/2q)$$

Therefore, we have an irreversible evolution towards a gaussian distribution, independent of $\underset{\sim}{u}_o$. The system has forgotten its initial condition. A priori, nothing implies that this asymptotic distribution is the Maxwell-Boltzmann equilibrium distribution .If we add this condition as a further requirement, we must choose the diffusion coefficient in velocity space to be :

(I.4.7) $$q = kT\beta / M$$

Therefore, with the following set of assumptions :

1. Langevin equation
2. characteristic time for the variation of $\underset{\sim}{A}(t)$ much smaller that the characteristic time for the variation of macroscopic quantities
3. net acceleration between t and $t + \Delta t$ depends on Δt only

4. distribution function for the net acceleration during Δt is gaussian
5. asymptotic distribution for the velocity is Maxwell-Boltzmann distribution

the distribution function in velocity space for the brownian particle is is completely determined by (I.4.5) and (I.4.7)

I.5. - Fokker-Planck equation in velocity space.

So far, we have obtained the probability distribution function corresponding to a well defined initial condition: at t=0, the velocity is $\underset{\sim}{u}_0$. To do this, we have introduced quite specific assumptions about the statistical properties of the fluctuating force. We shall now show that the problem of finding the distribution function can be reduced to the solution of a partial differential equation, the Fokker-Planck equation. In fact, this method will require less restrictive assumptions about the properties of the fluctuating force. When the same assumptions as above are made, the general Fokker-Planck equation takes a simple form and its solution reduces to (I.4.5). Another interesting feature of this method is that when further restrictions on the problem are imposed, they can be expressed as boundary conditions for the solution of the Fokker-Planck equation. Also, this equation will appear as the most adequate tool for the comparison with the results of the microscopic theory.

Again, we assume the existence of time intervals Δt such that macroscopic quantities do not vary very much during these time intervals whereas the fluctuating force has changed several times.

If we consider brownian motion as a Markoff process, i.e. if we

assume that the course which the brownian particle will take is entirely independent of its past history, we expect that the probability distribution function $W(\underset{\sim}{u}, t + \Delta t)$ will satisfy the following integral equation :

$$(I.5.1) \qquad W(\underset{\sim}{u}, t+\Delta t) = \int d(\Delta \underset{\sim}{u}) W(\underset{\sim}{u} - \Delta \underset{\sim}{u}, t) \Psi(\underset{\sim}{u} - \Delta \underset{\sim}{u}; \Delta \underset{\sim}{u})$$

where $\Psi(\underset{\sim}{u}; \Delta \underset{\sim}{u})$ is the transition probability for a velocity increase $\Delta \underset{\sim}{u}$ in Δt.

Let us now expand the lhs in a power series of Δt and the integrand in the rhs in a power series of $\Delta \underset{\sim}{u}$:

$$W(\underset{\sim}{u}, t) + \frac{\partial W}{\partial t} \Delta t + 0(\Delta t)^2 =$$

$$(I.5.2) \qquad \int d(\Delta \underset{\sim}{u}) \left\{ W(\underset{\sim}{u}, t) - \frac{\partial W}{\partial u_i} \Delta u_i + \frac{1}{2} \frac{\partial^2 W}{\partial u_i \partial u_j} \Delta u_i \Delta u_j + \dots \right\} \times$$

$$\times \left\{ \Psi(\underset{\sim}{u}; \Delta \underset{\sim}{u}) - \frac{\partial \Psi}{\partial u_i} \Delta u_i + \frac{1}{2} \frac{\partial^2 \Psi}{\partial u_i \partial u_j} \Delta u_i \Delta u_j + \dots \right\}$$

With the notation :

$$(I.5.3) \qquad \langle \alpha \rangle = \int d(\Delta \underset{\sim}{u}) \alpha \Psi(\underset{\sim}{u}; \Delta \underset{\sim}{u})$$

this equation can be rewritten :

$$(I.5.4) \qquad \frac{\partial W}{\partial t} \Delta t + 0(\Delta t)^2 = -\frac{\partial}{\partial u_i} \left[W \langle \Delta u_i \rangle \right] + \frac{1}{2} \frac{\partial^2}{\partial u_i \partial u_j} \left[W \langle \Delta u_i \Delta u_j \rangle \right] + 0\left(\langle \Delta u_i \Delta u_j \Delta u_k \rangle \right).$$

Taking into account the fact that in the Langevin equation, all systematic effects are accounted for in the friction term and that the flucua-

ting force is random, we have :

$$\text{(I.5.5)} \qquad \left\langle \int_0^{\Delta t} d\tau \, \underset{\sim}{A}(\tau) \right\rangle = \underset{\sim}{0}$$

$$\text{(I.5.6)} \qquad \left\langle \int_0^{\Delta t} d\tau \int_0^{\Delta t} d\tau' \, A_i(\tau) \, A_j(\tau') \right\rangle \sim \int_0^{\Delta t} d\tau \int_0^{\Delta t} d\tau' \, \delta(\tau - \tau') \sim \Delta t$$

Therefore, if we take the limit $\Delta t \to 0$, we obtain the general Fokker-Planck equation for the velocity distribution function :

$$\text{(I.5.7)} \qquad \frac{\partial W}{\partial t} = - \frac{\partial}{\partial u_i} \left[\frac{\langle \Delta u_i \rangle}{\Delta t} W \right] + \frac{1}{2} \frac{\partial^2}{\partial u_i \partial u_j} \left[\frac{\langle \Delta u_i \, \Delta u_j \rangle}{\Delta t} W \right]$$

From the Langevin equation, we have :

$$\text{(I.5.8)} \qquad \Delta \underset{\sim}{u} = - \beta \underset{\sim}{u} \, \Delta t + \underset{\sim}{B}(\Delta t)$$

If we further assume that the probability distribution for the net acceleration $\underset{\sim}{B}(\Delta t)$ due to the fluctuating force is given by (I.3.4) and that the asymptotic distribution must be the Maxwell-Boltzmann distribution the transition probability becomes :

$$\text{(I.5.9)} \qquad \psi(\underset{\sim}{u} ; \Delta \underset{\sim}{u}) = (4\pi\beta kT \, \Delta t / M)^{-3/2} \times \times \exp \left[-M \left| \Delta \underset{\sim}{u} + \beta \underset{\sim}{u} \, \Delta t \right|^2 / 4 \beta kT \, \Delta t \right]$$

Then , we have :

$$\text{(I.5.10)} \qquad \langle \Delta u_i \rangle = - \beta u_i \, \Delta t$$

$$\langle \Delta u_i \, \Delta u_j \rangle = (2 \beta kT / M) \delta_{i,j} + 0 (\Delta t)^2$$

and we obtain the special form of the Fokker-Planck equation :

$$\frac{\partial W}{\partial t} = \beta \left[\frac{\partial W u_i}{\partial u_i} + \frac{kT}{M} \frac{\partial^2 W}{\partial u_i^2} \right] \tag{I.5.11}$$

One verifies easily that its fundamental solution, i.e. the solution which reduces at t=0 to a delta function :

$$W(\underset{\sim}{u}, 0 ; \underset{\sim}{u}_0) = \delta(\underset{\sim}{u} - \underset{\sim}{u}_0) \tag{I.5.12}$$

is given by (I.4.5) . From it , it is of course trivial to derive the solution corresponding to an arbitrary initial distribution.

I.6.-Fokker-Planck equation in phase space.

The above procedure can be generalized to find an equation for the complete distribution function $W(\underset{\sim}{r}, \underset{\sim}{u}, t)$ in phase space . Instead of (I.5.1), we have now :

$$W(\underset{\sim}{r}, \underset{\sim}{u}, t + \Delta t) = \iint W(\underset{\sim}{r} - \Delta \underset{\sim}{r}, \underset{\sim}{u} - \Delta \underset{\sim}{u}, t) \psi(\underset{\sim}{r} - \Delta \underset{\sim}{r}, \underset{\sim}{u} - \Delta \underset{\sim}{u} ; \Delta \underset{\sim}{r}, \Delta \underset{\sim}{u}) \, d(\Delta \underset{\sim}{r}) \, d(\Delta \underset{\sim}{u}) \tag{I.6.1}$$

From the Langevin equation (we directly consider the case where an external force is present), we obtain :

$$\begin{aligned} \Delta \underset{\sim}{r} &= \underset{\sim}{u} \, \Delta t \\ \Delta \underset{\sim}{u} &= -(\beta \underset{\sim}{u} - \underset{\sim}{K}) \Delta t + \underset{\sim}{B}(\Delta t) \end{aligned} \tag{I.6.2}$$

Therefore, we have :

$$\psi(\underset{\sim}{r}, \underset{\sim}{u} ; \Delta \underset{\sim}{r}, \Delta \underset{\sim}{u}) = \psi(\underset{\sim}{u} ; \Delta \underset{\sim}{u}) \, \delta(\Delta \underset{\sim}{r} - \underset{\sim}{u} \Delta t) \tag{I.6.3}$$

We shall take for the transition probability $\psi(\underset{\sim}{u} ; \Delta \underset{\sim}{u})$ the assumption (I.5.9), in which we add a term $-\underset{\sim}{K} \Delta t$ in the exponential to take into account the effect of the external field. This assumption will lead

us to a generalization for the complete phase space of equation (I. 5.11). If we do not make a special choice for $\psi(\underset{\sim}{u};\Delta\underset{\sim}{u})$, we can follow the arguments of the previous paragraph and obtain a generalization of (I.5.7).

Integrating over $\Delta\underset{\sim}{r}$ and expanding again in a power series of Δt, $\Delta\underset{\sim}{u}$, one obtains :

$$\left(\frac{\partial W}{\partial t} + u_i \frac{\partial W}{\partial r_i}\right)\Delta t + 0(\Delta t)^2 = -\frac{\partial W\langle \Delta u_i\rangle}{\partial u_i} + \frac{1}{2}\frac{\partial^2 W\langle \Delta u_i \Delta u_j\rangle}{\partial u_i \partial u_j} + 0\left(\langle \Delta u_i \Delta u_j \Delta u_k\rangle\right) \tag{I.6.4}$$

If one computes the various averages and then takes the limit $\Delta t \to 0$, one obtains the Fokker-Planck equation :

$$\frac{\partial W}{\partial t} + u_i \frac{\partial W}{\partial r_i} + K_i \frac{\partial W}{\partial u_i} = \beta\left[\frac{\partial W u_i}{\partial u_i} + (kT/M)\frac{\partial^2 W}{\partial u_i^2}\right] \tag{I;6.5}$$

I.7. - Diffusion equation.

Let us now consider a spatially inhomogeneous system in which we have a certain number n of brownian particles. We assume that the dilution is such that we may neglect all interactions between these particles. Therefore, the probability distribution function $W(\{\underset{\sim}{r}\},\{\underset{\sim}{u}\},t)$ factorizes into a product of n factors :

$$W(\{\underset{\sim}{r}\},\{\underset{\sim}{u}\},t) = \prod_{i=1}^{n} W_i(\underset{\sim}{r}_i, \underset{\sim}{u}_i, t) \tag{I.7.1}$$

where W_i is the one particle distribution function which satisfies the Fokker-Planck equation .

We shall also assume that the density gradient is small.

In such a system, we have two kinds of processes : first , we have collisions with the particles of the surrounding fluid which insure that the velocity distribution function approaches the Maxwellian distribution ; next, we have a diffusion of the particles which will lead to spatial uniformization of the system. The time scale for the first process is given by the relaxation time β^{-1} ; this is much smaller than the time scale for the diffusion process . As a consequence, if we are interested in times long with respect to the relaxation time, we may expect that the distribution function for one particle will be of the form:

$$W_i(\underset{\sim}{r}_i, \underset{\sim}{u}_i, t) = n_i(\underset{\sim}{r}_i, t)\,(M_i/2\pi kT)^{3/2}\, e^{-M_i u_i^2/2kT} + \delta W_i(\underset{\sim}{r}_i, \underset{\sim}{u}_i, t) \qquad \text{(I.7.2)}$$

The first term describes the local equilibrium distribution which is reached for times much longer than the relaxation time.
The second term is a small correction which takes into account the existence of the diffusion process; it is of the order of the density gradient .

We shall now show that, under these circumstances, the function $n_i(\underset{\sim}{r}_i, t)$ obeys a diffusion equation .

If we integrate the Fokker-Planck equation (I.6.5) over the velocity, we obtain :

$$\frac{\partial \int d\underset{\sim}{u}_i\, W_i}{\partial t} + \frac{\partial}{\partial \underset{\sim}{r}_i} \cdot \int d\underset{\sim}{u}_i \underset{\sim}{u}_i W_i = 0 \qquad \text{(I.7.3)}$$

If we first multiply both sides of the Fokker-Planck equation by $u_{i\alpha}$ ($\alpha = x, y, z$) and then integrate over the velocity, we get :

$$\frac{\partial \int d\underset{\sim}{u}_i W_i u_{i\alpha}}{\partial t} + \frac{\partial}{\partial \underset{\sim}{r}_i} \cdot \int d\underset{\sim}{u}_i u_i W_i u_{i\alpha} = -\beta \int d\underset{\sim}{u}_i W_i u_{i\alpha} \tag{I.7.4}$$

If we combine these two equations, we obtain :

$$\frac{\partial}{\partial t}\left[\int d\underset{\sim}{u}_i W_i - \frac{1}{\beta} \frac{\partial}{\partial \underset{\sim}{r}_i} \cdot \int d\underset{\sim}{u}_i u_i W_i\right] = -\frac{1}{\beta} \frac{\partial^2}{\partial \underset{\sim}{r}_i \partial \underset{\sim}{r}_i} \int d\underset{\sim}{u}_i u_i u_i W_i \tag{I.7.5}$$

Now , using (I.7.2) and keeping only lowest order terms, we easily, obtain the diffusion equation :

$$\frac{\partial n_i(\underset{\sim}{r}_i, t)}{\partial t} = D \nabla^2_{\underset{\sim}{r}_i} n_i(\underset{\sim}{r}_i, t) \tag{I.7.6}$$

with

$$D = kT/\beta M \tag{I.7.7}$$

The density of the particles at a given point $\underset{\sim}{x}$ of space will be :

$$C(\underset{\sim}{x}, t) = \sum_{i=1}^{n} \int \delta(\underset{\sim}{x} - \underset{\sim}{r}_i) W(\{\underset{\sim}{r}\}, \{\underset{\sim}{u}\}, t)\ d\underset{\sim}{r}_i d\underset{\sim}{u}_i \tag{I.7.8}$$

Again, if we keep only lowest order terms, i.e. if we take :

$$C(\underset{\sim}{x}, t) = \sum_{i=1}^{n} n_i(\underset{\sim}{x}, t) \tag{I.7.9}$$

we verify easily that this also obeys the diffusion equation

$$\frac{\partial C(\underset{\sim}{x}, t)}{\partial t} = D \nabla^2 C(\underset{\sim}{x}, t) \tag{I.7.10}$$

Appendix I.1 - Proof of (I.3.3)

In the problem of random flights, one considers a particle which performs a sequence of steps $\underset{\sim}{r}_i \ldots \underset{\sim}{r}_i \ldots$ The magnitude and direction of all the different steps are independent of the preceding ones. One chooses a priori a distribution function $\tau_i(\underset{\sim}{r}_i)$ which gives the probability distribution that a given step $\underset{\sim}{r}_i$ lies between $\underset{\sim}{r}_i$ and $\underset{\sim}{r}_i + d\underset{\sim}{r}_i$. The problem is then to find the probability $W(\Delta\underset{\sim}{R}; \Delta t)$ that the particle has travelled a distance $\Delta\underset{\sim}{R}$ in the time interval Δt.

We shall give a proof of (I.3.3) for the simple case of one dimensional random walk with all steps of the same length and with equal a priori probability for a step to the left or to the right. Therefore, if the particle is at the origin at $t=0$, the probability that it will be at the point m after N steps $(-N \leq m \leq N)$, is given by :

$$W(m, N) = \frac{1}{2} W(m-1, N-1) + \frac{1}{2} W(m+1, N-1) \quad (N > 1) \tag{AI.1.1}$$

$$W(1, 1) = W(-1, 1) = 1/2 \tag{AI.1.2}$$

Using Fourier transforms :

$$P_N(\ell) = \sum_{m=-\infty}^{+\infty} W(m, N) e^{-ilm} \tag{AI.1.3}$$

we obtain from (AI.1.1) and (AI.1.2) :

$$P_N(\ell) = \cos l \; P_{N-1}(\ell) \qquad N > 1$$

$$P_1(\ell) = \cos 1 \tag{AI.1.4}$$

Therefore,

$$P_N(\ell) = (\cos 1)^N \tag{AI.1.5}$$

and hence inverting (AI.1.3) :

$$(AI.1;6) \qquad W(m,N) = (2\pi)^{-1} \int_{-\pi}^{+\pi} (\cos l)^N \, e^{ilm} \, dl$$

Now, with

$$(AI.1.7) \qquad (\cos l)^N = 2^{-N} \sum_{p=0}^{N} \frac{N!}{p!(N-p)!} \, e^{-l(N-2p)i}$$

we obtain easily :

$$(AI.1.9) \qquad W(m,N) = 2^{-N} \sum_{p=0}^{N} \frac{N!}{p!(N-p)!} \, \frac{\sin\pi(N-m-2p))}{\pi(N-m-2p)}$$

The last factor vanishes unless N-m-2p = 0. Therefore :

$$W(m,N) = 0 \quad \text{if N even and m odd or vice versa} \qquad (AI.1.9)$$

$$W(m,N) = 2^{-N} \, N! \{[(N-m)/2]! \, [(N+m)/2]! \}^{-1} \quad \text{if both N and m even or odd} \qquad (AI.1.10)$$

The first result is of course obvious. The second could have been obtained using combinatorial analysis. However, the method involving Fourier transforms can be generalized to more complicated problems and although exact results for arbitrary values of N cannot always be obtained, expressions such as (AI.1.6) are often useful to obtain an asymptotic result.

For our present problem , for $N \to \infty$ and m finite , using Stirling's formula :

$$(AI.1.11) \qquad \log n! = (n+\frac{1}{2}) \log n - n + \frac{1}{2} \log 2\pi \qquad (n \to \infty)$$

we obtain :

$$\log\ W(m,\ N) = (N + \frac{1}{2}\ )\log\ N\ \ - \frac{1}{2}(N + m\ + 1)\log\ (\frac{N}{2} + m)$$

$$(AI.I.12)\quad - \frac{1}{2}(N - m + 1)\log\ (\frac{N}{2} - m) - \frac{1}{2}\ \log\ 2\pi\ - N\log\ 2$$

$$\simeq\ \log\ (2/N\pi)^{1/2}\ - m^2/2N$$

and hence the asymptotic expression :

$$(AI.1.13)\qquad W(m, N) \approx\ (2/\pi N)^{1/2}\ \exp\ (-m^2/2N)$$

If each step has a length l and if τ is the time lapse between two steps, introducing the variables :

$$(AI.1.14)\qquad x = ml \qquad\qquad \Delta t\ = N\tau$$

the probability $\overline{W}(x,\ \Delta\ t)\Delta x$ that the particle lies between x and $x + \Delta\ x$ after $\Delta\ t$ is :($\Delta\ m\ = \Delta x/l$) :

$$\overline{W}(x,\ \Delta t)\ \Delta\ x\ = \sum_{m \in\ \Delta\ m} W(m, N)$$

$$(AI.1.15)\qquad = (1/2)\ W(x/l,\ \Delta\ t/\tau\ )\ \sum_{m\ \in\ \Delta\ m} 1$$

$$= (1/21)\ W(x/l, \Delta t/\tau\ )$$

where the factor $(1/2)$ takes into account the fact that for N given (odd or even) , only one half of the values of m contribute (those which are odd or even) .

Therefore, we obtain :

$$(AI.1.16)\overline{W}(x,\ \Delta\ t) = (4\ \pi\ D\ \Delta\ t)^{-1/2}\ \exp\ (-x^2/\ 4D\Delta t)$$

with

$$(AI.1.17)\qquad D = l^2/2\tau$$

(AI.1;16) is nothing else than (I.3.3) for this simple one dimensional problem. This asymptotic formula can be generalized for several three dimensional random flight problems. For instance, for a gaussian probability distribution for the j^{th} step :

$$\tau_j(\underset{\sim}{r}_j) = (2\pi l_j^2/3)^{-3/2} \exp(-3|\underset{\sim}{r}_j|^2/2l_j^2) \qquad \text{(AI.1.18)}$$

one obtains :

$$W_N(\underset{\sim}{R}) = (2\pi N\langle l^2\rangle/3)^{-3/2} \exp(-3|\underset{\sim}{R}|^2/2N\langle l^2\rangle) \qquad \text{(A.I.1.19)}$$

with

$$\langle l^2\rangle = N^{-1} \sum_{j=1}^{N} l_j^2 \qquad \text{(AI.1.20)}$$

The same expression is obtained if the probability distribution is identical for each step and spherically symmetric. Then $\langle l^2\rangle$ is the average displacement in each step (the l_j's are independent of the index j).

Appendix I.2. - Proof of (I.4.4)

We want the probability distribution of the quantity $\underset{\sim}{\alpha}$:

$$\underset{\sim}{\alpha} = \sum_{j=1}^{N} \underset{\sim}{\alpha}_j = \sum_j \psi_j \underset{\sim}{B}(\Delta t) \qquad \text{(AI.2.1)}$$

with

$$\psi_j = \exp[-\beta(t-j\Delta t)] \qquad \text{(AI.2.2)}$$

when the distribution function for $\underset{\sim}{B}(\Delta t)$ is given by (I.3.4). This is again a random flight problem, the steps being the $\underset{\sim}{\alpha}_j$'s. The probability distribution for each $\underset{\sim}{\alpha}_j$ is a gaussian and corresponds

to the function τ_j given in (AI.I.18) with :

$$\ell_j^2 = 6q \psi_j^2 \Delta t \qquad \text{(AI.2.3)}$$

Therefore, for a large number of steps , using (AI.I.19) , we have

$$W(\underset{\sim}{R}) = \left[2\pi \sum_{j=1}^{N} l_j^2/3 \right]^{-3/2} \exp\left[-3 \left| \underset{\sim}{R} \right|^2 / 2 \sum_{j=1}^{N} l_j^2 \right] \qquad \text{(AI.2.4)}$$

With

$$\sum_{j=1}^{N} l_j^2 = 6q \Delta t e^{-2\beta t} \sum_{j=1}^{N} e^{2\beta j \Delta t} \qquad \text{(AI.2.5)}$$

If we use the same approximation that led us from (I.4.2) to (I.4.3) , we may write :

$$\frac{2}{3} \sum_{j=1}^{N} l_j^2 = 4q \, e^{-2\beta t} \int_0^t d\xi \, e^{2\beta\xi} \qquad \text{(AI.2.6)}$$

Inserting (AI.2.6) into (AI.2.4) , we readily obtain (I.4.4)

References

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II. KINETIC EQUATIONS

II. 1 - Introduction.

In this chapter , we shall consider the microscopic description of an N-body system from the point of view of statistical mechanics. We shall restrict ourselves to classical systems which are homogeneous in space, although the formalism can be extended to include quantum systems and inhomogeneous situations, As this will be the most useful for us, we shall consider the case of a gas interacting through binary central forces. On the microscopic level, a complete description of the system is given by its hamiltonian , i.e. here :

$$(II.1.1) \qquad H = \sum_j \frac{p_j^2}{2m_j} + \lambda \sum_{i<j} V_{ij}(|q_i - q_j|) = H_o + \lambda V$$

where m_j is the mass of the j^{th} particle , q_j and p_j its position and momentum. λ is a dimensionless coupling constant.

Once we have the hamiltonian and the initial conditions, the evolution of the system is of course completely determined by Hamilton's equations of motion.

However, for a large system , a set of 6N differential equations is not very practical. Moreover, we can only measure a few macroscopic quantities and we never have, even at t = 0 , a detailed information about the positions and momenta of all the particles. Therefore, we shall use the idea of a representative ensemble in phase space. We imagine a large number of similar systems, with the same hamiltonian but differing by their initial states. If we take a sufficiently large set of equivalent systems, the ensemble will be characterized by a continuous density in phase space $\rho(\{p\}, \{q\}, t)$. As all points in

the ensemble move in time according to Hamilton's equations, the function ρ satisfies the Liouville equation :

$$\frac{\partial \rho}{\partial t} = [H, \rho] = - iL \rho \qquad \text{(II.1.2)}$$

where $[H, \rho]$ is the Poisson bracket of the Hamiltonian and ρ, and, hence, the Liouville operator L is :

$$L = -i \sum_j \left\{ \frac{\partial H}{\partial p_j} \frac{\partial}{\partial q_j} - \frac{\partial H}{\partial q_j} \frac{\partial}{\partial p_j} \right\} \qquad \text{(II.1.3)}$$

From this equation, one verifies easily that :

$$\int \rho(\{p\}, \{q\}, t) \{dp\, dq\}^N = \text{constant} \qquad \text{(II.1.4)}$$

If we choose this normalization constant to be equal to unity :

$$\int \rho(\{p\}, \{q\}, t) \{dp\, dq\}^N = 1 \qquad \text{(II.1.5)}$$

then, $\rho(\{p\}, \{q\}, t) \{dp\, dq\}^N$ is the probability of finding at time t a representative point in the volume element $\{dp\, dq\}^N$ of phase space.

A basic postulate in statistical mechanics is that all macroscopic quantities may be computed by taking the average value of the corresponding microscopic dynamical quantity over the distribution function of a suitable ensemble :

$$\langle A(t) \rangle = \int A(\{p\}, \{q\}) \rho(\{p\}, \{q\}, t) \{dp\, dq\}^N \qquad \text{(II.1.6)}$$

This description has the advantage that the whole mechanical behavior is given by a single linear equation, the Liouville equation (II.1.2).

To the decomposition (II.1.1) of the hamiltonian into un unperturbed part H_o (kinetic term) and a perturbed part λV (interaction) corresponds a similar decomposition of the Liouville operator :

$$L = L_o + \lambda \delta L \qquad \text{(II.1.7)}$$

This feature , as well as the strong analogy between the Liouville equation (II.1.2) and the Schrödinger equation in quantum mechanics will enable us to develop easily a perturbation technique to study the time evolution of the distribution function. In this chapter, we shall concentrate ourselves on the evolution of the velocity distribution function :

$$\rho_o(\{\underset{\sim}{p}\}, t) = \int \{dq\}^N \rho(\{\underset{\sim}{p}\}, \{\underset{\sim}{q}\}, t) \qquad \text{(II.1.8)}$$

Essentially, we shall solve formally the Liouville equation and write the formal solution as a power series of the perturbation. The introduction of a diagram technique to represent the various contributions will enable us to rearrange the terms and to write the equation of evolution in a form suitable for further discussions :

$$\frac{\partial \rho_o}{\partial t} = \int_o^t d\tau\, G(t-\tau)\, \rho_o(\tau) + \mathcal{D}(\{\rho_{\{\underset{\sim}{k}\}}(o)\}, t) \qquad \text{(II.1.9)}$$

First, we have a non-markovian term which relates $\rho_o(t)$ to its value at an earlier time τ . G(t) is an operator which describes the effect of the collisions which occur in the system on the evolution of the velocity distribution function. The non-markovian character of the first contribution is due to the fact that the collisions last over a finite time interval τ_{coll}. The second term gives the contribution to the evolution of $\rho_o(t)$ due to the existence of initial correlations in the

system , these being described by the functions $\rho_{\{k\}}(0)$.

We shall then show that, for systems interacting through short range forces and such that the initial correlations present at t=0 are over molecular distances, in the limit of a large system;

(II.1.10) $$N \to \infty , \quad \Omega \to \infty ; \quad N/\Omega = C \text{ finite}$$

(Ω : volume of the system)

and for long times :

(II.1.11) $$t \gg \tau_{coll}$$

the second term in the rhs of (II.1.9) may be neglected and that $\rho_o(t)$ satisfies a closed equation , which may be written in a pseudomarkovian form :

(II.1.12) $$i \frac{\partial \rho_o}{\partial t} = \Omega \, \psi(0) \, \rho_o$$

where $\psi(z)$ is the Laplace transform of the collision operator G(t) and $\psi(0)$ its limit when $z \to 0$. Ω is a functional of ψ and its derivatives for $z \to 0$ and takes into account the finite duration of the collision.

In this chapter, we shall show in detail how the kinetic equation (II.1.12) can be derived. We shall then sketch briefly how the same formalism can be extended to discuss the evolution of space correlations in the system. We shall also indicate the necessary modifications when an external force is present . The equations so obtained will be our basic tools for the next chapters.

We shall be able to give here only a very short outline of the theory. More details , as well as references,to the original papers can

be found in the monographs by Prigogine [1], Balescu [2] and Résibois [3].

II.2. Fourier analysis of the distribution function.

Let us expand the distribution function in a Fourier series with respect to the position variables :

$$\rho(\{\underset{\sim}{p}\},\{\underset{\sim}{q}\},t) = \Omega^{-N} \sum_{\underset{\sim}{k}_1 \cdots \underset{\sim}{k}_N} \rho_{\underset{\sim}{k}_1 \cdots \underset{\sim}{k}_N}(\{\underset{\sim}{p}\},t) \times$$

$$\times \exp\left[i \sum_{j=1}^{N} \underset{\sim}{k}_j \cdot \underset{\sim}{q}_j \right] \qquad \text{(II.2.1)}$$

The factor Ω^{-N} is introduced to allow the normalization of ρ to unity:

$$\int \{d\underset{\sim}{p}\, d\underset{\sim}{q}\}^N \rho(t) = \int \{d\underset{\sim}{p}\}^N \rho_o(t) = 1) \qquad \text{(II.2.2)}$$

The formal expansion (II.2.1) is very interesting. Indeed, it is easily verified that the Fourier coefficients $\rho_{\underset{\sim}{k}_1 \cdots \underset{\sim}{k}_N}$ have a very simple physical meaning . First of all, we notice that, in a system which is homogeneous in space, i.e. such that the distribution function is invariant with respect to space translations :

$$\rho(\{\underset{\sim}{q}_j + \underset{\sim}{a}\},\{\underset{\sim}{p}_j\},t) = \rho(\{\underset{\sim}{q}_j\},\{\underset{\sim}{p}_j\},t) \qquad \text{(II.2.3)}$$

only those coefficients such that :

$$\sum_{i=1}^{N} \underset{\sim}{k}_i = \underset{\sim}{0} \qquad \text{(II.2.4)}$$

are different from zero. Therefore, Fourier coefficients such that (II.2.4) is not fulfilled are closely connected with the existence of spatial inhomogeneities in the system.

Also , we shall,most of the time,be interested in the average value of microscopic quantities which depend only on a small , finite number s of degrees of freedom. To compute these, all we need are the reduced distribution functions :

$$(II.2.5) \qquad f_s(\underset{\sim}{p}_1 \cdots \underset{\sim}{p}_s \underset{\sim}{q}_1 \cdots \underset{\sim}{q}_s, t) = \int d\underset{\sim}{q}_{s+1} \cdots d\underset{\sim}{q}_N d\underset{\sim}{p}_{s+1} \cdots d\underset{\sim}{p}_N \rho(\{\underset{\sim}{p}\}, \{\underset{\sim}{q}\}, t)$$

In such reduced distribution functions, the only Fourier coefficients which play a role are obviously those which have at most s wave vectors different from zero.

One of the most important coefficients is that with all wave vectors equal to zero. It is the velocity distribution function :

$$(II.2.6) \qquad \rho_o(\{\underset{\sim}{p}\}, t) = \int \{d\underset{\sim}{q}\}^N \rho(\{\underset{\sim}{p}\}, \{\underset{\sim}{q}\}, t)$$

From (II.2.2), we notice that this function is normalized to unity.

To find out the meaning of the other Fourier coefficients, let us consider for instance the average density.

$$\langle n(\underset{\sim}{x}, t) \rangle = \int \{d\underset{\sim}{p}\, d\underset{\sim}{q}\}^N \sum_j \delta(\underset{\sim}{x} - \underset{\sim}{q}_j)\, \rho(\{\underset{\sim}{p}\}, \{\underset{\sim}{q}\}, t)$$

$$(II.2.7) \qquad = N/\Omega \left[1 + \sum_{\underset{\sim}{k}} e^{i\underset{\sim}{k} \cdot \underset{\sim}{x}} \int \{d\underset{\sim}{p}\}^N \rho_{\underset{\sim}{k}, \{\underset{\sim}{0}\}}(\{\underset{\sim}{p}\}, t) \right]$$

In this way , we see that the Fourier coefficients with one wave vector different from zero are connected with the local deviations from the mean density N/Ω .

As another example, let us consider the binary correlation function :

$$g(\underset{\sim}{x},\underset{\sim}{x}',t) = \sum_{ij}\left\{\int d\underset{\sim}{q}_i\, d\underset{\sim}{q}_j\, \delta(\underset{\sim}{x}-\underset{\sim}{q}_i)\delta(\underset{\sim}{x}'-\underset{\sim}{q}_j)\left\{\int d\underset{\sim}{p}_i\, d\underset{\sim}{p}_j\, f_2(\underset{\sim}{q}_i\underset{\sim}{q}_j\underset{\sim}{p}_i\underset{\sim}{p}_j t)\right.\right.$$

(II.2.8)
$$\left.\left. -\int d\underset{\sim}{p}_i\, f_1(\underset{\sim}{q}_i\underset{\sim}{p}_i t)\int d\underset{\sim}{p}_j\, f_1(\underset{\sim}{q}_j\underset{\sim}{p}_j t)\right\}\right.$$

$$= \sum_{ij}\sum_{\underset{\sim}{k}_i}\sum_{\underset{\sim}{k}_j}\left\{\left\{\int d\underset{\sim}{p}\right\}^N \rho_{\underset{\sim}{k}_i,\underset{\sim}{k}_j}(\{\underset{\sim}{p}\},t) - \left\{\int d\underset{\sim}{p}\right\}^N \rho_{\underset{\sim}{k}_i}(\{\underset{\sim}{p}\},t)\times\right.$$

$$\left.\times\left\{\int d\underset{\sim}{p}\right\}^N \rho_{\underset{\sim}{k}_j}(\{\underset{\sim}{p}\},t)\right\}\exp\left[i(\underset{\sim}{k}_i\cdot\underset{\sim}{x}+\underset{\sim}{k}_j\cdot\underset{\sim}{x}')\right]$$

In an homogeneous system, this reduces to :

(II.2.9)
$$g(\underset{\sim}{x},\underset{\sim}{x}',t) = \sum_{ij}\sum_{\underset{\sim}{k}}\left\{\int d\underset{\sim}{p}\right\}^N \rho_{\underset{\sim}{k},-\underset{\sim}{k}}(\{\underset{\sim}{p}\},t)\, e^{i\underset{\sim}{k}.(\underset{\sim}{x}-\underset{\sim}{x}')}$$

Correlations among s particles therefore depend on the Fourier coefficients with at most s indices different from zero. For a large system, the spectrum of $\underset{\sim}{k}$ becomes continuous and the rhs of (II.2.9) vanishes for $|\underset{\sim}{x}-\underset{\sim}{x}'|\to\infty$ if $\rho_{\underset{\sim}{k},-\underset{\sim}{k}}$ is sufficiently regular.

Another interesting feature of (II.2.1) is that this is in fact an expansion in terms of the eigenfunctions of the unperturbed Liouville operator. Indeed, from (II.1.7), (II.1.3) and (II.1.1), we have :

(II.2.10)
$$L_o = -i\sum_j \frac{\underset{\sim}{p}_j}{m_j}\cdot\frac{\partial}{\partial\underset{\sim}{q}_j}$$

If we use the same notation for eigenfunctions as in quantum mechanics:

(II.2.11)
$$|\{\underset{\sim}{k}\}\rangle = \Omega^{-N/2}\exp\left[i\sum_j \underset{\sim}{k}_j\cdot\underset{\sim}{q}_j\right]$$

we have :

(II.2.12)
$$L_o|\{\underset{\sim}{k}\}\rangle = \left[\sum_j (\underset{\sim}{k}_j\cdot\underset{\sim}{p}_j/m_j)\right]|\{\underset{\sim}{k}\}\rangle$$

These eigenfunctions are orthogonal and normalized to unity :

$$(II.2.13) \qquad \Omega^{-N}\int\{dq\}^N \exp\left[-i\sum_j (\underset{\sim}{k}_j - \underset{\sim}{k}'_j).\underset{\sim}{q}_j\right] = \langle\{k\}|\{k'\}\rangle = \prod_j \delta_{\underset{\sim}{k}_j,\underset{\sim}{k}'_j}$$

From these properties, the time dependence of the Fourier coefficients $\rho_{\{\underset{\sim}{k}\}}$ in a system of non interacting particles ($\lambda = 0$) is easily found :

$$(II.2.14) \qquad \rho_{\{\underset{\sim}{k}\}}(\{p\},t) = \bar{\rho}_{\{\underset{\sim}{k}\}}(\{p\}) \exp\left[i\sum_j (\underset{\sim}{k}_j.\underset{\sim}{p}_j/m_j)t\right] (\lambda=0)$$

When the particles are interacting , the time dependence of the $\rho_{\{\underset{\sim}{k}\}}(t)$ is of course much more complex. Besides the oscillating exponential factor corresponding to the free propagation of the particles, we have a further time dependence in the coefficients $\bar{\rho}_{\{\underset{\sim}{k}\}}(\{p\})$ in the rhs of (II.2.14) because of the collisions occuring in the system.

II.3. Formal solution of the Liouville equation. Resolvent operator

The formal solution of the Liouville equation is of course very easily written :

$$(II.3.1) \qquad \rho(t) = e^{-iLt}\rho(0)$$

From this, we obtain for the various Fourier coefficients of the distribution function :

$$\rho_{\{\underset{\sim}{k}\}}(t) = \sum_{\{\underset{\sim}{k}'\}} \langle \{\underset{\sim}{k}\} | e^{-iLt} | \{\underset{\sim}{k}'\} \rangle \rho_{\{\underset{\sim}{k}'\}}(0)$$

$$= \Omega^{-N} \sum_{\{\underset{\sim}{k}'\}} \int \{d\underset{\sim}{q}\}^N \exp\left[-i \sum_j \underset{\sim}{k}_j \cdot \underset{\sim}{q}_j\right] e^{-iLt} \times \tag{II.3.2}$$

$$\times \exp\left[i \sum_j \underset{\sim}{k}'_j \cdot \underset{\sim}{q}_j\right] \rho_{\{\underset{\sim}{k}'\}}(0)$$

As L is an operator in the complete phase space, the matrix elements in the rhs of (II.3.2) are still operators in velocity space.

The operator e^{-iLt} can be expanded formally in a power series of the interaction :

$$e^{-iLt} = e^{-iL_o t} - i\lambda \int_o^t dt_1 \, e^{-iL_o(t-t_1)} \delta L \, e^{-iL_o t_1}$$

$$+ (-i\lambda)^2 \int_o^t dt_1 \int_o^{t_1} dt_2 \, e^{-iL_o(t-t_1)} \delta L \, e^{-iL_o(t_1-t_2)} \delta L \, e^{-iL_o t_2} \tag{II.3.3}$$

$$+ \ldots$$

This equality is most easily verified if one takes the time derivative of both sides of (II.3.3) .

However, the behavior of the system can be discussed much more easily if, rather than the operator e^{-iLt} , one considers its Laplace transform, the resolvent operator R(z) :

$$R(z) = -i \int_o^\infty dt \, e^{izt} \, e^{-iLt} = \frac{1}{z - L} \quad (z \in S^+) \tag{II.3.4}$$

From (II.3.2) and (II.3.4) , we obtain after an inverse Laplace transform :

$$\rho_{\{\underset{\sim}{k}\}}(t) = -\frac{1}{2\pi i} \int_C dz \, e^{-izt} \langle \{\underset{\sim}{k}\} | R(z) | \{\underset{\sim}{k}'\} \rangle \rho_{\{\underset{\sim}{k}'\}}(0) \tag{II.3.5}$$

where the contour C is a parallel to the real axis in the upper half plane, above all singularities of the integrand. (II. 3. 5) can be easily verified for a finite system . Indeed, then , the operator L is a hermitian operator and all its eigenvalues, although unknown , are real. For an infinite system ($\Omega \to \infty$) , the properties of the Liouville operator are not known. We shall however assume that (II. 3. 5) remains valid when we perform the limiting procedure (II. 1. 10) .

The resolvent operator can be expanded in a power series of the perturbation

$$R(z) = \sum_{n=0}^{\infty} \frac{1}{z - L_o} \left(\delta L \frac{1}{z - L_o}\right)^n \qquad \text{(II. 3. 6)}$$

This result can also be obtained from (II. 3. 3) through a Laplace transform, using the convolution theorem.

(II. 3. 5) and (II. 3. 6) will be our basic equations for the following discussion. Of course this means that we assume that perturbation theory up to an infinite order is valid. Whether this is true or not is an unanswered question and we shall not discuss it.

The unperturbed resolvent operator is diagonal in the $|\{\underset{\sim}{k}\}\rangle$ representation. Its matrix elements are very simple :

$$\langle\{\underset{\sim}{k}\}| R_o(z) |\{\underset{\sim}{k}\}\rangle = \langle\{\underset{\sim}{k}\}| \frac{1}{z - L_o} |\{\underset{\sim}{k}\}\rangle$$

$$= \frac{1}{z - \sum_j \underset{\sim}{k}_j . \underset{\sim}{v}_j} \qquad \text{(II. 3. 7)}$$

where

$$\underset{\sim}{v}_j = \underset{\sim}{p}_j / m_j \qquad \text{(II. 3. 8)}$$

is the velocity of the j^{th} particle.

As to the operator δL, we obtain from (II.1.7), (II.1.3) and (II.1.1):

$$-i\delta L = \sum_{i<j} \left(\frac{\partial V_{ij}}{\partial \underset{\sim}{q}_i} \cdot \frac{\partial}{\partial \underset{\sim}{p}_i} + \frac{\partial V_{ij}}{\partial \underset{\sim}{q}_j} \cdot \frac{\partial}{\partial \underset{\sim}{p}_j} \right) \tag{II.3.9}$$

If we expand the potential in a Fourier series :

$$V_{ij}\left(|\underset{\sim}{q}_i - \underset{\sim}{q}_j|\right) = (8\pi^3/\Omega) \sum_{\underset{\sim}{k}} V_k \, e^{i\underset{\sim}{k}\cdot(\underset{\sim}{q}_i - \underset{\sim}{q}_j)} \tag{II.3.10}$$

we have:

$$-i\delta L = (8\pi^3 i/\Omega) \sum_{i<j} \sum_{\underset{\sim}{k}} V_k \, \underset{\sim}{k} \cdot \left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j} \right) \times$$

$$\times \, e^{i\underset{\sim}{k}\cdot(\underset{\sim}{q}_i - \underset{\sim}{q}_j)} \tag{II.3.11}$$

It is easy to verify that the only non vanishing matrix elements are those where the initial and final states have only two different wave vectors, the total wave vector being conserved :

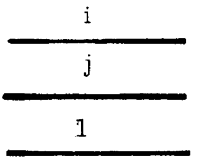
$$\left\langle \underset{\sim}{k}_1 \ldots \underset{\sim}{k}_i \ldots \underset{\sim}{k}_j \ldots \underset{\sim}{k}_N \middle| \delta L \middle| \underset{\sim}{k}_1 \ldots \underset{\sim}{k}'_i \ldots \underset{\sim}{k}'_j \ldots \underset{\sim}{k}_N \right\rangle$$

$$= \delta_{\underset{\sim}{k}_i + \underset{\sim}{k}_j, \underset{\sim}{k}'_i + \underset{\sim}{k}'_j} (8\pi^3/\Omega) \, V_{|\underset{\sim}{k}_i - \underset{\sim}{k}'_i|} (\underset{\sim}{k}_i - \underset{\sim}{k}'_i) \cdot \left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j} \right) \tag{II.3.12}$$

The fact that only two wave vectors are modified and that the total wave vector is conserved is of course due to our choice of binary central forces. An interesting consequence of the condition of conservation of the total wave vector is that the Fourier coefficients are divided into subsets corresponding to the different values of the total wave vector. Each subset evolves in time independently of all the others. Therefore, for instance, a system which is initially homogeneous in space will remain so in the course of time.

II.4 - Diagram representation of the formal solution of the Liouville equation.

The classification of the various terms in the series (II.3.6) is best performed if one uses a diagram technique . Let us associate with each state $|\{\underset{\sim}{k}\}\rangle = |\underset{\sim}{k}_1 \ldots \underset{\sim}{k}_N\rangle$ with n non vanishing wave vectors a set of n lines running from the right to the left. Each line is labelled with an index corresponding to the particle; when necessary, we shall also indicate the wave vector.An example is given in fig. II.4.1.



Diagrammatic representation of the state

$|\{\underset{\sim}{0}\}\, \underset{\sim}{k}_i\, \underset{\sim}{k}_j\, \underset{\sim}{k}_l\rangle$

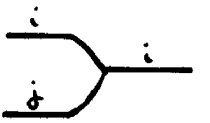
Fig. II.4.1

The matrix elements of δL provoke a modification of two wave vectors $\underset{\sim}{k}_i\, \underset{\sim}{k}_j \rightarrow \underset{\sim}{k}'_i\, \underset{\sim}{k}'_j$. Taking into account the fact that among these, none, one or two may correspond to the wave vector $\underset{\sim}{0}$, we have 6 basic diagrams (see fig. II.4.2) .

$\langle .. \underset{\sim}{k}_i .. \underset{\sim}{k}_j | \delta L | .. \underset{\sim}{k}'_i .. \underset{\sim}{k}'_j .. \rangle$

$\underset{\sim}{k}_i + \underset{\sim}{k}_j = \underset{\sim}{k}'_i + \underset{\sim}{k}'_j$

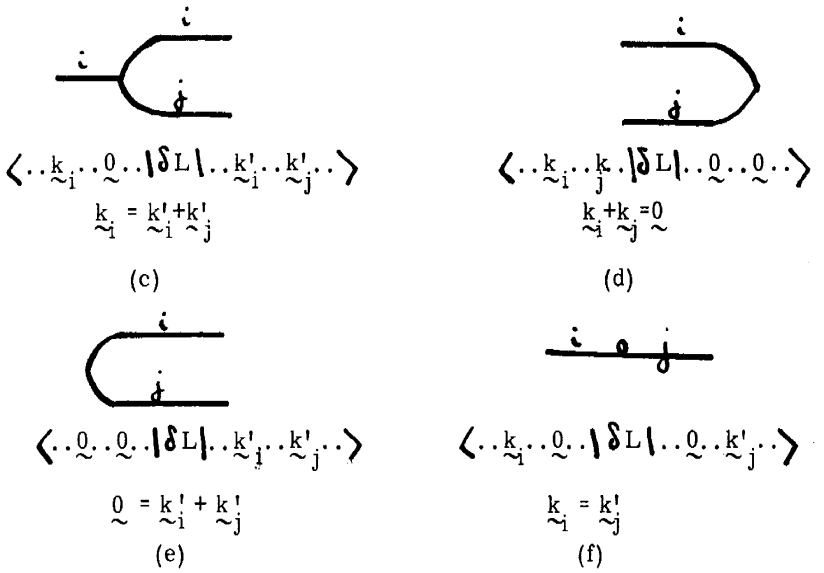
(a)



$\langle .. \underset{\sim}{k}_i .. \underset{\sim}{k}_j .. | \delta L | .. \underset{\sim}{k}'_i .. \underset{\sim}{0} .. \rangle$

$\underset{\sim}{k}_i + \underset{\sim}{k}_j = \underset{\sim}{k}'_i$

(b)

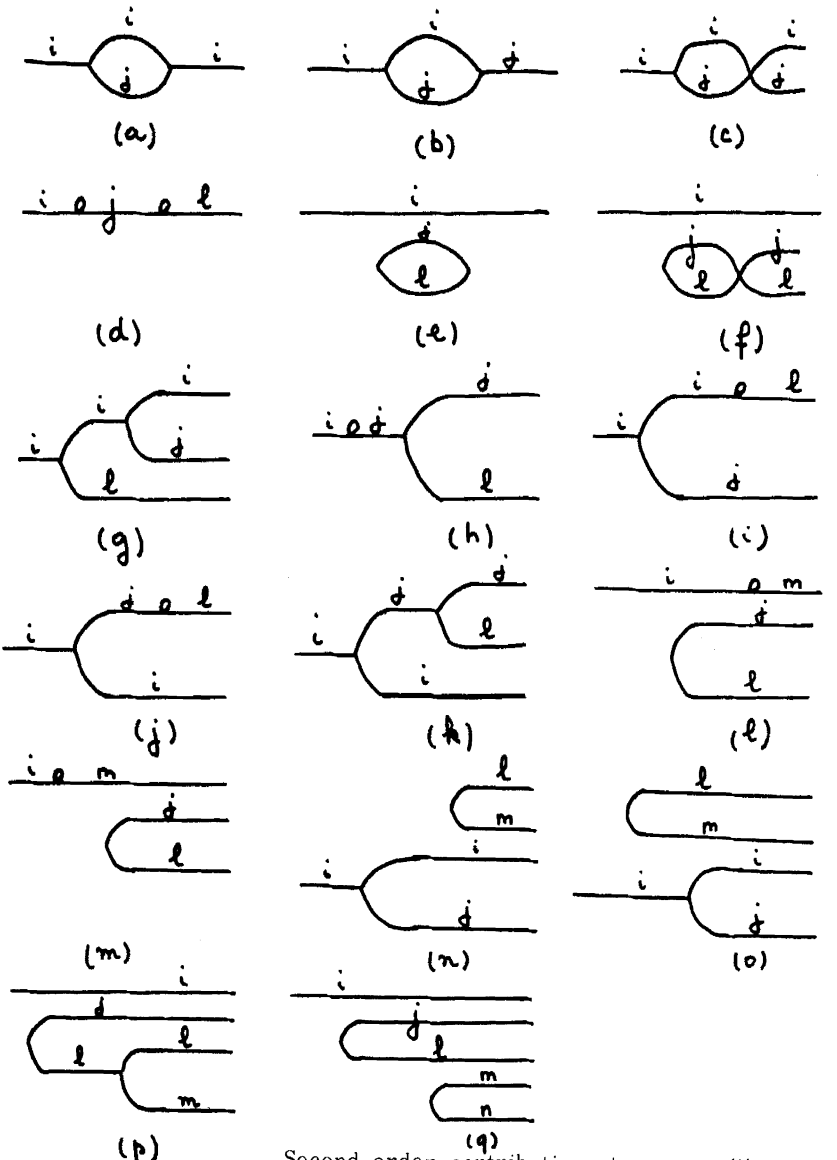


Basic interaction vertices .

Fig. II.4.2.

Taking into account the fact that the states $|\{\underset{\sim}{k}\}\rangle$ describe well defined correlations in the system, the diagrams indicate very clearly what changes in these correlations occur as a consequence of the interactions. The present formalism thus appear as a description of mechanics in terms of a dynamics of correlations.

With the diagrams, it is easy to represent any contribution to the formal solution of the Liouville equation. To obtain the n^{th} order contribution to the evolution of $\rho_{\{\underset{\sim}{k}\}}(t)$, we first draw the final state $|\{\underset{\sim}{k}\}\rangle$. Then, we go to the right through n vertices, using all possible combinations of the six basic vertices which conserve the total wave vector. As an example , the second order contributions to the evolution of $\rho_{\underset{\sim}{k}_i}(t)$ are given in fig. II.4.3).



Second order contributions to $\rho_{\underset{\sim}{k}_i}(t)$

Fig. 4.3

Also, it is very easy, once we have a given diagram, to write down its analytic contribution . Let us for instance consider diagram (g) in fig. II. 4.3.

Reading the diagram from the left to the right, we obtain (we do not write explicitly wave vector equal to $\underset{\sim}{0}$) :

$$\left\langle \{\underset{\sim}{k}\} \left| \frac{1}{z-L_o} \left(\delta L \frac{1}{z-L_o}\right)^2 \right| \{\underset{\sim}{k}'\} \right\rangle_{(g)} = \left\langle \underset{\sim}{k}_i \left| \frac{1}{z-L_o} \right| \underset{\sim}{k}_i \right\rangle \left\langle \underset{\sim}{k}_i \left| \delta L \right| \underset{\sim}{k}'_i, \underset{\sim}{k}'_1 \right\rangle \times$$

$$\text{(II.4.1)} \left\langle \underset{\sim}{k}'_i, \underset{\sim}{k}'_1 \left| \frac{1}{z-L_o} \right| \underset{\sim}{k}'_i, \underset{\sim}{k}'_1 \right\rangle \left\langle \underset{\sim}{k}'_i, \underset{\sim}{k}'_1 \left| \delta L \right| \underset{\sim}{k}''_i, \underset{\sim}{k}''_j, \underset{\sim}{k}'_1 \right\rangle \times$$

$$\times \left\langle \underset{\sim}{k}''_i, \underset{\sim}{k}''_j, \underset{\sim}{k}'_1 \left| \frac{1}{z-L_o} \right| \underset{\sim}{k}''_i, \underset{\sim}{k}''_j, \underset{\sim}{k}'_1 \right\rangle \delta_{\underset{\sim}{k}_i, \underset{\sim}{k}'_i + \underset{\sim}{k}'_1} \delta_{\underset{\sim}{k}_i, \underset{\sim}{k}''_i + \underset{\sim}{k}''_j + \underset{\sim}{k}'_1}$$

In other words, we write a sequence of matrix elements of δL, each corresponding in a well defined order to the vertices; in between these matrix elements, we sandwich propagators (see II.3.7), which are matrix elements of $R_o(z)$ for the corresponding intermediate state; we also have such a propagator for the initial and final states.

II.5. Classification of diagrams.

We shall now discuss the topological structure of the diagrams which appear in the solution of the Liouville equation.

In the most general diagram, we may distinguish three different regions. Let us denote by $|\{\underset{\sim}{k}''\}\rangle$ the initial state of correlation (at the right), by $|\{\underset{\sim}{k}'\}\rangle$ the intermediate state where we have the minimum number of lines.(which may of course appear several times in the diagram and by $|\{\underset{\sim}{k}\}\rangle$ the final state. If s is the minimum number of lines in the diagram, it may of course happen that we have several different states with that number of lines. We then choose as $|\{\underset{\sim}{k}'\}\rangle$ the last one starting from the right . As an example, in fig. II.5.1b we have two different states with one line : $|\underset{\sim}{k}_\alpha, \{\underset{\sim}{0}\}\rangle$ and $|\underset{\sim}{k}_j, \{\underset{\sim}{0}\}\rangle$. As the latter is the second one when we start from the right, we choose it as our state $|\{\underset{\sim}{k}'\}\rangle$. Another example (with two lines) can be found in fig. II.5.1e.

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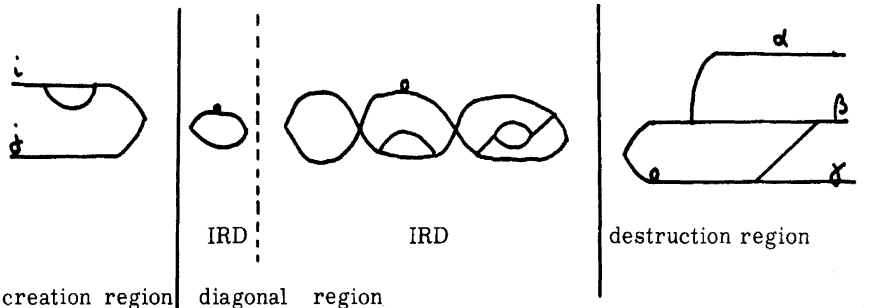
In the most general case where $|\{\underset{\sim}{k}''\}\rangle \neq |\{\underset{\sim}{k}'\}\rangle \neq |\{\underset{\sim}{k}\}\rangle$ we have :

1. a destruction region, i.e. a region where we go from the state $|\{\underset{\sim}{k}''\}\rangle$ to the state $|\{\underset{\sim}{k}'\}\rangle$ in such a way that no intermediate state is identical to $|\{\underset{\sim}{k}'\}\rangle$; in such a region, we go from a state with given correlations to a state where we have less correlations.

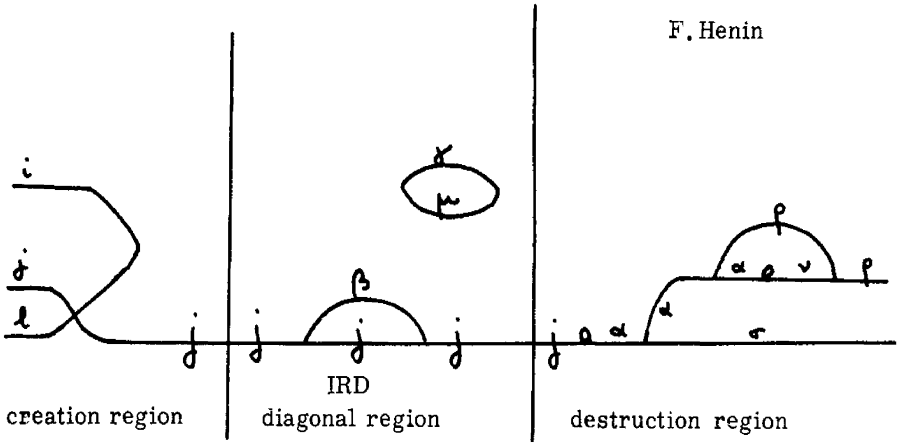
2. a diagonal region, i.e. a region where we go from the state $|\{\underset{\sim}{k}'\}\rangle$ back to the state $|\{\underset{\sim}{k}'\}\rangle$; in general such a region contains a succession of irreducible diagonal fragments. By definition, an irreducible diagonal fragment is such that we go from a given state back to that state through a path such that no intermediate state is identical to the initial state.

3. a creation region, , i.e. a region where we go from the state $|\{\underset{\sim}{k}'\}\rangle$ to the final state $|\{\underset{\sim}{k}\}\rangle$ in such a way that no intermediate state is identical to $|\{\underset{\sim}{k}'\}\rangle$; in this region, we go from the state of correlations $|\{\underset{\sim}{k}'\}\rangle$ to a state of higher correlations.

Examples of this decomposition are given in fig. II.5.1 (diagrams (a) and (b) contain the three different types of regions while diagrams (c) , (d) and (e) have only one or two of them) .

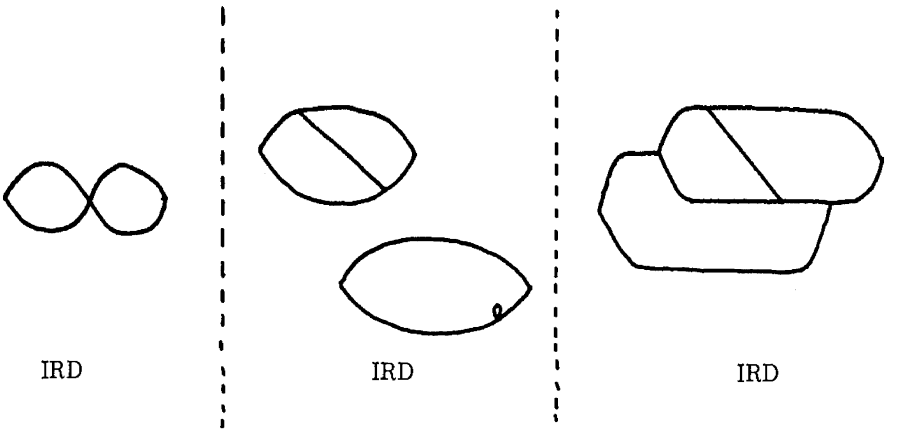


(α)



$$|\{\underset{\sim}{k}\}\rangle = |\underset{\sim}{k}_i, \underset{\sim}{k}_j, \underset{\sim}{k}_\ell = \underset{\sim}{k}'_j - \underset{\sim}{k}_j - \underset{\sim}{k}_i\rangle ; |\{\underset{\sim}{k}'\}\rangle = |\underset{\sim}{k}'_j\rangle \; ; \; |\{\underset{\sim}{k}''\}\rangle = |\underset{\sim}{k}_\sigma, \underset{\sim}{k}_\rho = \underset{\sim}{k}'_j - \underset{\sim}{k}_\sigma\rangle$$

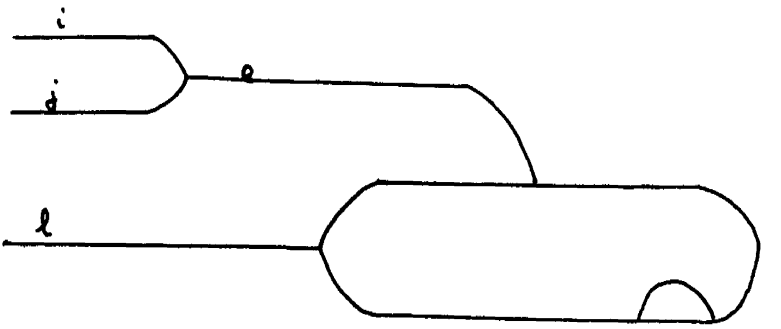
(b)



diagonal diagram

$$|\{\underset{\sim}{k}\}\rangle \equiv |\{\underset{\sim}{k}'\}\rangle \equiv |\{\underset{\sim}{k}''\}\rangle \equiv |\{0\}\rangle$$

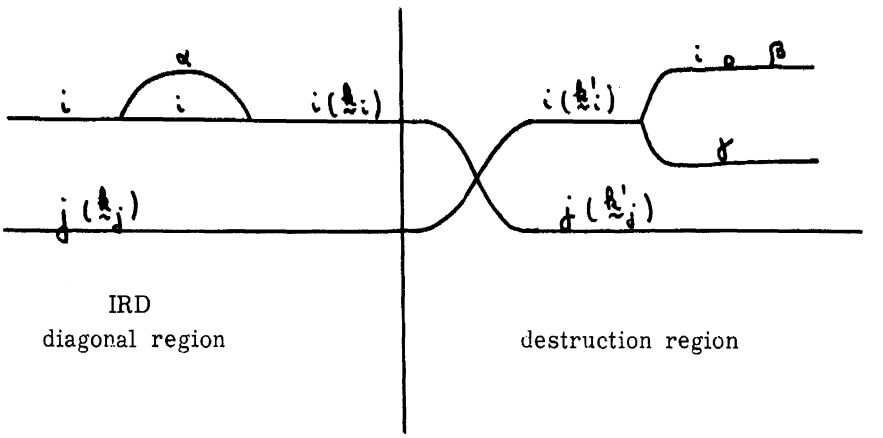
(c)



creation diagram

$$|\{\underset{\sim}{k}\}\rangle = |\underset{\sim}{k}_i, \underset{\sim}{k}_j, \underset{\sim}{k}_\ell = -\underset{\sim}{k}_i - \underset{\sim}{k}_j\rangle \qquad |\{\underset{\sim}{k}'\}\rangle \equiv |\{\underset{\sim}{k}''\}\rangle \equiv |\{0\}\rangle$$

(d)



$$|\{\underset{\sim}{k}\}\rangle \equiv |\{\underset{\sim}{k}'\}\rangle = |\underset{\sim}{k}_i, \underset{\sim}{k}_j\rangle \qquad |\{\underset{\sim}{k}''\}\rangle = |\underset{\sim}{k}'_j, \underset{\sim}{k}_\beta, \underset{\sim}{k}_\gamma = \underset{\sim}{k}_i + \underset{\sim}{k}_j - \underset{\sim}{k}'_j - \underset{\sim}{k}_\beta\rangle$$

(e)

IRD = irreducible diagonal fragment

Examples of decomposition of diagrams in creation, diagonal and destruction regions.

Fig. II.5.1

As we shall see later on, the time dependence of the various contributions will be closely related to this decomposition.

II.6 - Initial conditions.

We shall always consider initial conditions such that macroscopic properties like the pressure, density etc.. are finite at every point of the system, even when the limiting case of an infinite system is considered. The interest of this class of initial conditions is obvious from the physical point of view; it can be shown that once the existence and finiteness of the reduced distribution functions for a finite number of degrees of freedom is imposed at $t=0$, it will remain so at an arbitrary later time.

This choice of initial conditions introduces mathematical restrictions on the class of functions ρ we consider. It can be shown that this initial condition requires the following volume dependence for the various Fourier coefficients :

$$\rho_{\underset{\sim}{k}_1 \cdots \underset{\sim}{k}_N} = (8\pi^3/\Omega)^{\nu} \tilde{\rho}_{\underset{\sim}{k}_1 \cdots \underset{\sim}{k}_N} \qquad \text{(II.6.1)}$$

where ν is the number of independent non vanishing wave vectors which

appear in the set $\underset{\sim}{k}_1 \ldots \underset{\sim}{k}_N$. (By this, we mean the total number of non vanishing wave vectors minus the number of relations of the form $\underset{\sim}{k}_i + \ldots + \underset{\sim}{k}_j = \underset{\sim}{0}$ which they satisfy). For instance :

$$\rho_{\underset{\sim}{k}_1, \underset{\sim}{k}_2} = (8\pi^3/\Omega)^2 \, \tilde{\rho}_{\underset{\sim}{k}_1, \underset{\sim}{k}_2} \qquad (\underset{\sim}{k}_1 \neq -\underset{\sim}{k}_2)$$

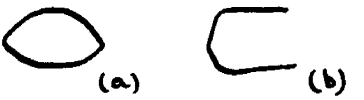
(II. 6. 2)

$$\rho_{\underset{\sim}{k}, -\underset{\sim}{k}} = (8\pi^3/\Omega) \, \tilde{\rho}_{\underset{\sim}{k}, -\underset{\sim}{k}}$$

The coefficients $\tilde{\rho}_{\underset{\sim}{k}_1 \ldots \underset{\sim}{k}_N}$ do no longer depend explicitly on Ω or N, although they might still depend on the ratio N/Ω.

With these assumptions, although in the formal solution of the Liouville equation, we find terms growing more and more rapidly $(N, N^2 \ldots)$, all contributions to the reduced distribution functions for a finite number of degrees of freedom remain finite. The proof of these theorems is rather lengthy and cannot be given here. However, we shall illustrate them with two examples. We shall consider the contribution of the two diagrams of fig. II. 6. 1 to the one particle velocity distribution function :

(II. 6. 3) $$\varphi_1(\underset{\sim}{v}, t) = \int d\underset{\sim}{p}_2 \ldots d\underset{\sim}{p}_N \, \rho_o(\{\underset{\sim}{p}\}, t)$$



Lowest order diagonal and destruction contributions to $\rho_o(t)$

Fig. II. 6. 1

The contribution of the cycle (fig. II. 6. 1a) to the evolution of $\rho_o(t)$ is (see equ. (II. 3. 5), (II. 3. 7), (II. 3. 12) and (II. 4. 1))

$$\left[\rho_o(t)\right]_o = -\frac{1}{2\pi i}\lambda^2 \int_C dz\, e^{-izt} \sum_{i<j} \sum_{\underset{\sim}{k}} \langle 0 | \frac{1}{z-L_o} | 0 \rangle \times$$

$$\times \langle 0 | \delta L | \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} \rangle \langle \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} | \frac{1}{z-L_o} | \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} \rangle \times$$

(II.6.4)
$$\times \langle \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} | \delta L | 0 \rangle \langle 0 | \frac{1}{z-L_o} | 0 \rangle \rho_o(0)$$

$$= \lambda^2 (8\pi^3/\Omega)^2 \sum_{i<j} \sum_{\underset{\sim}{k}} (1/2\pi i) \int_C dz \frac{e^{-izt}}{z^2} (V_k)^2 \times$$

$$\times \underset{\sim}{k}.\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \frac{1}{z - \underset{\sim}{k}.(\underset{\sim}{v}_i - \underset{\sim}{v}_j)} \underset{\sim}{k}.\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \rho_o(0)$$

In the limit of a large system (see II.1.10), the summation over $\underset{\sim}{k}$ becomes an integral :

(II.6.5)
$$(8\pi^3/\Omega) \sum_{\underset{\sim}{k}} \rightarrow \int d^3k$$

Hence

$$\left[\rho_o(t)\right]_o = \lambda^2 (8\pi^3/\Omega) \sum_{i<j} \int d^3k\, (1/2\pi i) \int_C dz \frac{e^{-izt}}{z^2} \times$$

(II.6.6)
$$\times |V_k|^2 \underset{\sim}{k}.\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \frac{1}{z - \underset{\sim}{k}.(\underset{\sim}{v}_i - \underset{\sim}{v}_j)} \underset{\sim}{k}.\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \rho_o(0)$$

$$= 0(NC)$$

if we take into account the fact that the sum over the particles contains N^2 terms.

Similarily, using (II.3.11), the contribution of the destruction diagram (fig. II.6.1b) is :

$$\left[\rho_o(t)\right]_C = -\lambda (8\pi^3/\Omega)^2 \sum_{i<j} \sum_{\underset{\sim}{k}} \int_C dz\, e^{-izt} (2\pi i)^{-1} \times$$

$$\times \langle 0 | \frac{1}{z - L_o} | 0 \rangle \langle 0 | \delta L | \underset{\sim}{k}_i = \underset{\sim}{k},\ \underset{\sim}{k}_j = -\underset{\sim}{k} \rangle \times$$

(II.6.7)

$$\times \left\langle \underset{\sim}{k}_i = \underset{\sim}{k}\ ,\ \underset{\sim}{k}_j = -\underset{\sim}{k} \right| \frac{1}{z - L_o} \left| \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} \right\rangle \tilde{\rho}^{(0)}_{\underset{\sim}{k}_i = \underset{\sim}{k},\ \underset{\sim}{k}_j = -\underset{\sim}{k}}$$

$$= \lambda (8\pi^3/\Omega)^2 \sum_{i<j} \sum_{\underset{\sim}{k}} (1/2\pi i) \int_C dz\, \frac{e^{-izt}}{z} V_{\underset{\sim}{k}} \underset{\sim}{k} \cdot \left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \times$$

$$\times \frac{1}{z - \underset{\sim}{k} \cdot (\underset{\sim}{v}_i - \underset{\sim}{v}_j)} \tilde{\rho}^{(0)}_{\underset{\sim}{k}_i = \underset{\sim}{k},\ \underset{\sim}{k}_j = -\underset{\sim}{k}}$$

For large systems, this becomes :

$$\left[\rho_o(t)\right]_C = \lambda (8\pi^3/\Omega) \sum_{i<j} \int d^3k\, (1/2\pi i) \int_C dz\, \frac{e^{-izt}}{z} V_k$$

(II.6.8)

$$\underset{\sim}{k} \cdot \left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \frac{1}{z - \underset{\sim}{k} \cdot (\underset{\sim}{v}_i - \underset{\sim}{v}_j)} \tilde{\rho}^{(0)}_{\underset{\sim}{k}_i = \underset{\sim}{k},\ \underset{\sim}{k}_j = -\underset{\sim}{k}}$$

$$= 0(NC)$$

Let us now introduce these two results in (II.6.3) . Because of the integrations over the velocities, all contributions vanish except if $i = 1$. This means, that, among the $N(N-1)$ diagrams a or b of fig. II.6.1, we only keep the $(N-1)$ diagrams such that $i = 1$. Therefore we obtain :

$$\left[\varphi_1(\underset{\sim}{v}_1, t)\right]_0 = \lambda^2 (8\pi^3/\Omega) \sum_{j>1} \int d^3k\, (1/2\pi i) \int_C dz\, \frac{e^{-izt}}{z^2} \times$$

$$\times |V_k|^2 \underset{\sim}{k} \cdot \frac{\partial}{\partial \underset{\sim}{p}_1} \int d\underset{\sim}{p}_2 \ldots d\underset{\sim}{p}_N \frac{1}{z - \underset{\sim}{k} \cdot (\underset{\sim}{v}_1 - \underset{\sim}{v}_j)} \times$$

$$(II.6.9) \qquad * \; \underset{\sim}{k} \cdot \left(\frac{\partial}{\partial \underset{\sim}{R}_1} - \frac{\partial}{\partial \underset{\sim}{R}_j}\right) \rho_o^{(0)}$$

$$= 0(C)$$

$$\left[\varphi_1 \left(\underset{\sim}{v}_1, t\right)\right]_C = \lambda \left(8\pi^3/\Omega\right) \sum_{j>1} \int d^3k \, (1/2\pi i) \int_C dz \, \frac{e^{-izt}}{z} \; *$$

$$(II.6.10) \qquad * \; V_k \underset{\sim}{k} \cdot \frac{\partial}{\partial \underset{\sim}{R}_1} \int d\underset{\sim}{R}_2 \cdots d\underset{\sim}{R}_N \; \frac{1}{z - \underset{\sim}{k} \cdot (\underset{\sim}{v}_1 - \underset{\sim}{v}_j)} \tilde{\rho}_{\underset{\sim}{k}_1 = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k}}^{(0)}$$

$$= 0(C)$$

The general mechanism which insures convergence at an arbitrary time for the reduced distribution function of a finite number of degrees of freedom is thus twofold ; first , our assumption (II. 6. 1) (which for instance introduced a factor Ω^{-1} in (II. 6. 7)), then the suppression of the contributions of many diagrams once we perform the integrations over all but a finite number of degrees of freedom.

In many problems we shall further reduce the class of initial conditions we consider . For instance we shall often restrict ourselves to the class of initial conditions where the correlations are over distances of the order of molecular distances. This will be discussed when necessary.

The property of finiteness of the reduced distribution functions plays a very important role in the obtention of irreversible equations for the macroscopic quantities. Indeed, once finiteness is ascertained with respect to N and Ω, we can further look at the time behavior of the system and find out that in the long time limit, some terms may become negligible. This is not the case for the complet distribution function because of the divergences with respect to N in the

limit of a large system. However, for the sake of simplicity it appears often convenient not to worry about this N divergence and to write down asymptotic equations for the complete distribution function (kinetic equations, see § 9) . This procedure is perfectly legitimate provided we keep in mind the fact that all asymptotic equations we shall derive are valid only when they are used for the computation of average quantities which depend on a finite number of degrees of freedom.

II.7 - Time dependence

In order to get some feeling about the simplifications which may arise when we discuss the long time behavior of the system, let us consider in detail some simple and typical contributions which we meet in the evolution of homogeneous systems. To make things even clearer, let us choose a special form of a repulsive potential which will enable us to perform all calculations completely :

$$V(r) = V_o \, e^{-\varkappa r} \tag{II.7.1}$$

$\varkappa^{-1}$ is here the range of the intermolecular force. The Fourier transform of this potential is :

$$V_k = V_o \frac{8\pi\varkappa}{(k^2+\varkappa^2)^2} \tag{II.7.2}$$

Let us now first investigate the time dependence of the contribution of the simplest diagonal fragment to the evolution of the velocity distribution function : the cycle (fig. II.6.1a) . Using (II.3.6) ,(II.3.11) and (II.7.2), we have :

$$(II.7.3)\qquad \left[\rho_o(t)\right]_{cycle} = -(1/2\pi i)\int_C dz\ \frac{e^{-izt}}{z^2}\,\psi_2(z)\,\rho_o(0)$$

with :

$$(II.7.4)\qquad \psi_2(z) = \lambda^2 \langle 0|\delta L \frac{1}{z - L_o}\delta L|0\rangle$$

$$= -\lambda^2(8\pi K V_o)^2(8\pi^3/\Omega)\sum_{i<j}\int d^3k\ (k^2+K^2)^{-4}$$

$$\underset{\sim}{k}.(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j})\frac{1}{z - \underset{\sim}{k}.(\underset{\sim}{v}_i - \underset{\sim}{v}_j)}\ \underset{\sim}{k}.(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j})$$

$$= -\lambda^2\sum_{\alpha=x,y,z}\sum_{\beta=x,y,z}(8\pi^3/\Omega)\sum_{ij}(\frac{\partial}{\partial p_{i\alpha}} - \frac{\partial}{\partial p_{j\alpha}})$$

$$(II.7.5)\qquad I^{+}_{\alpha\beta}(z, \underset{\sim}{p}_i, \underset{\sim}{p}_j)\ (\frac{\partial}{\partial p_{i\beta}} - \frac{\partial}{\partial p_{j\beta}})$$

where

$$I^{+}_{\alpha\beta}(z, \underset{\sim}{p}_i, \underset{\sim}{p}_j, k) = (8\pi K V_o)^2\int d^3k\ \frac{k_\alpha k_\beta}{(k^2+K^2)^4\left[z - \underset{\sim}{k}.(\underset{\sim}{v}_i - \underset{\sim}{v}_j)\right]}$$

$$(II.7.6)\qquad (z \in S^{+})$$

Using cylindrical coordinates with the z axis along the relative velocity :

$$(II.7.7)\qquad \underset{\sim}{g} = \underset{\sim}{v}_i - \underset{\sim}{v}_j$$

one obtains easily :

$$I^{+}_{\alpha\beta}(z, \underset{\sim}{p}_i, \underset{\sim}{p}_j, K) = (\pi/3)(8\pi K V_o)^2\ \delta_{\alpha,\beta}\ \times$$

$$\times\left[\left(\delta_{\alpha,x}+\delta_{\alpha,y}\right)\frac{1}{4}\int_{-\infty}^{+\infty}dk_{\parallel}\,\frac{1}{(z-k_{\parallel}g)(k_{\parallel}^{2}+\kappa^{2})^{2}}\right.$$

$$\left.+\,\delta_{\alpha,z}\int_{-\infty}^{+\infty}dk_{\parallel}\,\frac{k_{\parallel}^{2}}{(z-k_{\parallel}g)(k_{\parallel}^{2}+\kappa^{2})^{3}}\right] \tag{II.7.8}$$

As can be easily seen when performing the $k_{\parallel}$ integration, $I^{+}_{\alpha\beta}(z)$ is regular in S^{+} and has poles in S^{-} at

$$z = -i\kappa g \tag{II.7.9}$$

The quantity $(\kappa g)^{-1}$ represents the time during which the two particles i and j are interacting, i.e. the collision time τ_{coll}. Using this result, we can easily perform the z integration in (II.7.3). We obtain :

$$\left[\rho_{o}(t)\right]_{cycle} = -it\,\psi_{2}(0)+\psi_{2}'(0) + \mathrm{Res}\left[\frac{e^{-izt}\psi_{2}(z)}{z^{2}}\right]_{z=-ik g} \tag{II.7.10}$$

Therefore, we have three types of contributions: one proportional to t, a second one which is of order τ_{coll}/t when compared to the first and finally an exponentially decaying contribution proportional to $\exp(-t/\tau_{coll})$. This last term becomes quite negligible for times much longer than the collision time.

If we do not make a special choice of the intermolecular potential, it is easily verified (see an example in chapter III, § 2) that the function $I^{+}_{\alpha\beta}$ has the form of a Cauchy integral :

$$I^{+}_{\alpha\beta}(z) = \int_{-\infty}^{+\infty} d\omega\,\frac{f(\omega)}{z-\omega} \qquad (z \in S^{+}) \tag{II.7.11}$$

Provided $f(\omega)$ satisfies some general conditions [4], this function is regular in S^+ and can be continued analytically in S^-. Its singularities in S^- are at a finite distance of the real axis, of the order of τ_{coll}^{-1}. If we assume these singularities to be simple poles (although other types of singularities can also be discussed [3]), the general result (I.7.10) is valid (instead of a single residue, we must take a sum over the residues at all poles in S^-).

Let us now consider the contribution of the simplest destruction fragment to the evolution of $\rho_o(t)$ (fig. II.6.1b). In the limit of an infinite system, we have (see (II.6.8)):

$$(II.7.12) \qquad \left[\rho_o(t)\right]_C = -(1/2\pi i)\int_C dz\ \frac{e^{-izt}}{z}\,\mathcal{D}_1(z)$$

with

$$\mathcal{D}_1(z) = (8\pi^3/\Omega) \sum_{i<j} \int d^3k\, V_k\, \underset{\sim}{k}\cdot\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \times$$

$$(II.7.13) \qquad \times \frac{1}{z - \underset{\sim}{k}\cdot(\underset{\sim}{v}_i - \underset{\sim}{v}_j)}\ \tilde{\rho}_{\underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k}}^{(0)}$$

In contrast with the operator $\psi_2(z)$, the singularities of the destruction operator $\mathcal{D}_1(z)$ depend not only on the type of intermolecular potential we choose, but also on the $\underset{\sim}{k}$ dependence of the function $\tilde{\rho}_{\underset{\sim}{k}, -\underset{\sim}{k}}$, i.e: on the initial conditions. Let us denote by κ_{corr}^{-1} the range of the initial correlations. We may for instance suppose that the binary correlation function $g(\underset{\sim}{x}, \underset{\sim}{x}', 0)$ (see II.2.9) is of the form :

$$(II.7.14) \qquad g(\underset{\sim}{x}, \underset{\sim}{x}', 0) = g\left(\left|\underset{\sim}{x} - \underset{\sim}{x}'\right|, 0\right) = e^{-\kappa_{corr}\left(\left|\underset{\sim}{x} - \underset{\sim}{x}'\right|\right)}$$

Then we have :

$$\tilde{\rho}_{\underset{\sim}{k},-\underset{\sim}{k}}(0) \sim \frac{\kappa_{corr}}{(k^2+\kappa_{corr}^2)^2} \qquad \text{(II.7.15)}$$

Therefore, besides the pole at $z = -i\kappa g$ due to the Fourier coefficient of the potential, we now have poles at:

$$z = -i\,\kappa_{corr}\,g \qquad \text{(II.7.16)}$$

in the rhs of (II.7.12). We thus obtain:

$$\left[\rho_o(t)\right]_C = \mathfrak{D}_1(0) + \mathrm{Res}\left[\frac{e^{-izt}}{z}\mathfrak{D}_1(z)\right]_{z=-i\kappa g} + \mathrm{Res}\left[\frac{e^{-izt}}{z}\mathfrak{D}_1(z)\right]_{z=-i\,\kappa_{corr}\,g} \qquad \text{(II.7.17)}$$

As for the diagonal fragment, taking into account the fact that $\mathfrak{D}_1(z)$ is of the form of a Cauchy integral, one generalizes this result very easily for the case where one does not assume a particular form of the interaction and the correlation function.

For times t which are much longer than both the collision time and the characteristic time $(\kappa_{corr}g)^{-1}$, only the first term remain in the rhs of (II.7.17). In what follows we shall restrict ourselveses situations where the initial correlations are due to molecular interactions. Then the range of the correlations is of the order of the range the interaction and both characteristic times are identical.

Let us now consider the simplest creation fragment:

(fig. II.7.1)

Simplest creation fragment

Fig. II.7.1

It is a contribution to the evolution of $\rho_{\underset{\sim}{k},-\underset{\sim}{k}}(t)$. Analytically, we have:

$$(II.7.18)\quad \left[\rho_{\underset{\sim}{k},-\underset{\sim}{k}}(t)\right]_{\supset} = -(1/2\pi i)\int_C dz\ \frac{e^{-izt}}{Z}\ C_1(z)\ \rho_o(0)$$

with

$$(II.7.19)\quad C_1(z) = (8\pi^3/\Omega)\ V_k\ \frac{1}{z-\underset{\sim}{k}.(\underset{\sim}{v}_i-\underset{\sim}{v}_j)}\ \underset{\sim}{k}.\left(\frac{\partial}{\partial \underset{\sim}{p}_i}-\frac{\partial}{\partial \underset{\sim}{p}_j}\right)$$

The main difference with the two preceding cases is that we have no longer a summation over the wave vector. However, our aim is to compute average values of dynamical quantities in phase space. If we compute the contribution of (II.7.17) to the complete phase space distribution function $\rho(\{\underset{\sim}{p}\},\{\underset{\sim}{q}\},t)$, we have :

$$(II.7.20)\quad \left[\rho(\{\underset{\sim}{p}\},\{\underset{\sim}{q}\},t)\right]_{\supset} = -(1/2\pi i)\int_C dz\ \frac{e^{-izt}}{z}\ \Gamma_1(z)\ \rho_o(0)$$

where

$$(II.7.21)\quad \Gamma_1(z) = \int d^3k\ \exp\left[i\underset{\sim}{k}.(\underset{\sim}{q}_i-\underset{\sim}{q}_j)\right]\ C_1(z)$$

With our assumption (II.7.1) for the potential , we obtain:

$$(II.7.22)\quad \left[\rho(\{\underset{\sim}{p}\},\{\underset{\sim}{q}\},t)\right]_{\supset} = \Gamma_1(0) + \mathrm{Res}\left[\frac{e^{-izt}\Gamma_1(z)}{z}\right]_{z=-i\kappa g}$$

The last term is proportional to $\exp\left[-\kappa(|\underset{\sim}{r}-\underset{\sim}{g}t|)\right]$ where $\underset{\sim}{r}=\underset{\sim}{q}_i-\underset{\sim}{q}_j$. It will become negligible for times t such that :

$$(II.7.23)\quad t \gg r/g$$

Later on, we shall only be interested in the value of the distribution function for relative distances of the order of the range of the intermolecular forces. Then the characteristic time r/g will be of the order

of the collision time and for $t \gg \tau_{coll}$, the asymptotic contribution will reduce to $\Gamma_1(0)$. This means that, for the computation of the quantities defined above, we may take the asymptotic expression :

$$\left[\rho_{\underset{\sim}{k},-\underset{\sim}{k}}(t)\right]_{\supset} = C_1(0)\,\rho_o(0) \tag{II.7.24}$$

The contribution of other types of diagrams (diagonal fragments inserted on a line, free propagating lines, destruction diagrams involving exchange vertices (fig. II, 4.2 a, f) can be discussed in a similar way but shall not be considered here (see ref. [1])

II.8 - Evolution of the velocity distribution function.

From (II.3.5) and (II.3.6), we have :

$$\rho_o(t) = -(1/2\pi i)\int_C dz\; e^{-izt} \sum_{\{\underset{\sim}{k}\}} \sum_{n=0}^{\infty} \left\langle 0 \left| \frac{1}{z-L_o}\left(\delta L \frac{1}{z-L_o}\right)^n \right| \{\underset{\sim}{k}\} \right\rangle \times$$

$$\times\, \rho_{\{\underset{\sim}{k}\}}(0) \tag{II.8.1}$$

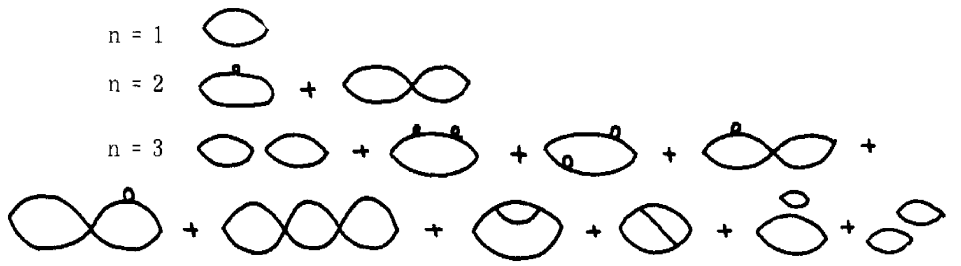
If we separate out the diagonal part, we obtain :

$$\rho_o(t) = -(1/2\pi i)\int_C dz\; e^{-izt} \sum_{n=0}^{\infty} \left\langle 0 \left| \frac{1}{z-L_o}\left(\delta L \frac{1}{z-L_o}\right)^n \right| 0 \right\rangle \rho_o(0)$$

$$-(1/2\pi i)\int_C dz\; e^{-izt} \sum_{\{\underset{\sim}{k}\} \neq \{\underset{\sim}{0}\}} \sum_{n=1}^{\infty} \left\langle 0 \left| \frac{1}{z-L_o}\left(\delta L \frac{1}{z-L_o}\right)^n \right| \{\underset{\sim}{k}\} \right\rangle \rho_{\{\underset{\sim}{k}\}}(0) \tag{II.8.2}$$

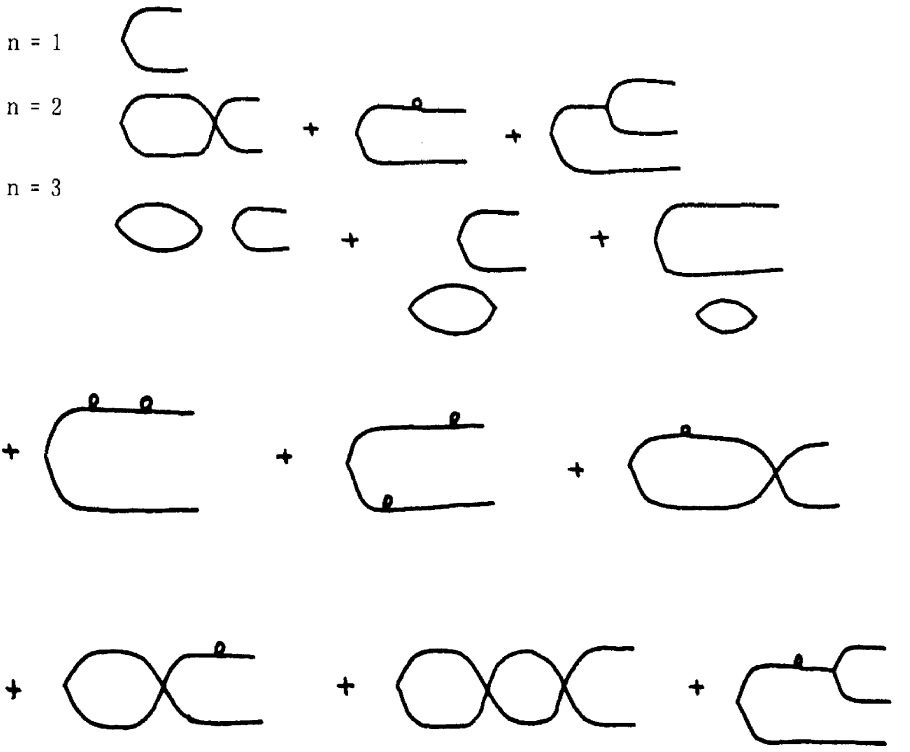
It is quite obvious that all contributions to the first term in the rhs of (II.8.2) will be successions of irreducible diagonal fragments (see fig. II.8.1) . As to the second term, we shall start from the right with a

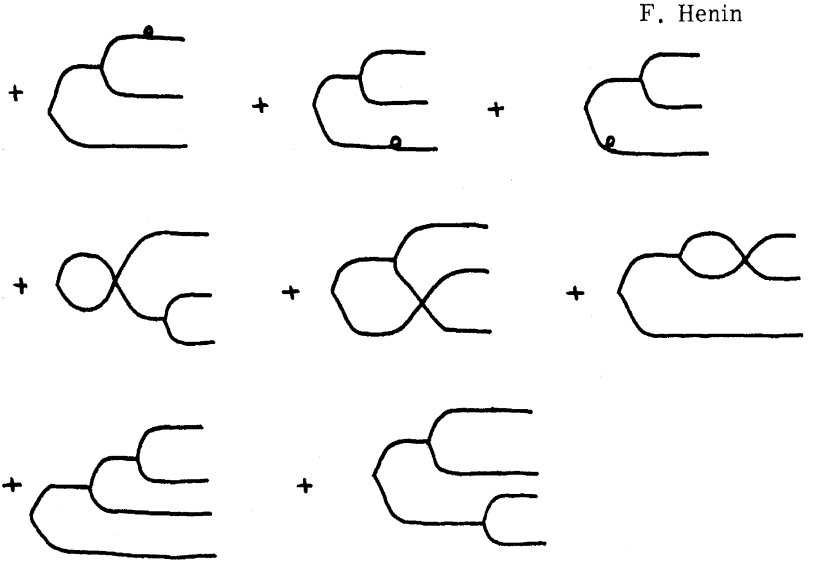
destruction region until we reach the vacuum of correlations $\{0\}$. Then we can again go on towards the left with a succession of irreducible diagonal fragments (see fig. II. 8. 2)



First diagonal contributions to $\rho_0(t)$

Fig. 11. 8. 1





First non diagonal contributions to $\rho_0(t)$

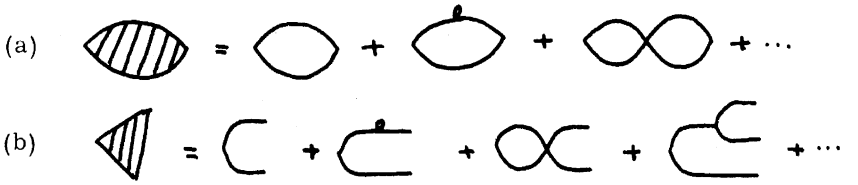
Fig. II. 8. 2

If we use the diagrams of fig.(II. 8. 3) to denote

(a) the sum of all irreducible diagonal fragments whose initial (and final state) is the vacuum of correlations

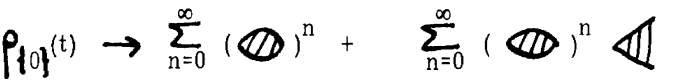
(b) the sum af all destruction fragments whose final state is the vacuum of correlations

we easily obtain a regrouping of all terms in the rhs of (II. 8. 2) in terms of diagrams (fig. II. 8. 4)



Diagrammatic representations of diagonal and destruction operators.

Fig. II. 8. 3



Diagrammatic representation of the evolution equation for the velocity distribution function

Fig. II. 8. 4

Let us introduce the following operators :

$$\frac{1}{z}\psi(z) = \sum_{m=2}^{\infty} \langle 0 \mid (\delta L \frac{1}{z-L_o})^m \mid 0 \rangle_{irr}$$

$$= \frac{1}{z} \sum_{m=1}^{\infty} \langle 0 \mid (\delta L \frac{1}{z-L_o})^m \delta L \mid 0 \rangle_{irr} \qquad \text{(II. 8. 3)}$$

$$D_{\{\underset{\sim}{k}\}}(z) = \sum_{m=1}^{\infty} \langle 0 \mid (\delta L \frac{1}{z-L_o})^m \mid \{\underset{\sim}{k}\} \rangle_{irr} \qquad \text{(II. 8. 4)}$$

where the index irr. means that only terms such that all intermediate states are different from the vacuum of correlations $|\{0\}\rangle$ must be taken into account. This condition means that all propagators in $\psi(z)$ and $D_{\{\underset{\sim}{k}\}}(z)$ are different from z.

With these operators (II. 8. 2) may now easily be written as :

$$\rho_o(t) = -(1/2\pi i) \int_C dz \, \frac{e^{-izt}}{z} \sum_{n=0}^{\infty} \left[\frac{1}{z}\psi(z)\right]^n \{\rho_o(0) + \sum_{\{\underset{\sim}{k}\} \neq \{\underset{\sim}{0}\}} D_{\{\underset{\sim}{k}\}}(z) \rho_{\{\underset{\sim}{k}\}}(0)\} \qquad \text{(II. 8. 5)}$$

Differentiating with respect to time , we obtain :

$$\frac{\partial \rho_o(t)}{\partial t} = (1/2\pi) \int_C dz \, e^{-izt} \sum_{n=0}^{\infty} \left[\frac{1}{z}\psi(z)\right]^n \{\rho_o(0)$$

$$+ i \sum_{\{\underset{\sim}{k}\} \neq \{\underset{\sim}{0}\}} D_{\{\underset{\sim}{k}\}}(z)\, \rho_{\{\underset{\sim}{k}\}}(0) \Big\}$$

$$= (1/2\pi) \int_C dz\, \frac{e^{-izt}}{z} \psi(z) \sum_{n=0}^{\infty} \left[\frac{1}{z}\psi(z)\right]^n \Big\{ \rho_o(0)$$

$$+ \sum_{\{\underset{\sim}{k}\} \neq \{\underset{\sim}{0}\}} D_{\{\underset{\sim}{k}\}}(z)\, \rho_{\{\underset{\sim}{k}\}}(0) \Big\}$$

$$+ (1/2\pi) \int_C dz\, e^{-izt} \rho_o(0) + (1/2\pi) \int_C dz\, e^{-izt} \times$$

$$\times \sum_{\{\underset{\sim}{k}\} \neq \{\underset{\sim}{0}\}} D_{\{\underset{\sim}{k}\}}(z)\, \rho_{\{\underset{\sim}{k}\}}(0) \qquad \text{(II.8.6)}$$

The second term vanishes because its integrand has no singularities. As to the remaining terms, let us perform the z integration. Introducing time dependent operators $G(t)$ and $\mathcal{D}_{\{\underset{\sim}{k}\}}(t)$ which are respectively the inverse Laplace transforms of $\psi(z)$ and $D_{\{\underset{\sim}{k}\}}(z)$:

$$G(t) = -(1/2\pi i) \int_C dz\, e^{-izt} \psi(z) \qquad \text{(II.8.7)}$$

$$\mathcal{D}_{\{\underset{\sim}{k}\}}(t) = -(1/2\pi i) \int_C dz\, e^{-izt} D_{\{\underset{\sim}{k}\}}(z) \qquad \text{(II.8.8)}$$

and using the convolution theorem as well as (II.8.5), we obtain :

$$i \frac{\partial \rho_o(t)}{\partial t} = \int_o^t d\tau\, G(t-\tau)\, \rho_o(\tau) + \sum_{\{\underset{\sim}{k}\} \neq \{\underset{\sim}{0}\}} \mathcal{D}_{\{\underset{\sim}{k}\}}(t)\, \rho_{\{\underset{\sim}{k}\}}(0) \qquad \text{(II.8.9)}$$

This generalized "master equation", which has been obtained in a straightforward way from a rearrangement of the terms in the formal so-

lution of the Liouville equation describes the exact behavior of the velocity distribution function for any time. It may seem much more complicated than the original Liouville equation. However, as it will appear below, it has the great advantage that for a very wide class of initial states, it has simple properties in the long time limit.

Let us first notice that we have decomposed the time variation of $\rho_0(t)$ in two contributions of a very different kind. First of all, we have a non-markovian contribution which is expressed in terms of ρ_0 only ; this contribution describes scattering processes; the integration over the past corresponds to the physical fact that the scattering processes have a finite duration (collision time) . On contrast with the first term, the second term in the rhs of (II. 8. 9) does not depend on ρ_0 but on the initial correlations present in the system. This term describes the destruction of these initial correlations.

II. 9 - Kinetic equation.

Let us now consider the case of systems interacting through short range forces and such that the initial correlations are over a molecular range . For such systems, the duration of a collision is very short and many simplifying features appear if we consider the asymptotic behavior of the system, i.e. its behavior for times t such that

(II. 9. 1) $$t \gg \tau_{coll}$$

Generalizing our discussion of § 7 , we shall assume that the operators $\psi(z)$ and $\sum_{\{k\}} D_{\{k\}}(z)\, \rho_{\{k\}}(0)$ have the following properties :

1. they are analytical functions of z in the whole complex plane except

for a finite discontinuity along the real axis . These operators are analytical in S^+ and can be continued analytically in the lower half plane.

These properties are consequences of the definition of these operators provided perturbation calculus converges. They have been verified in detail for the lowest order contribution to $\psi(z)$ and $\sum_{\{\underset{\sim}{k}\}} D_{\{\underset{\sim}{k}\}}(z)\rho_{\{\underset{\sim}{k}\}}(z)$ in §7 ; there it has been shown that both these contributions are Cauchy integrals. A detailled discussion of the operator $\psi(z)$ at higher orders has been recently done for the problem of anharmonic solids and some quantum field theory problems [5].

2. The singularities of the analytical continuation in S^- are poles at a finite distance from the real axis. This assumptinn must be considered as a sufficient condition for the validity of the kinetic equation we shall derive. We have seen how it can be realized for a simple type of interaction potential and a simple initial condition in §7. For more complicated interactions or initial conditions, singularities other than poles could appear and the following proofs must be amended but we shall not consider such cases here.

With these properties of the diagonal and destruction operator in the z plane, our results of § 7 can be easily generalized for the discussion of the two kinds of contributions in (II.8.9) .

Let us first consider the destruction term. Using (II.8.8) , we obtain :

$$\lim_{t \gg \tau_{coll}} \sum_{\{\underset{\sim}{k}\}} \mathcal{D}_{\underset{\sim}{k}}(t)\rho_{\{\underset{\sim}{k}\}}(0) = \lim_{t \gg \tau_{coll}} \sum_j \mathrm{Res}\left[\sum_{\{\underset{\sim}{k}\}} D_{\{\underset{\sim}{k}\}}(z)\, e^{-izt}\rho_{\{\underset{\sim}{k}\}}(0)\right]_{z=\zeta_j}$$

(II.9.2) $$= 0$$

where the ζ_j's are the poles in the lower half plane of the function

$\sum_{\{\underset{\sim}{k}\}} D_{\{\underset{\sim}{k}\}}(z)\, \rho_{\{\underset{\sim}{k}\}}(0)$. (II.9.2) corresponds to our result of 7 that the lowest order destruction contribution to the evolution of $\rho_o(t)$ is asymptotically constant; upon time differentiation, we obtain zero. Therefore, once (II.9.1) is fulfilled and the initial correlations are short range, the master equation becomes :

$$i\frac{\partial \rho_o}{\partial t} = \lim_{t \gg \tau_{coll}} \int_o^t d\tau\, G(t-\tau)\rho_o(\tau) \tag{II.9.3}$$

while (II.8.5) reduces to :

$$\rho_o(t) = \mathrm{Res}\left[\frac{e^{-izt}}{z} \sum_{n=1}^{\infty} \left(\frac{1}{z}\psi(z)\right)^n\right]_{z=0} \bar{\rho}_o(0) + \rho_o(o)$$

$$= \sum_{p=0}^{\infty}\sum_{q=0}^{\infty} (1/p!\, q!)\,(-it)^p \left\{\frac{d^p}{dz^p}\left[\psi(z)\right]^{p+q}\right\}_{z=0} \bar{\rho}_o(0) + \rho_o(o) \tag{II.9.4}$$

where the function $\psi(z)$ which has to be used for $z \to 0$ is the analytical continuation of the function defined in S^+ .[1)]

It can be shown , through some lengthy algebraic manipulations that this gives rise to the kinetic equation :

$$i\frac{\partial \rho_o(t)}{\partial t} = \Omega\, \psi(0)\, \rho_o(t) \tag{II.9.5}$$

where Ω is a complicated functional of ψ and its derivatives for $z \to 0$:

$$\Omega = \sum_{\alpha=0}^{\infty} \Omega_\alpha \tag{II.9.6}$$

$$\Omega_o = 1 \tag{II.9.7}$$

$$\Omega_\alpha = \lim_{z \to 0} \Omega_\alpha(z) \qquad \alpha > 1 \tag{II.9.8}$$

1) $\bar{\rho}_o(0)$ is a modified initial creation and is given by the expression between in the rhs of (II.8.5)

The $\Omega_\alpha(z)$ are given by a recursion formula :

$$\Omega_\alpha(z) = (1/\alpha) \sum_{\beta=0}^{\alpha-1} \left\{ \frac{\partial}{\partial z} \Omega_{\alpha-1} - \beta(z)\psi(z) \right\} \Omega_\beta(z) \qquad \text{(II.9.8)}$$

The operator Ω takes into account the finite duration of the collision. We shall not give this derivation here but rather use some simple considerations which will emphasize the meaning of both the operator ψ and Ω

The operator ψ has the dimension of the inverse of a time (see II.8.3) . As this operator describes the collisions occuring in the system, this time is of the order of the relaxation time. (for instance, in dilute gases (Boltzmann equation), the relaxation time is connected with binary collisions, i.e. those terms in ψ which involve only two particles). Derivation with respect to z of ψ increases by one the power of one of the unperturbed propagators. In our simple example of § 7, we have seen that this amounts to bring an extra factor τ_{coll}. Therefore, any contribution to rhe rhs of (II.9.4) corresponding to a given value of p and q is of the order :

$$(t/\tau_{rel})^p (\tau_{coll}/\tau_{rel})^q \qquad \text{(II.9.9)}$$

Let us first neglect τ_{coll}/τ_{rel}, i.e. let us consider the collisions as instantaneous events. Then, we may restrict ourselves in (II.9.4) to the term q = 0 and we obtain :

$$\rho_o(t) = \sum_{p=0}^{\infty} (1/p!) (-it\psi(0))^p \rho_o(0) + 0 (\tau_{coll}/\tau_{rel}) \qquad \text{(II.9.10)}$$

This leads us to :

$$\frac{\partial \rho_o(t)}{\partial t} = - i \psi(0) \rho_o(t) + 0 (\tau_{coll}/\tau_{rel}) \qquad \text{(II.9.11)}$$

This equation is a very simple generalization of Boltzmann's equation; besides two-body collisions, it includes collisions between an arbitrary number of particles. However, if we do not neglect collisions between more than two particles, it is not consistent. Indeed, for a dilute gas of hard spheres for instance, where we can restrict ourselves to two-body collisions, it can be shown that the relaxation time is given by :

$$\tau_{rel}^{-1} = C a^2 \bar{v} \qquad \text{(II.9.12)}$$

where a is the diameter of the particles and $\bar{v}$ their average velocity. As the only dimensionless parameter we have is a^3C, we must expect that, when we take into account higher order collision processes, we shall have an expansion analogous to the virial expansion :

$$\tau_{rel}^{-1} = Ca^2\bar{v}\left[1 + \alpha a^3C + \beta(a^3C)^2 + \ldots\right] \qquad \text{(II.9.13)}$$

Now, we also have :

$$\tau_{coll} = a/\bar{v} \qquad \text{(II.9.14)}$$

and thus

$$\tau_{coll}/\tau_{rel} = 0\,(a^3C) \qquad \text{(II.9.15)}$$

Therefore, the procedure we have followed is certainly not consistent: we cannot keep higher order collision processes (i.e. corrections of order a^3C in τ_{rel}) and neglect terms of the order of τ_{coll}/τ_{rel} in the rhs of (II.9.4). In order to understand the general evolution equation (II.9.5), let us keep in (II.9.4) the first correction, that which is proportional to τ_{coll}/τ_{rel} (i.e. the contribution q =1). Then we have :

$$\rho_o(t) = \sum_{p=0}^{\infty} (1/p!)\,(-it\,\psi(0))^p\,\rho_o(0)$$

$$+ \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} (1/(p+q)!)(-it\psi(0))^{p} \psi'(0)(-it\psi(0))^{q} \rho_{o}(0)$$

(II.9.16)

$$+ 0(\tau_{coll}/\tau_{rel})^{2}$$

Upon differentiation with respect to t, it is easy to show that one obtains :

$$\text{(II.9.17)} \quad \frac{\partial \rho_{o}(t)}{\partial t} = -i(1 + \psi'(0))\psi(0)\rho_{o}(t) + 0(\tau_{coll}/\tau_{rel})^{2}$$

The operator $\psi'(0)$, which takes into account, in first order, the finite duration of the collision, is precisely identical to the operator Ω_{1} in (II.9.6) .

II.10-Evolution of the correlations in an homogeneous system.

As all derivations are very similar to the derivation of the generalized master equation for the velocity distribution function, we shall only indicate how they proceed and what are the final results .

The most general diagram contributing to the evolution of a given correlation contains all three types of regions defined in § 5. We shall now write :

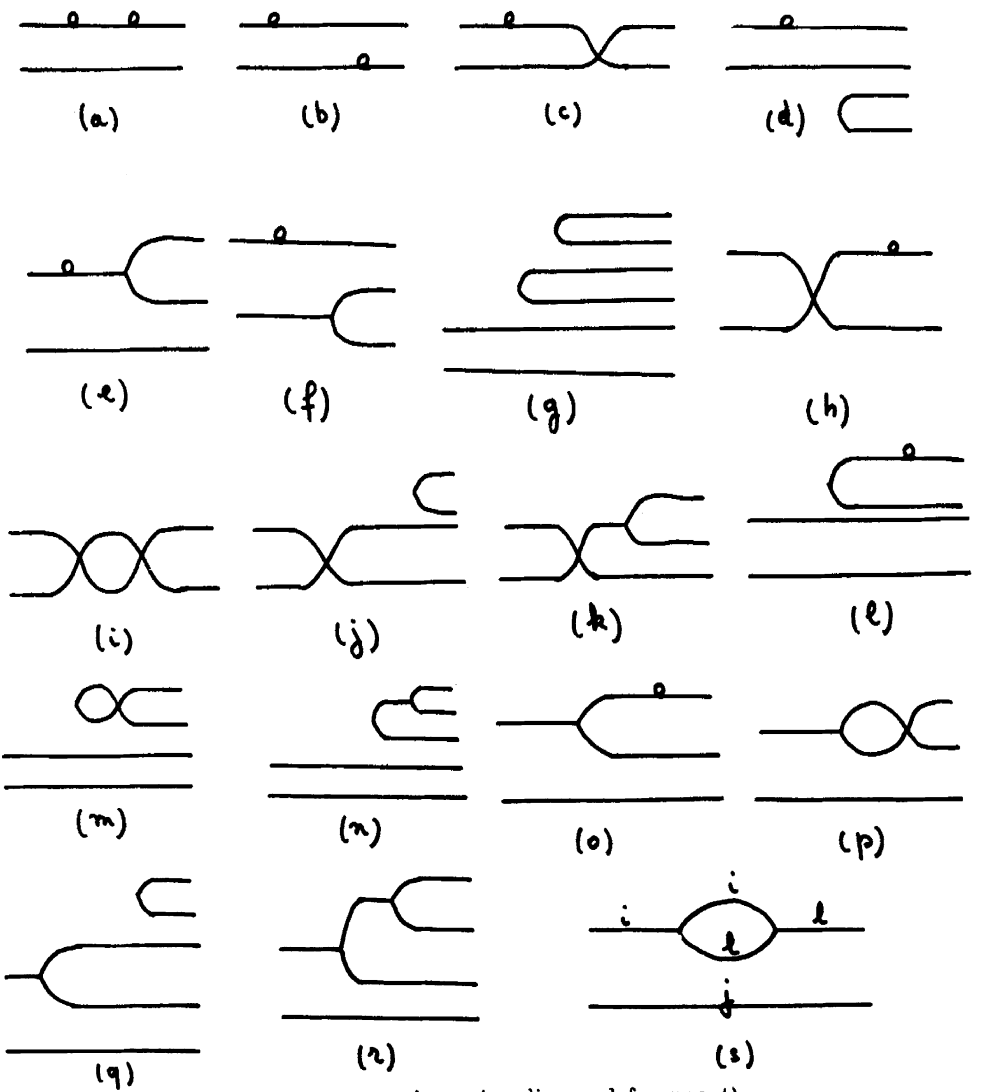
$$\text{(II.10.1)} \qquad \rho_{\{\underset{\sim}{k}\}}(t) = \rho'_{\{\underset{\sim}{k}\}}(t) + \rho''_{\{\underset{\sim}{k}\}}(t)$$

where, by definition :

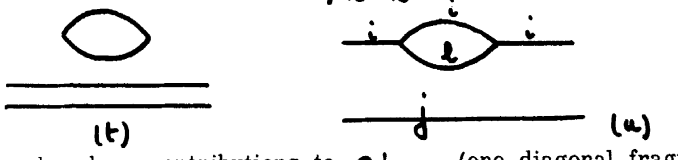
$\rho'_{\{\underset{\sim}{k}\}}(t)$ contains all diagrams without creation region

$\rho''_{\{\underset{\sim}{k}\}}(t)$ contains all diagrams which end by a creation region

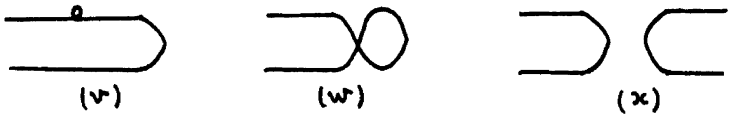
This decomposition is performed in detail for all second order diagrams contributing to the evolution of $\rho_{\underset{\sim}{k},-\underset{\sim}{k}}$ in fig;II.10.1.



Second order contributions $\rho'_{\underset{\sim}{k},-\underset{\sim}{k}}$ (no diagonal fragment)



Second order contributions to $\rho'_{\underset{\sim}{k}',-\underset{\sim}{k}}$ (one diagonal fragment)



Second order contributions to $\rho''_{\underset{\sim}{k},-\underset{\sim}{k}}$

Second order contributions to the evolution of the binary correlation $\rho_{\underset{\sim}{k},-\underset{\sim}{k}}$

Fig. II. 10. 1

To discuss the evolution of $\rho'_{\{\underset{\sim}{k}\}}(t)$, one decomposes the relevant diagrams into those which are diagonal and those which contain a destruction region (see fig. II. 10. 1) . In this way, one verifies easily that these functions obey an evolution equation very similar to the general master equation for the velocity distribution function :

$$i\frac{\partial \rho'_{\{\underset{\sim}{k}\}}(t)}{\partial t} = \int_0^t d\tau\, G_{\{\underset{\sim}{k}\}}(t-\tau)\rho'_{\{\underset{\sim}{k}\}}(\tau) + \sum_{\{\underset{\sim}{k}'\}}{}' \mathcal{D}_{\{\underset{\sim}{k}\}\{\underset{\sim}{k}'\}}(t, \rho_{\{\underset{\sim}{k}'\}}(0)) \tag{II. 10. 2}$$

where $G_{\{\underset{\sim}{k}\}}(t)$ is the inverse Laplace transform of the diagonal operator:

$$\psi_{\{\underset{\sim}{k}\}}(z) = \sum_{n=1}^{\infty} \langle \{\underset{\sim}{k}\} | \delta L \left(\frac{1}{z - L_o} \delta L\right)^n | \{\underset{\sim}{k}\} \rangle_{irr} \tag{II. 10. 3}$$

while $\mathcal{D}_{\{\underset{\sim}{k}\}\{\underset{\sim}{k}'\}}(t, \rho_{\{\underset{\sim}{k}'\}}(0))$ is the inverse Laplace transform of the destruction operator :

$$D_{\{\underset{\sim}{k}\}\{\underset{\sim}{k}'\}}(z)\, \rho_{\{\underset{\sim}{k}'\}}(0) = \sum_{m=1}^{\infty} \langle \{\underset{\sim}{k}\} | \left(\delta L \frac{1}{z - L_o}\right)^m | \{\underset{\sim}{k}'\} \rangle_{dest.} \rho_{\{\underset{\sim}{k}'\}}(0) \tag{II. 10. 4}$$

The dash on the summation over $\{\underset{\sim}{k}'\}$ in (II. 10. 2) means that only those states $|\{\underset{\sim}{k}'\}\rangle$ which are such that the transition $\{\underset{\sim}{k}\} \leftarrow \{\underset{\sim}{k}'\}$ describes a

destruction of correlations must be taken into account.

The evolution of $P'_{\{\underset{\sim}{k}\}}(t)$ is due to the dissipation of the initial correlations through the collision processes. For long times, a pseudomarkovian equation similar to (II.9.5) can also be derived from (II.10.2) .

As to the evolution of $P''_{\{\underset{\sim}{k}\}}(t)$, the main point is to notice that if we have at the left a given creation diagram, corresponding to a transition $\{\underset{\sim}{k}\} \leftarrow \{\underset{\sim}{k'}\}$, we may have at the right of this creation diagram any of the diagrams which contribute to the evolution of $P'_{\{\underset{\sim}{k'}\}}(\tau)$ (if $\{\underset{\sim}{k'}\} \equiv \{\underset{\sim}{0}\}$, we may have all the diagrams which contribute to the evolution of the velocity distribution function), if τ is the time corresponding to the first creation vertex. This remark makes it possible to show rigorously that one has :

$$P''_{\{\underset{\sim}{k}\}}(t) = \sum_{\{\underset{\sim}{k'}\}}{}' \int_0^t C_{\{\underset{\sim}{k}\}\{\underset{\sim}{k'}\}}(t-\tau) P'_{\{\underset{\sim}{k'}\}}(\tau)\, d\tau \qquad \text{(II.10.5)}$$

where the dash on the summation over $\{\underset{\sim}{k'}\}$ means that only those states $|\{\underset{\sim}{k'}\}\rangle$ corresponding to a lower state of correlations than $|\{\underset{\sim}{k}\}\rangle$ must be taken into account.

$C_{\{\underset{\sim}{k}\}\{\underset{\sim}{k'}\}}(t)$ is the inverse Laplace transform of the creation operator :

$$C_{\{\underset{\sim}{k}\}\{\underset{\sim}{k'}\}}(z) = \sum_{m=1}^{\infty} \langle \{\underset{\sim}{k}\} | \left(\frac{1}{z - L_o} \delta L \right)^m | \{\underset{\sim}{k'}\} \rangle \qquad \text{(II.10.6)}$$

Equation (II.10.5) describes the continuous creation of fresh correlations by direct mechanical interactions from less excited states.

F. Henin

II.11 - Approach to equilibrium of the velocity distribution function.

For weakly coupled or dilute systems, the approach to equilibrium is usually discussed by means of an $\mathcal{H}$-theorem. More precisely, one shows that the quantity

$$\mathcal{H} = \int |dp|^N \rho_o \ln \rho_o \tag{II.11.1}$$

decreases monotonically in time and that the stationary solution (which is unique) corresponds to the equilibrium distribution.

Unfortunately, this theorem cannot be completely generalized when higher order contributions are taken into account. We shall only consider the case of systems where there exists a parameter such that a perturbation expansion in powers of that parameter has a meaning (coupling constant λ for weakly coupled systems, concentration C for dilute systems). As an example, we shall consider the case where an expansion in powers of λ has a meaning. Then, with the following expansions :

$$\rho_o(t) = \rho_o^{(o)}(t) + \lambda \rho_o^{(1)}(t) + \lambda^2 \rho_o^{(2)}(t) + \ldots \tag{II.11.2}$$

$$\psi(0) = \lambda^2 \psi_2(0) + \lambda^3 \psi_3(0) + \lambda^4 \psi_4(0) + \ldots \tag{II.11.3}$$

$$\Omega = 1 + \lambda^2 \psi_2'(0) + \ldots \tag{II.11.4}$$

the kinetic equation (II.9.5) gives us a set of equations :

$$\frac{\partial \rho_o^{(0)}(t)}{\partial \lambda^2 t} = -i \psi_2(0) \rho_o^{(0)}(t) \tag{II.11.5}$$

$$\frac{\partial \rho_o^{(1)}(t)}{\partial \lambda^2 t} = -i \psi_2(0) \rho_o^{(1)}(t) - i \psi_3(0) \rho_o^{(0)}(t) \tag{II.11.6}$$

$$(II.11.7)\quad \frac{\partial \rho_o^{(2)}(t)}{\partial \lambda^2 t} = -i\,\psi_2(0)\,\rho_o^{(2)}(t) - i\psi_3(0)\,\rho_o^{(1)}(t) - i\psi_4(0)\,\rho_o^{(0)}(t) - i\psi_2'(0)\psi_2(0)\,\rho_o^{(0)}(t)$$

etc...

The $\mathcal{H}$-theorem for the lowest order approximation (for weakly coupled systems, see chapter III, §§ 2 and 3) shows us that $\rho_o^{(0)}(t)$ decreases monotonically towards its equilibrium value :

$$(II.11.8)\qquad \rho_o^{(0)}(t \to \infty) = f^{(0)}(H_o)$$

For times much longer than the relaxation time for $\rho_o^{(0)}(t)$, the next approximation is then given by :

$$(II.11.9)\quad \frac{\partial \rho_o^{(1)}(t)}{\partial \lambda^2 t} = -i\psi_2(0)\,\rho_o^{(1)}(t) - i\psi_3(0)\,f^{(0)}(H_o)$$

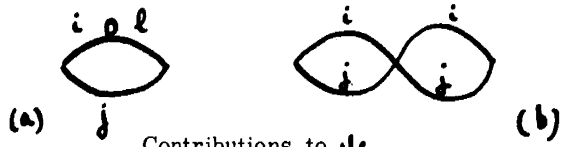
The interesting feature [*] is now that one can show that :

$$(II.11.10)\qquad \psi_n(0)\; g(H_o) = 0$$

where g is an arbitrary function of the unperturbed hamiltonian. A general method to verify this property can be found in [3]. This method is based on the discussion of an integral equation and rather formal. A more cumbersome method [1) 6)] consists in the splitting of each ψ_n in a number of operators according to the number of particles which appear in the diagram. For instance, in the operator $\psi_3(0)$, we have

[*] This is valid for gases where the interaction is velocity independent. For anharmonic solids for instance, the situation is more complicated because of the action dependence of the potential and this property is not valid. This makes it very difficult to study the approach to equilibrium at higher orders than λ^4. [1) 5) 7)]

two diagrams (fig. II. 11. 1) : one with three particles (a) which we call $\psi_3^{(3)}$, the next one (b) with two particles which we call $\psi_3^{(2)}$.



Contributions to ψ_3

Fig. II. 11. 1

One then shows that :

$$\psi_n^{(\nu)}(0)\ g(H_o) = 0 \qquad \text{(II. 11. 11)}$$

As an example, let us verify this for $n=3$, $\nu = 3$ (diagram a, fig. II. 11. 1)

We have :

$$\psi_3^{(3)}(0)\ g(H_o) = \lim_{z \to 0} \sum_{ijl} \sum_{\underset{\sim}{k}} \langle 0 | \delta L \,|\, \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} \rangle \times$$

$$\text{(II. 11. 12)} \quad \langle \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} \left| \frac{1}{z - L_o} \right| \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} \rangle \langle \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} | \delta L | \underset{\sim}{k}_l = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} \rangle \times$$

$$\times \langle \underset{\sim}{k}_l = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} \left| \frac{1}{z - L_o} \right| \underset{\sim}{k}_l = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} \rangle \langle \underset{\sim}{k}_l = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} | \delta L | 0 \rangle\ g(H_o)$$

Using (II. 1. 1) , (II. 2. 12) and (II. 3. 11) as well as :

$$\lim_{z \to 0} a/(z - a) = -1 \qquad \text{(II. 11. 13)}$$

we easily obtain :

$$\psi_3^{(3)}(0)\ g(H_o) \sim \lim_{z \to 0} \sum_{ijl} \int d^3k \left| V_k \right|^2 V_k \underset{\sim}{k} \cdot \left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j} \right) \times$$

$$\text{(II. 11. 14)} \qquad \times \frac{\underset{\sim}{k} \cdot (\underset{\sim}{v}_i - \underset{\sim}{v}_l)}{z - \underset{\sim}{k} \cdot (\underset{\sim}{v}_i - \underset{\sim}{v}_j)} \frac{\partial^2 g(H_o)}{\partial H_o^2}$$

Now, let : $i \to j$, $j \to i$, $\underset{\sim}{k} \to -\underset{\sim}{k}$ and take half sum of the rhs of (II.11.14) and the term obtained through this interchange of dummy variables. We obtain :

$$(II.11.15)\quad \psi_3^{(3)}(0)\, g(H_o) \sim \lim_{z \to 0} \sum_{ijl} \int d^3k \left| V_k \right|^2 V_k \; \underset{\sim}{k} . (\underset{\sim}{v}_i - \underset{\sim}{v}_j) \; \frac{\partial^3 g(H_o)}{\partial H_o^3}$$

$$= 0$$

because the integrand is an odd function of $\underset{\sim}{k}$.

Let us now go back to the discussion of the set of equations (II.11.5), (II.11.6), (II.11.7), etc... for long times. Using (II.11.10), we notice that (II.11.9) reduces to :

$$(II.11.16)\quad \frac{\partial \rho_o^{(1)}(t)}{\partial \lambda^2 t} = -i \psi_2(0) \rho_o^{(1)}(t)$$

As only the lowest order operator remains in this equation , we again obtain the result :

$$(II.11.17)\quad \rho_o^{(1)}(t \to \infty) = f^{(1)}(H_o)$$

It is then trivial , using again (II.11.10) to show by a recurrence procedure that :

$$(II.11.18)\quad \rho_o^{(n)}(t \to \infty) = f^{(n)}(H_o)$$

Therefore, we obtain :

$$(II.11.19)\quad \rho_o(t \to \infty) = f(H_o)$$

which is the equilibrium distribution . The function $f(H_o)$ is arbitrary (normalized to unity) as far as this proof is concerned but is completely determined from the initial condition (see ref. [1]) .

Let us stress the fact that this generalized $\mathcal{H}$-theorem is not so powerful as the $\mathcal{H}$-theorem for the lowest order approximation. Indeed, the $\mathcal{H}$-theorem for the lowest order approximation actually amounts to proof that all eigenvalues of the hermitian operator $-i\psi_2$ are either negative or zero and that there is a unique eigenfunction (the equilibrium distribution) corresponding to the eigenvalue zero. In the case of stronger coupling, what we have actually done here is to verify that there exists one zero eigenvalue for the complete evolution operator, with the equilibrium distribution as eigenfunction. A true $\mathcal{H}$-theorem would require a proof that the eigenvalue zero is unique and that all other eigenvalues are negative. This is of course very likely, at least for systems where a perturbation expansion has a meaning, i.e. when the lowest order terms give the dominant features of the behaviour of the system.

II.12 - Approach to equilibrium of the correlations in an homogeneous system.

The asymptotic solution for the equation (II.10.2) for the part $\rho'_{\{\underset{\sim}{k}\}}$ of the correlation can be discussed in a way similar to the above discussion for the equation for the velocity distribution function. The main result is :

(II.12.1) $$\rho'_{\{\underset{\sim}{k}\}}(t\to\infty) = 0$$

As a result, in the equation for $\rho''_{\{\underset{\sim}{k}\}}(t)$, we only keep those creation fragments which start from the vacuum of correlations :

(II.12.2) $$\rho''_{\{\underset{\sim}{k}\}}(t) = \int_0^t d\tau\, C_{\{\underset{\sim}{k}\#\underset{\sim}{0}\}}(t-\tau)\, \rho_0(\tau)$$

These results mean that the initial correlations tend to dissipate. In the long time limit, only the fresh correlations which are continuously created from the velocity distribution function remain.

For times such that the velocity distribution function has reached its equilibrium value, we have ;

$$\rho_{\{\underset{\sim}{k}\}}(t) = \rho''_{\{\underset{\sim}{k}\}}(t) = \int_0^t d\tau\, C_{\{\underset{\sim}{k}\}\{\underset{\sim}{0}\}}(\tau)\, f(H_0) \tag{II.12.3}$$

or, using the Laplace transform of the creation operator (see II.10.6):

$$\rho_{\{\underset{\sim}{k}\}}(t) = \rho''_{\{\underset{\sim}{k}\}}(t) = -(1/2\pi)\int_0^t d\tau \int_C dz\; e^{-izt}\; C_{\{\underset{\sim}{k}\}\{\underset{\sim}{0}\}}(z)\, f(H_0)$$

$$= (1/2\pi i)\int_C dz\,(e^{-izt} - 1)\, z^{-1}\, C_{\{\underset{\sim}{k}\}\{\underset{\sim}{0}\}}(z)\, f(H_0) \tag{II.12.4}$$

Now , as in our discussion of § 7, we take into account the fact that we shall always be interested in average values of dynamical quantities, i.e. in expressions which involve a sum over the wave vector. In such quantities, the operator $C_{\{\underset{\sim}{k}\}\{\underset{\sim}{0}\}}(z)$ is replaced by an operator $\Gamma(z)$ which is a Cauchy integral (see for instance II.7.21) . We then have :

$$(1/2\pi i)\int_C dz\;\; (e^{-izt} - 1)\, z^{-1}\, \Gamma(z)$$

$$= \sum_j \operatorname{res}\left[(e^{-izt} - 1)\, z^{-1}\Gamma(z)\right]_{\zeta_j = z} \tag{II.12.5}$$

where the ζ_j's are the poles in S^- of $\Gamma(z)$.
For long times, this becomes :

$$\lim_{t\to\infty} \sum_j \operatorname{res}\left[(e^{-izt} - 1)\, z^{-1}\Gamma(z)\right]_{z=\zeta_j} = -\sum_j \operatorname{res}\,(z^{-1}\,\Gamma(z))_{\zeta_j = z} \tag{II.12.6}$$

$$= \Gamma(0)$$

This result allows us take [x]:

$$\rho_{\{\underset{\sim}{k}\}}(\infty) = \rho''_{\{\underset{\sim}{k}\}}(\infty) = C_{\{\underset{\sim}{k}\}\{\underset{\sim}{0}\}}^{(0)} f(H_o)$$

(II.12.7)

$$= \lim_{z \to 0} \langle \{\underset{\sim}{k}\} | \sum_{m=1} \left(\frac{1}{z - L_o} \delta L \right)^m | 0 \rangle f(H_o)$$

If we denote by

$$\rho_{\{\underset{\sim}{k}\}}^{(m)} = \lim_{z \to 0} \langle \{\underset{\sim}{k}\} | \left(\frac{1}{z - L_o} \delta L \right)^m | 0 \rangle f(H_o) \qquad \text{(II.12.8)}$$

the set of all to $\rho_{\{\underset{\sim}{k}\}}$, contributions involving m vertices we have:

$$\rho_{\{\underset{\sim}{k}\}}^{(m)} = \langle \{\underset{\sim}{k}\} | \frac{\partial^{m} f(H_o)}{\partial H_o^m} \frac{V^m}{m!} | 0 \rangle \qquad \text{(II.12.9)}$$

where V is the intermolecular potential (see (II.1.1)). (II.12.9) can be proven, using a recurrence procedure. For m = 1, we have, using (II.3.9):

$$\rho_{\underset{\sim}{k}_i}^{(1)} = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} = \lim_{z \to 0} \langle \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} | \frac{1}{z - L_o} \delta L | 0 \rangle f(H_o)$$

$$= (8\pi^3/\Omega) \lim_{z \to 0} \frac{1}{z - \underset{\sim}{k} \cdot (\underset{\sim}{v}_i - \underset{\sim}{v}_j)} V_{\underset{\sim}{k}} \cdot \left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j} \right) f(H_o)$$

(II.12.10)

$$= (8\pi^3/\Omega) V_{\underset{\sim}{k}} \frac{\partial f(H_o)}{\partial H_o}$$

$$= \langle \underset{\sim}{k}_i = \underset{\sim}{k}, \underset{\sim}{k}_j = -\underset{\sim}{k} | V \frac{\partial f(H_o)}{\partial H_o} | 0 \rangle$$

---

[x] Some care has always to be taken in the use of (II.12.7). The use of such an expression does not lead to difficulties when one is interested in average quantities which are linear functionals of the correlations. When non linear functionals must be considered, one must go back to (II.12.4) as has been shown in recent work on anharmonic solids [5].

Assuming (II. 12.9) to hold for a given value of m, we have :

$$\rho^{(m+1)}_{\{\underset{\sim}{k}\}} = \lim_{z\to 0} \langle \{\underset{\sim}{k}\} | \left(\frac{1}{z-L_o}\delta L\right)^{m+1} | 0\rangle f(H_o)$$

$$= \lim_{z\to 0} \sum_{\{\underset{\sim}{k}'\}} \langle \{\underset{\sim}{k}\} | \frac{1}{z-L_o}\delta L | \{\underset{\sim}{k}'\}\rangle \rho^{(m)}_{\{\underset{\sim}{k}'\}}$$

(II. 12.11)

$$= \lim_{z\to 0} \sum_{\{\underset{\sim}{k}'\}} \langle \{\underset{\sim}{k}\} | \frac{1}{z-L_o}\delta L | \{\underset{\sim}{k}'\}\rangle\langle \{\underset{\sim}{k}'\} | \frac{\partial^m f(H_o)}{\partial H_o^m}\frac{V^m}{m!} | 0\rangle$$

$$= \lim_{z\to 0} \langle \{\underset{\sim}{k}\} | \frac{1}{z-L_o}\delta L \frac{V^m}{m}\frac{\partial^m f(H_o)}{\partial H_o^m} | 0\rangle$$

Now, if $\{\underset{\sim}{k}\}$ contains ν non vanishing wave vectors $\underset{\sim}{k}_1 \ldots \underset{\sim}{k}_\nu$, we obtain :

$$\rho^{(m+1)}_{\underset{\sim}{k}_1 \ldots \underset{\sim}{k}_\nu} = \lim_{z\to 0} \frac{1}{z - \sum_{i=1}^{\nu} \underset{\sim}{k}_i \cdot \underset{\sim}{v}_i} \langle \{\underset{\sim}{k}\} | \delta L \frac{V^m}{m!}\frac{\partial^m f(H_o)}{\partial H_o^m} | 0\rangle$$

$$= -i(8\pi^3/\Omega)^{N+1} \lim_{z\to 0} \frac{1}{z - \sum_{i=1}^{\nu} \underset{\sim}{k}_i \cdot \underset{\sim}{v}_i} \times$$

$$\times \int \{d\underset{\sim}{q}\}^N \exp\left[-i \sum_{i=1}^{\nu} \underset{\sim}{k}_i \cdot \underset{\sim}{q}_i\right] \sum_{l=1}^{N} \frac{\partial V}{\partial \underset{\sim}{q}_l} \cdot \frac{\partial}{\partial \underset{\sim}{p}_l} \frac{V^m}{m!}\frac{\partial^m f(H_o)}{\partial H_o^m}$$

$$= i(8\pi^3/\Omega)^{N+1} \lim_{z\to 0} \frac{1}{z - \sum_{i=1}^{\nu} \underset{\sim}{k}_i \cdot \underset{\sim}{v}_i} \int \{d\underset{\sim}{q}\}^N \exp\left[-i \sum_{i=1}^{\nu} \underset{\sim}{k}_i \cdot \underset{\sim}{q}_i\right] \times$$

$$\times \sum_{l=1}^{N} \underset{\sim}{v}_l \cdot \frac{\partial V}{\partial \underset{\sim}{q}_l} \frac{V^m}{m!}\frac{\partial^{m+1} f(H_o)}{\partial H_o^{m+1}}$$

$$= i(8\pi^3/\Omega)^{N+1} \lim_{z\to 0} \frac{1}{z - \sum_{i=1} \underset{\sim}{k}_i \cdot \underset{\sim}{v}_i} \times$$

$$\times \int \{dq\}^N \exp\left[-i \sum_{i=1}^{\nu} \underset{\sim}{k}_i \cdot \underset{\sim}{q}_i\right] \sum_{l=1}^{N} \underset{\sim}{v}_l \cdot \frac{\partial V^{m+1}}{\partial \underset{\sim}{q}_l} \frac{1}{(m+1)!} \frac{\partial^{m+1} f(H_o)}{\partial H_o^{m+1}}$$

$$= i(8\pi^3/\Omega)^{N+1} \lim_{z \to 0} \frac{1}{z - \sum_{i=1}^{\nu} \underset{\sim}{k}_i \cdot \underset{\sim}{v}_i} \times$$

(II.12.12)

$$\times \int \{dq\}^N \exp\left[-i \sum_{i=1}^{\nu} \underset{\sim}{k}_i \cdot \underset{\sim}{q}_i\right] \sum_{l=1}^{\nu} \underset{\sim}{v}_l \cdot \frac{\partial V^{m+1}}{\partial \underset{\sim}{q}_l} \frac{1}{(m+1)!} \frac{\partial^{m+1} f(H_o)}{\partial H_o^{m+1}}$$

Integrating by parts over $\underset{\sim}{q}_1$, one obtains easily (II.12.9) with m replaced by m+1.

Combining (II.12.9) and (II.12.7), we easily obtain:

$$(II.12.13) \qquad \rho_{\{\underset{\sim}{k}\}}^{equ.} = \sum_{m=1}^{\infty} \langle \{\underset{\sim}{k}\} | \frac{\partial^m f(H_o)}{\partial H_o^m} \frac{V^m}{m!} | 0 \rangle = \langle \{\underset{\sim}{k}\} | f(H) | 0 \rangle$$

which is the correct value of the equilibrium correlation.

Therefore, once the velocity distribution function has reached its equilibrium value, the fresh correlations which are continuously created from ρ_o are the equilibrium correlations. (II.12.7) gives us a dynamical description of the equilibrium correlations. A comparison with Mayer's cluster formalism can be done but will not be oonsidered here.

II.13. Response to an external constraint.

As an example, let us consider a system of charged particles which is at equilibrium at t=0: at t=0, we switch on a spatially homogeneous external electrical field $\underset{\sim}{E}(t)$.

To the hamiltonian (II,1.1), we now have to add a term describing the effect of the external field:

$$H_E = \sum_i e_i \underset{\sim}{E}(t) \cdot \underset{\sim}{q}_i \qquad \text{(II.13.1)}$$

where e_i is the the carge of the i^{th} particle.

The Liouville operator corresponding to this problem is then:

$$iL = iL_o + i\,\delta L + iL_E \qquad \text{(II.13.2)}$$

with

$$iL_E = \sum_i e_i \underset{\sim}{E} \cdot \frac{\partial}{\partial \underset{\sim}{p}_i} \qquad \text{(II.13.3)}$$

As we have assumed the system to be at equilibrium at t=0, the initial condition is :

$$\rho(0) = \rho_{equ.} = \frac{\exp\left[-(H_o + \lambda V)/kT\right]}{\int \{dp\, dq\}^N \exp\left[-(H_o + \lambda V)/kT\right]} \qquad \text{(II.13.4)}$$

If the external field is sufficiently weak, we can restrict ourselves to a linear theory in E; therefore, we have:

$$\rho(t) = \rho_{equ.} + \Delta\rho(t) \qquad \text{(II.13.5)}$$

where $\Delta\rho$ is linear in E. Using :

$$(L_o + \delta L)\,\rho_{equ.} = 0 \qquad \text{(II.13.6)}$$

$$\partial \rho_{equ} / \partial t = 0 \qquad \text{(II.13.7)}$$

the Liouville equation reduces to :

$$\frac{\partial \Delta\rho}{\partial t} = -i\,(L_o + \delta L)\Delta\rho - iL_E\,\rho_{equ.} \qquad \text{(II.13.8)}$$

when terms of order E^2 and higher are neglected.

This equation can be solved formally very easily :

$$(II.13.9)\quad \Delta\rho(t) = -i \int_0^t dt' \exp\left[-i(L_0 + \delta L)(t-t')\right] L_E(t') \rho_{equ.}$$

This solution takes into account the initial condition(II.13.9)) ($\Delta\rho(0)=0$).

Let us again expand the distribution function in a Fourier series of the position variables. Then, for the velocity distribution function $\rho_o(t)$ (which is the only coefficient we require if we want, for instance, to compute the current in the system), we obtain :

$$(II.13.10)\qquad \rho_o(t) = \rho_o^{equ.}(t) + \Delta\rho_o(t)$$

Taking into account the fact that $\underset{\sim}{E}$ is spatially constant, we have:

$$(II.13.11)\qquad \langle \{\underset{\sim}{k}\} | L_E(t) | \{\underset{\sim}{k}'\} \rangle = L_E(t)\, \delta_{\{\underset{\sim}{k}\}\{\underset{\sim}{k}'\}}$$

and therefore :

$$(II.13.12)\qquad \Delta\rho_o(t) = -i \sum_{\{\underset{\sim}{k}\}} \int_0^t dt' \langle o | \exp\left[-i(L_0 + \delta L)(t-t')\right] | \{\underset{\sim}{k}\} \rangle \times$$

$$\times L_E(t') \rho^{equ.}_{\{\underset{\sim}{k}\}}$$

Any time dependent field can be represented by a superposition of oscillating fields with various frequencies. Therefore, we shall restrict ourselves to the case of an external oscillating field :

$$(II.13.12)\qquad \underset{\sim}{E}(t) = \underset{\sim o}{E}\, e^{-i\omega t}$$

Using the convolution theorem and (II.13.13) , we easily can write :

$$(II.13.14)\quad \Delta\rho_o(t) = -(1/2\pi i)\sum_{\{\underset{\sim}{k}\}}\int_C dz\, e^{-izt}\langle 0|R(z)|\{\underset{\sim}{k}\}\rangle\frac{1}{z-\omega}\times \times \sum_i e_i \underset{\sim}{E}_0 \cdot \frac{\partial}{\partial p_i}\rho^{equ.}_{\{\underset{\sim}{k}\}}$$

where R(z) is the resolvent operator defined by (II.3.6) , in the absence of external field. The matrix elements of this operator have been discussed in detail in § 8, where we established the generalized master equation for the evolution of the velocity distribution function in the absence of external field. Using these results, we obtain :

$$(II.13.15)\quad \Delta\rho_o(t) = -(1/2\pi i)\int_C dz\, \frac{e^{-izt}}{z}\sum_{n=0}\left[\frac{1}{z}\psi(z)\right]^n\left\{\frac{1}{z-\omega}\sum_i e_i \underset{\sim}{E}_o\cdot\frac{\partial}{\partial p_i}\rho^{equ.}_o + \sum_{\{\underset{\sim}{k}\}} D_{\{\underset{\sim}{k}\}}(z)\frac{1}{z-\omega}\sum_i e_i \underset{\sim}{E}_o\cdot\frac{\partial}{\partial p_i}\rho^{equ.}_{\{\underset{\sim}{k}\}}\right\}$$

where the operators $\psi(z)$ and $D_{\{\underset{\sim}{k}\}}(z)$ are given by (II.8. 3) a nd (II.8.4) respectively.

Differentiating with respect to t and using (II.8.7) , (II.8.8) , we obtain :

$$(II.13.6)\quad \frac{\partial\Delta\rho_o(t)}{\partial t} + iL_E\rho^{equ.}_o + i\sum_{\{k\}}\int_o^t d\tau\, \mathcal{D}_{\{\underset{\sim}{k}\}}(t-\tau)L_E(\tau)\rho^{equ.}_{\{\underset{\sim}{k}\}} = \int_o^t d\tau\, G(t-\tau)\Delta\rho_o(\tau)$$

This transport equation is valid at any order in the coupling constant and the concentration.

The term $iL_E\rho^{equ.}_o$ in the lhs is the usual flow term

which describes the effect of the field on the unperturbed particles (i.e. between successive collisions).

As to the non markovian term in the lhs of (II.13.16) it describes the effect of the external field on the particles during the collisions. To see this, let us consider the static case ($\omega=0$). Then, for times long with respect to the collision time, we have (see (II.8.8.)) :

$$\text{(II.13.17)} \qquad \sum_{\{\underset{\sim}{k}\}} \int_0^t d\tau\, \mathcal{D}_{\{\underset{\sim}{k}\}}(\tau)\, L_E \rho^{equ.}_{\{\underset{\sim}{k}\}} = \sum_{\{\underset{\sim}{k}\}} D^{(0)}_{\{\underset{\sim}{k}\}} L_E \rho^{equ.}_{\{\underset{\sim}{k}\}}$$

As we have seen, the equilibrium correlations are created from the equilibrium velocity distribution (see (II.12.7)) and we can write :

$$\sum_{\{\underset{\sim}{k}\}} D^{(0)}_{\{\underset{\sim}{k}\}}\, L_E \rho^{equ.}_{\{\underset{\sim}{k}\}} = \sum_{\{\underset{\sim}{k}\}} D^{(0)}_{\{\underset{\sim}{k}\}}\, L_E\, C^{(0)}_{\{\underset{\sim}{k}\}}\, \rho^{equ.}_0$$

$$= \lim_{z\to 0} \sum_{\{\underset{\sim}{k}\}} \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \langle 0 | \left(\delta L \frac{1}{z-L_0}\right)^m | \{\underset{\sim}{k}\} \rangle L_E \langle \{\underset{\sim}{k}\} | \left(\frac{1}{z-L_0} \delta L\right)^n | 0 \rangle \rho^{equ}_0$$

$$\text{(II.13.18)} \qquad = \lim_{z\to 0} \sum_{\{\underset{\sim}{k}\}} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \langle 0 | \delta L \left(\frac{1}{z-L_0} \delta L\right)^p \frac{1}{z-L_0} L_E \frac{1}{z-L_0} \left(\delta L \frac{1}{z-L_0}\right)^q \delta L | 0 \rangle \times$$

$$\times\, \rho^{equ.}_0$$

If we compare the operator in the rhs with the operator $\psi(z)$ given by (II.8.3), we notice that they differ only through the replacement of one the unperturbed propagator $S\, 1/(z-L_0)$ in $\psi(z)$ by :

$$\text{(II.13.19)} \qquad \frac{1}{z-L_0} L_E \frac{1}{z-L_0} = \frac{1}{z-L_0-L_E} - \frac{1}{z-L_0} + 0(E^2)$$

In other words, the operator in the lhs of (II.13.16) describes the corre-

ction to a collision process which one obtains when one takes into account (to first order in E) the effect of the external field on one of the intermediate state.

II.14 - Stationary transport equation in the static case.

After a long time, we may expect that a system submitted to an external, spatially homogeneous, constant, electrical field will reach a stationary state :

$$\Delta\rho_o(t) \to \Delta\rho_o^{st} \tag{II.14.1}$$

where $\Delta\rho_o^{st.}$ is time independent. As the contributions to the rhs of (II.13.16) come from times τ such that :

$$t - \tau \lesssim \tau_{coll} \tag{II.14.2}$$

we also have, for t very long :

$$\Delta\rho_o(\tau) = \Delta\rho_o(t) = \Delta\rho_o^{st.} \tag{II.14.3}$$

Taking also into account (II.8.8), the general transport equation becomes :

$$iL_E\rho_o^{equ.} + \sum_{\{\underset{\sim}{k}\}} D_{\{\underset{\sim}{k}\}}(0) iL_E \rho_{\{\underset{\sim}{k}\}}^{equ.} = \lim_{t\to\infty} \int_o^t d\tau\, G(t-\tau)\Delta\rho_o^{st.} \tag{II.14.4}$$

or

$$iL_E\rho_o^{equ.} + \sum_{\{\underset{\sim}{k}\}} D_{\{\underset{\sim}{k}\}}(0)\, iL_E \rho_{\{\underset{\sim}{k}\}}^{equ.} = -i\Psi(0)\Delta\rho_o^{st} \tag{II.14.5}$$

In chapter V, we shall use this equation as a starting point in a discussion of brownian motion of a heavy charged particle submitted to the action of an external constant electrical field and moving in a medium of light particles.

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III. BROWNIAN MOTION IN AN HOMOGENEOUS, WEAKLY COUPLED SYSTEM

III. 1 - Introduction

We shall consider here a weakly coupled gas, i.e. a system such that the coupling constant is very small :

(III. 1. 1) $$\lambda \to 0$$

The relaxation time of such a system is proportional to λ^{-2} (see the Born approximation) :

(III. 1. 2) $$\tau_{rel} \sim \lambda^{-2}$$

We shall consider the evolution of such a system for times of the order of the relaxation time, i.e. we shall take the following limit :

(II. 1. 3) $$\lambda \to 0 \quad , \quad t \to \infty \, , \; \lambda^2 t \text{ finite}$$

As the collision time is independent of the strength of the interaction, we clearly have :

(II. I. 4) $$\tau_{coll} / \tau_{rel} \to 0$$

and the evolution of the system will be described by a markovian equation.

The weak coupling condition implies that we exclude all forces with a strong repulsive core. Strictly speaking, there are no known intermolecular forces for which the theory of weakly coupled systems may be applied.

In all physical cases, the interaction becomes too strong at very short distances to be handled in a weak coupling theory . Nevertheless, we shall consider it here because it is the simplest example where the brownian

motion problem can be discussed starting from a microscopic basis. This model has been discussed by Prigogine and Balescu [1)2)] and will already show up interesting features when compared with the phenomenological theory of chapter I, and in any case, we can expect that it will give us a good description of the effect of the collisions which are not too close.

We shall first find the equation for the reduced distribution function for one particle assuming that initially there are no long range correlations. Then, we shall specialize to the problem of brownian motion where the particle moves in a fluid at equilibrium. The equation so obtained for the one particle velocity distribution function will be of the Fokker-Planck type. However, in contrast with the assumptions of the stochastic theory, the friction coefficient will appear as velocity dependent. In fact, this dependence will be important only for velocities equal to or higher than the mean thermal velocity of the fluid.

III.2 - Equation of evolution of the velocity distribution function for weakly ooupled systems.

From the discussion of chapter II, § 9, it is quite clear that if we take into account (III.1.4), we must neglect all non markovian corrections to the kinetic equation, i.e. take

(III.2.1) $$\Omega = 1$$

in (II.9.5).

When we do this, to be consistent, we must keep in the operator Ψ only the lowest order contribution, of order λ^2. The only diagram which we have therefore to keep in the operator Ψ is the cycle (fig. II.6 1a). The evolution equation then becomes :

$$\frac{\partial \rho_o(t)}{\partial t} = -i\lambda^2 \psi_2 \rho_o(t) \qquad \text{(III.2.2)}$$

where ψ_2 is the operator associated with the cycle. We have already discussed this operator in ch. II. § 7, using the simple case of an exponential interaction law. If we do not make any special choice of the potential, we have (see II.7.4) ;

$$-i\psi_2(z) = (8\pi^3/\Omega)^2 \; i \sum_{i<j} \sum_{\underset{\sim}{k}} |V_k|^2 \underset{\sim}{k}\cdot\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \times$$

$$\times \frac{1}{z - \underset{\sim}{k}\cdot(\underset{\sim}{v}_i - \underset{\sim}{v}_j)} \quad \underset{\sim}{k}\cdot\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \quad \left(z \in S^+\right) \qquad \text{(II.2.3)}$$

We have now to find out the limiting value of $\psi_2(z)$ when $z \to 0^+$, i.e. the analytical continuation of this operator when z approaches the real axis. As we have already said this can be done easily, in the limit of a large system , using the theory of Cauchy integrals. Indeed, when the limit

$$N \to \infty \;,\; \Omega \to \infty, \quad N/\Omega = C \text{ finite} \qquad \text{(III.2.4)}$$

in taken , the spectrum of values of $\underset{\sim}{k}$ becomes continuous and the summation over $\underset{\sim}{k}$ in (III.2.3) becomes an integral :

$$(8\pi^3/\Omega) \sum_{\underset{\sim}{k}} \to \int d^3k \qquad \text{(III2.5)}$$

Then we have :

$$-i\psi_2(z) = (8\pi^3/\Omega)\, i \sum_{i<j} \int d^3k\, |V_k|^2 \underset{\sim}{k}\cdot\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \times$$

$$\times \frac{1}{z - \underset{\sim}{k}\cdot(\underset{\sim}{v}_i - \underset{\sim}{v}_j)} \quad \underset{\sim}{k}\cdot\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \qquad \text{(III.2.6)}$$

If we take as one of the integration variable the variable :

(II.2.7) $$x = \underset{\sim}{k}.(\underset{\sim}{v}_i - \underset{\sim}{v}_j)$$

the dependence on z is of the form :

(III.2.8) $$F(z) = \int_{-\infty}^{+\infty} dx \ \frac{f(x)}{z - x} \qquad (z \in S^+)$$

This is precisely a Cauchy integral. Its analytical continuation is :

(III.2.9) $$F(0^+) = -\int_{-\infty}^{+\infty} dx \ \mathcal{P}(1/x) f(x) - \pi i \int_{-\infty}^{+\infty} dx \ \delta(x) \ f(x)$$

The rhs of (III.2.6) is an even function of $\underset{\sim}{k}$. Therefore, the contribution involving the principal part vanishes and we are left with the following kinetic equation for a weakly coupled gas :

(III.2.10) $$\frac{\partial \rho_o(t)}{\partial t} = (8\pi^4 \lambda^2/\Omega) \sum_{i<j} \int d^3k \ |V_k|^2 \ \underset{\sim}{k}.\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \times$$
$$\times \ \delta\left[\underset{\sim}{k}.(\underset{\sim}{v}_i - \underset{\sim}{v}_j)\right] \ \underset{\sim}{k}.\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right)\rho_o(t)$$

Let us notice that with this equation it is very easy to verify Boltzmann's $\mathcal{H}$-theorem. Indeed, with Boltzmann's $\mathcal{H}$-quantity defined as :

(III.2.11) $$\mathcal{H} = \int |d\underset{\sim}{p}|^N \rho_o \ln \rho_o$$

the kinetic equation allows us to write :

(III.2.12) $$\frac{\partial \mathcal{H}}{\partial t} = -(8\pi^4 \lambda^2/\Omega) \sum_{i<j} \int d^3k \ |V_k|^2 \delta\left[\underset{\sim}{k}.(\underset{\sim}{v}_i - \underset{\sim}{v}_j)\right] \ \frac{1}{\rho_o(t)} \times$$
$$\times \left[\underset{\sim}{k}.\left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right)\rho_o(t)\right]^2 \leqslant 0$$

The function $\mathcal{H}$ (which is related to the entropy) decreases monotonically

to its equilibrium value. The rhs of (III.2.12) vanishes once ρ_o has reached its equilibrium value :

$$\rho_o^{equ.} = f(H_o) \tag{III.2.13}$$

The function f cannot be determined by (III.2.12) but is determined by the initial conditions. We shall see in the next paragraph that the assumption of initial molecular chaos leads to the Maxwell-Boltzmann distribution.

III.3 - Kinetic equation for the one particle velocity distribution function.

Let us call φ_s the reduced distribution function for s momenta:

$$\varphi_s(\underset{\sim}{v}_1, \ldots \underset{\sim}{v}_s, t) = \int d\underset{\sim}{p}_{s+1} \ldots d\underset{\sim}{p}_N \; \rho_o(\{\underset{\sim}{p}\}, t) \tag{III.3.1}$$

Integrating (III.2.10) with respect to all momenta except $\underset{\sim}{v}_1$ and taking into account the fact that the distribution function vanishes at infinity, we obtain :

$$\frac{\partial \varphi_1(\underset{\sim}{v}_1, t)}{\partial t} = (8\pi^4 \lambda^2/\Omega\, m_1^2) \sum_{j>1} \int d\underset{\sim}{v}_j \int d^3k \, |V_k|^2 \, \underset{\sim}{k} \cdot \frac{\partial}{\partial \underset{\sim}{v}_1} \times$$

$$\times \, \delta\left[\underset{\sim}{k} \cdot (\underset{\sim}{v}_1 - \underset{\sim}{v}_j)\right] \underset{\sim}{k} \cdot \left(\frac{\partial}{\partial \underset{\sim}{v}_1} - \frac{m_1}{m_j} \frac{\partial}{\partial \underset{\sim}{v}_j}\right) \varphi_2(\underset{\sim}{v}_1, \underset{\sim}{v}_j, t) \tag{III.3.2}$$

This equation gives us the evolution of the one-particle velocity distribution function in terms of the two-particle distribution function. Therefore , it is not a closed equation and if we do not make any further assumptions, we have actually to deal with an infinite hierarchy of equations.

According to our basic assumption (Ch. II. , § 9) , we consider a system where all correlations are of finite extension. Now, the velocity distribution function is an average over the positions of all particles of the complete distribution function. When we do this, if we consider two given particles, it is quite clear that the contribution of those configurations where the particles are correlated is much smaller than that of those configurations where they are uncorrelated. This allows us to neglect the effect of these correlations on the velocity distribution function, i.e. to make the assumption of molecular chaos at t = 0 :

$$\rho_0^{(t=0)} = \prod_j \varphi_1(\underset{\sim}{v}_j, t) \tag{III.3.3}$$

Once molecular chaos is taken as an initial condition, it can be shown to persist for all times in the limit of infinite systems [1) 3)]. We shall not give the proof here.

With the initial condition (III.3.3) , we may write in the rhs of (III.3.2) :

$$\varphi_2(\underset{\sim}{v}_1, \underset{\sim}{v}_j, t) = \varphi_1(\underset{\sim}{v}_1, t)\varphi_1(\underset{\sim}{v}_j, t) \tag{III.3.4}$$

and we obtain :

$$\frac{\partial \varphi_1(\underset{\sim}{v}_1, t)}{\partial t} = (8\pi^4 \lambda^2/\Omega m_1^2) \sum_j \int d\underset{\sim}{v}_j \int d^3k \left|V_k\right|^2 \underset{\sim}{k} \cdot \frac{\partial}{\partial \underset{\sim}{v}_1} \times$$

$$\times \delta\left[\underset{\sim}{k} \cdot (\underset{\sim}{v}_1 - \underset{\sim}{v}_j)\right] \underset{\sim}{k} \cdot \left(\frac{\partial}{\partial \underset{\sim}{v}_1} - \frac{m_1}{m_j} \frac{\partial}{\partial \underset{\sim}{v}_j}\right) \varphi_1(\underset{\sim}{v}_1, t)\varphi_1(\underset{\sim}{v}_j, t) \tag{III.3.5}$$

A similar equation can of course be easily obtained for the reduced distribution function of any particle of the system. Therefore, we are now dealing with a closed set of equations.

Let us now verify that the equilibrium distribution corresponding to the initial condition (III.3.3) is indeed the Maxwell-Boltzmann distribution. Using (III.2.12) and the assumption of molecular chaos, at equilibrium, we must have :

$$\text{(III.3.6)} \qquad \underset{\sim}{k} \cdot \left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right) \varphi_1(\underset{\sim}{v}_i, t)\, \varphi_1(\underset{\sim}{v}_j, t) = 0$$

whenever $\underset{\sim}{k}$ is such that :

$$\text{(III.3.7)} \qquad \underset{\sim}{k} \cdot (\underset{\sim}{v}_i - \underset{\sim}{v}_j) = 0$$

We verify easily that (III.3.6) implies :

$$\text{(III.3.8)} \qquad \underset{\sim}{k} \cdot \left(\frac{\partial \ln \varphi_1(\underset{\sim}{v}_i, t)}{\partial \underset{\sim}{p}_i} - \frac{\partial \ln \varphi_1(\underset{\sim}{v}_j, t)}{\partial \underset{\sim}{p}_j}\right) = 0$$

Whenever (III.3.8) and (III.3.7) are simultaneously satisfied, we must have :

$$\frac{\dfrac{\partial \ln \varphi_1(\underset{\sim}{v}_i)}{\partial \underset{\sim}{p}_i}}{\dfrac{\underset{\sim}{p}_i - \underset{\sim}{p}_o}{m_i}} = \frac{\dfrac{\partial \ln \varphi_1(\underset{\sim}{v}_j)}{\partial \underset{\sim}{p}_j}}{\dfrac{\underset{\sim}{p}_j - \underset{\sim}{p}_o}{m_j}} = \alpha$$

where α and $\underset{\sim}{p}_o$ are constants .

Integrating (III.3.9) , we obtain :

$$\text{(III.3.10)} \qquad \ln \varphi_1(\underset{\sim}{v}_i) = \alpha (\underset{\sim}{p}_i - \underset{\sim}{p}_o)^2 / 2m_i + \ln \gamma_i$$

where γ_i is a constant .

This gives :

$$\text{(III.3.11)} \qquad \varphi_1(\underset{\sim}{v}_i) = \gamma_i \exp\left[\alpha \left|\underset{\sim}{p}_i - \underset{\sim}{p}_o\right|^2 / 2m_i\right]$$

The normalization condition requires :

$$\alpha < 0 \qquad \gamma_i = 4\pi(-m_i \alpha / 2\pi)^{3/2} \tag{III.3.12}$$

We also consider systems where the average velocity is zero ; hence

$$\underset{\sim}{p}_o = \underset{\sim}{0} \tag{III.3.13}$$

Defining the temperature through :

$$kT = \langle m_i v^2/2 \rangle = \int d\underset{\sim}{v}_i \; (v_i^2/2) \varphi_1(\underset{\sim}{v}_i) m_i \tag{III.3.14}$$

one obtains easily the usual Maxwell - Boltzmann law ;

$$\varphi_1(\underset{\sim}{v}) = 4\pi (m/2\pi kT)^{3/2} \exp(-mv^2/2kT) \tag{III.3.15}$$

In this way, we have verified our statement at the end of the previous paragraph.

III.4 - Brownian motion in a fluid at equilibrium.

We shall now consider the simple case where the particle 1 moves in a fluid at equilibrium . We then have :

$$\varphi_1(\underset{\sim}{v}_j, t) = 4\pi (m_j/2\pi kT)^{3/2} \exp(-m_j v_j^2/2kT) \qquad j \neq 1 \tag{III.4.1}$$

Then, equ.(III.3.5) becomes (assuming the masses of all fluid particles to be equal to m) :

$$\frac{\partial \varphi_1(\underset{\sim}{v}_1, t)}{\partial t} = (32\pi^5 \lambda^2 C/m_1^2)(m/2\pi KT)^{3/2} \int d\underset{\sim}{v} \exp(-mv^2/2kT) \times$$
$$\times \int d^3k \, |V_k|^2 \, \underset{\sim}{k} \cdot \frac{\partial}{\partial \underset{\sim}{v}_1} \delta[\underset{\sim}{k} \cdot (\underset{\sim}{v}_1 - \underset{\sim}{v})] \underset{\sim}{k} \left(\frac{\partial}{\partial \underset{\sim}{v}_1} + \frac{m_1 \underset{\sim}{v}_1}{kT} \right) \varphi_1(\underset{\sim}{v}_1, t) \tag{III.4.2}$$

In this way, we have obtained a closed equation for $\varphi_1(\underset{\sim}{v}_1, t)$.

The $\underset{\sim}{k}$ integration is easily performed in a reference frame where the relative velocity

$$\underset{\sim}{g} = \underset{\sim}{v}_1 - \underset{\sim}{v} \tag{III.4.3}$$

is along the z axis :

$$a_i \int d^3k \, |V_k|^2 \, k_i k_j \, \delta(\underset{\sim}{k} \cdot \underset{\sim}{g}) \, b_j = \pi B \left(a_x \frac{1}{g} b_x + a_y \frac{1}{g} b_y \right)$$

$$= \pi B \left(\underset{\sim}{a} \cdot \frac{1}{g} \underset{\sim}{b} - \underset{\sim}{a} \cdot \underset{\sim}{g} \frac{1}{g^3} \underset{\sim}{g} \cdot \underset{\sim}{b} \right) \tag{III.4.4}$$

where

$$B = \int_0^\infty dk \; k^3 \, |V_k|^2 \tag{III.4.5}$$

depends only on the intermolecular potential .

The last expression in (III.4.4) is valid in an arbitrary reference frame . Using dimensionless quantities :

$$\underset{\sim}{u} = \sqrt{\frac{m}{2kT}} \, \underset{\sim}{v}_1 \qquad \underset{\sim}{w} = \sqrt{\frac{m}{2kT}} \, \underset{\sim}{g} \tag{III.4.6}$$

we obtain :

$$\frac{\partial \varphi_1(\underset{\sim}{u}, t)}{\partial t} = (8 \sqrt{2} \, \pi^{9/2} \, \lambda^2 CB / m_1^2) \, (m/kT)^{3/2} \times$$

$$\times \left\{ \frac{\partial}{\partial u_i} \int d\underset{\sim}{w} \; e^{-(\underset{\sim}{w} - \underset{\sim}{u})^2} \; \frac{1}{w} \left(\frac{\partial}{\partial u_i} + 2 \frac{m_1}{m} u_i \right) - \frac{\partial}{\partial u_i} \int d\underset{\sim}{w} \; e^{-(\underset{\sim}{w} - \underset{\sim}{u})^2} \times \right.$$

$$\left. \times \; w_i w_j \frac{1}{w^3} \left(\frac{\partial}{\partial u_j} + 2 \frac{m_1}{m} u_j \right) \right\} \varphi_1(\underset{\sim}{u}, t) \tag{III.4.7}$$

In a reference frame where $\underset{\sim}{u}$ is along the z axis, we have :

$$I_1 = \int d\underset{\sim}{w}\, e^{-(\underset{\sim}{w}-\underset{\sim}{u})^2}\,(1/w) = 2\pi\int_0^\infty dw\, w \int_{-1}^{+1} d\cos\theta\, e^{-(w^2+u^2-2wu\cos\theta)}$$

(III. 4. 8)
$$= (\pi/u)\int_0^\infty dw\left\{e^{-(w-u)^2} - e^{-(w+u)^2}\right\} = (\pi^{3/2}/u)\,\Phi(u)$$

where

(III. 4. 9)
$$\Phi(u) = (2/\sqrt{\pi})\int_0^u dx\, e^{-x^2}$$

is the error function .

We also have :

$$a_i \int d\underset{\sim}{w}\, e^{-(\underset{\sim}{w}-\underset{\sim}{u})^2}\, w_i w_j w^{-3} b_j = (1/2)(\underset{\sim}{a}.I_1\underset{\sim}{b} - \underset{\sim}{a}.\underset{\sim}{u}\,\frac{1}{u^2}\; I_1\,\underset{\sim}{u}.\underset{\sim}{b})$$

(III. 4. 10)
$$- (1/2)\,(\underset{\sim}{a}.I_2\underset{\sim}{b} - 3\,\underset{\sim}{a}.\underset{\sim}{u}\,\frac{1}{u^2}\; I_2\,\underset{\sim}{u}\,.\,\underset{\sim}{b})$$

$$I_2 = 2\pi\int_0^\infty dw\, w \int_{-1}^{+1} d\cos\theta\,\cos^2\theta\; e^{-(w^2+u^2\, wu\cos\theta)}$$

$$= (\pi/2u^2)\int_0^\infty dw\, w\, e^{-(w^2+u^2)} \quad \frac{d^2}{dw^2} \int_{-1}^{+1} d\cos\theta\, e^{2wu\cos\theta}$$

(III. 4. 11)
$$= (\pi/2u^2)\left\{\int_0^\infty dw\left[\frac{d^2}{dw^2}\, w\, e^{-(w^2+u^2)}\right]\int_{-1}^{+1} d\cos\theta\, e^{2wu\cos\theta} + 2e^{-u^2}\right\}$$

$$= \pi^{3/2}\left\{u^{-2}\,\Phi'(u) - u^{-3}(1-u^2)\Phi(u)\right\}$$

where

(II. 4. 12)
$$\Phi'(u) = \frac{d\Phi(u)}{du} = (2/\sqrt{\pi})\, e^{-u^2}$$

Introducing (III. 4. 8) and (III. 4. 10) into (III. 4. 7) , one can finally write (III. 4. 7) as :

$$\frac{\partial \varphi_1(\underset{\sim}{u}, t)}{\partial t} = \tau^{-1}\left\{a(u)\quad \frac{\partial^2}{\partial u_i^2} + b(u)\left[\left(u_i \frac{\partial}{\partial u_i}\right)^2 - u_i \frac{\partial}{\partial u_i}\right]\right.$$

$$(III.4.13)\quad -2\left(1-\frac{m_1}{m}\right)\left[u^{-3}\phi(u)-u^{-2}\phi'(u)\right]u_i\frac{\partial}{\partial u_i}+4\frac{m_1}{m}\phi'(u)\Big\}\varphi_1(\underset{\sim}{u},t)\,,$$

where

$$(III.4.14)\quad a(u)=\frac{1}{2u^3}\left[u\phi'(u)+(2u^2-1)\phi(u)\right]$$

$$(III.4.15)\quad b(u)=u^{-1}\,\frac{da(u)}{du}$$

and where τ has the dimension of a time :

$$(III.4.16)\quad \tau^{-1}=(32\pi^6 C\lambda^2 B/m_1^2)\,(m/2kT)^{3/2}$$

III.5. Link with stochastic theory .

Equation (III.4.13) can be easily written in the form of the general Fokker - Planck equation (I.5.7) :

$$\frac{\partial\varphi}{\partial t}=\frac{\partial}{\partial u_i}\left[-\frac{\langle\Delta u_i\rangle}{\Delta t}\varphi\right]+\frac{1}{2}\,\frac{\partial^2}{\partial u_i\partial u_j}\left[\frac{\langle\Delta u_i\Delta u_j\rangle}{\Delta t}\varphi\right]$$

(III.5.1)

with

$$(III.5.2)\quad \frac{\langle\Delta u_i\rangle}{\Delta t}=-4\frac{u_i}{u}\left(1+\frac{m_1}{m}\right)g(u)\,\tau^{-1}$$

$$(III.5.3)\quad \frac{\langle\Delta u_i\Delta u_j\rangle}{\Delta t}=\left\{6\,\frac{u_iu_j}{u^3}\left[g(u)-\frac{1}{3}\phi(u)\right]+\frac{2}{u}\delta_{i,j}\left[\phi(u)-g(u)\right]\right\}\tau^{-1}$$

where

$$(III.5.4)\quad g(u)=\frac{1}{2}\,u^{-1}\left[u^{-1}\phi(u)-\phi'(u)\right]$$

This equation has been obtained from first principles as an asymptotic equation describing the motion of a particle of mass m_1 in a gas at thermal equilibrium , with the assumption of weak coupling. The avera-

rage values $\langle \Delta u_i \rangle, \langle \Delta u_i \Delta u_j \rangle$ are such that the velocity distribution function reaches monotonically the Maxwell-Boltzmann distribution after a long time. No other assumption than the hypothesis of initial molecular chaos has been necessary to obtain this result.

The relaxation time, i.e. the characteristic time for the evolution of $\varphi(\underset{\sim}{u}, t)$ is given by (III.4.16) :

$$\tau_{rel}^{-1} = (32\pi^6 \lambda^2_{BC}) / m_1^2)(m/2kT)^{3/2} \qquad \text{(III.5.5)}$$

As expected, it decreases when the concentration increases. It is also a function of the temperature and the intermolecular forces (see III. 4.5 for B) ; it depends upon the ratio of the interaction energy and the mean thermal energy of the particles of the fluid. It decreases whenever this ratio increases.

If we compare (III.5.2) with the corresponding expression derived from the Langevin equation, we notice that the microscopic theory introduces a coefficient of dynamical friction η which is velocity dependent :

$$\eta = 4 \tau^{-1} \left(1 + \frac{m_1}{m}\right) \frac{g(u)}{u} \qquad \text{(III.5.6)}$$

Let us introduce the following dimensionless quantities :

$$\gamma = (m/m_1)^{1/2} \qquad \text{(III.5.7)}$$

$$x = (m_1/2kT)^{1/2} v_1 = u/\gamma \qquad \text{(III.5.8)}$$

γ is the ratio of the masses of the fluid particle and the brownian particle ; x is the ratio of the velocity of the brownian particle and its thermal velocity. With these quantities, we have :

(III.5.9) $$\eta = (4(1+\gamma^2)\frac{g(\gamma x)}{\gamma x}\frac{\tau^{-1}}{\gamma^2}$$

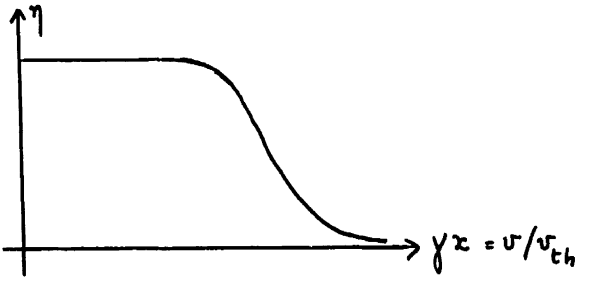
For $x \ll 1$, (and $\gamma \leq 1$) we have

(III.5.10) $$\eta \simeq (8/3\sqrt{\pi})(1+\gamma^2)\tau^{-1}\gamma^{-2}$$

In this case, the dynamical friction coefficient is approximately constant:

If $\gamma x \gg 1$, i.e. if the particle has a high velocity, the dynamical friction coefficient is very small :

(III.5.12) $$\eta \simeq 4(1+\gamma^2)\frac{1}{\gamma^3 x^3}\tau^{-1}\gamma^{-2} \simeq \frac{4\tau^{-1}}{\gamma^3 x^3}$$



Dependence of dynamical friction coefficient on velocity

Fig. III.5.1

For $\gamma x \ll 1$, we also have :

(III.5.13) $$\frac{\langle \Delta u_i \, \Delta u_j \rangle}{\langle \Delta t \rangle} = \delta_{i,j}(8/3\sqrt{\pi})\tau^{-1}$$

For $\gamma \ll 1$ and $x \simeq 1$, i.e. for a heavy particle moving with thermal velocity in a medium of light particles at equilibrium , the Fokker Planck equation takes the simple form :

(III.6.14) $$\frac{\partial \varphi}{\partial t} = (4/3\sqrt{\pi})(1/\tau\gamma^2)\frac{\partial}{\partial x_i}\left(\frac{\partial}{\partial x_i} + 2x_i\right)\varphi$$

analogous to (I.5.11) .

The expressions (III.5.2) and (III.5.3) for the average value of the velocity and square of the velocity have been obtained first by Chandrasekhar [4] .

In an analysis of tue dynamical friction in systems of stars, Chandrasekhar first considered single stellar encounters idealized as two-body problems. If a star of mass m_1 and velocity $\underset{\sim}{v}_1$ collides with a star of mass m and velocity $\underset{\sim}{v}$, the increments parallel ($\delta \underset{\sim}{v}_{1//}$) and perpendicular ($\delta \underset{\sim}{v}_{1\perp}$) to its direction of motion can be easily written. The net increments $\Delta \underset{\sim}{v}_{1//}$ and $\Delta \underset{\sim}{v}_{1\perp}$, due to a large number of successive encounters with field stars during a time interval Δt such that $\underset{\sim}{v}_1$ does not change appreciably, are easily computed. Assuming the velocity distribution for field stars to be a gaussian, one obtains :

(III.6.15) $$\Delta \underset{\sim}{v}_{1//} = \eta \, v_1$$

(III.6.16) $$\Delta \underset{\sim}{v}_{1\perp} = 0$$

(for more details, see Prof. Ferraro's notes in this volume)

III.6. Application.

These results have been used to discuss transport processes in fully ionized gases. A good account of this can be found in Spitzer's book [5] . However, the application is not straightforward. Indeed , the interaction law in this case is the Coulomb potential :

(III.6.1) $$V(r) = e^2/r$$

which Foûrier transform is :

(III. 6. 2) $$V_k = e^2/2\pi^2 k^2$$

Therefore the coefficient B which appears in the Fokker-Planck equation is :

(III. 6. 3) $$B = (e^4/4\pi^4) \int_0^\infty dk(1/k)$$

We notice that B diverges logarithmically both at the upper and lower limits of integration. This is due to the fact that the Coulomb potential has an infinite repulsive core at small distances (hence the upper limit divergence) and has a long range (hence the lower limit divergence). The long distance divergence is well known and appears also in the equilibrium properties. In fact, because of the long range of the potential, the interactions in such a medium have a collective character : configurations involving many particles play a dominant role. Both in equilibrium and non equilibrium properties[6)7)8)], this problem can be settled by a summation over a well defined class of diagrams. The result of this summation is to introduce a screening effect : in simple cases, the effective interaction vanishes exponentially for distances greater than the Debye radius κ^{-1} :

(III. 6. 4) $$V_{eff} = e^2 e^{-\kappa r}/r$$

with

(III. 6. 5) $$\kappa^2 = 4\pi e^2 C/kT$$

One way to take into account these effects semi-empirically is to introduce a cut-off at both limits of integration :

(III. 6. 6) $$B = (e^4/4\pi^4) \int_\kappa^{1/a} dk(1/k)$$

The lower cut-off K takes into account the screening effect while the upper one eliminates the effect of the very close collisions. The theory of weakly coupled gases may then be used.

However, this approach is not very satisfactory and the true way to solve this problem, although we shall not discuss it here, is, within a perturbation theory, to sum first all relevant contributions. From (III.6.4), it is quite apparent that the adequate procedure is not to limit ourselves to first power in the coupling constant e^2 or the concentration C, but to retain all terms proportional to any power of K, i.e. of e^2C, in the expansions. This summation introduces a dynamical screening effect, i.e. a screening which depends on the velocity of the brownian particle [9]. However, if the velocity of the particle is such that $(kT/m)^{1/2} \ll 1$, the dynamical effects may be neglected and the Debye potential is a good approximation. For more rapid particles, one can still write a Fokker-Planck equation but there appears a further velocity dependence of the coefficients due to the collective effects (excitation of plasma oscillations).

III.7 - Brownian motion in a fluid which is not at equilibrium.

In this case, we must relax assumption (III.4.1) and use equation (III.3.5). The main feature is that, whereas, in the equilibrium case, we have a single closed equation for the distribution function of the brownian particle, in the non equilibrium case, we have a whole set of equations for the velocity distribution functions of the Brownian particle and the fluid particles.

Following the same procedure as above for the integration over the wave vector, we easily obtain :

$$\frac{\partial \varphi_1(\underset{\sim}{v}_1, t)}{\partial t} = (8\pi^5 \lambda^2 c_B/m_1^2) \int d\underset{\sim}{v} \left\{ \frac{\partial}{\partial \underset{\sim}{v}_1} \quad \frac{1}{g} \quad \left(\frac{\partial}{\partial \underset{\sim}{v}_1} - \frac{\partial}{\partial \underset{\sim}{v}} \right) \right.$$

$$(III.7.1) \qquad -\frac{\partial}{\partial \underset{\sim}{v}_1}\cdot \underset{\sim}{g}\,\frac{1}{g^3}\underset{\sim}{g}\cdot\left(\frac{\partial}{\partial v_1}-\frac{\partial}{\partial v}\right)\Big\}\varphi_1(\underset{\sim}{v}_1,t)\,\varphi(\underset{\sim}{v},t)$$

This second order differential equation can be easily recast in the form of a generalized Fokker-Planck equation :

$$(III.7.2) \qquad \frac{\partial \varphi_1(\underset{\sim}{v}_1,t)}{\partial t} = \left\{\frac{\partial}{\partial v_{1_i}}\left(-\overline{\Delta v_{1_i}/\Delta\tau}\right)+\frac{1}{2}\,\frac{\partial^2}{\partial v_{1_j}\partial v_{1_j}}\left(\overline{\Delta v_{1_i}\Delta v_{1_j}/\Delta\tau}\right)\right\}\times \varphi_1(\underset{\sim}{v}_1,t)$$

where the transition moments are given by:

$$\overline{\Delta v_{1_i}/\Delta\tau} = (8\pi^5\lambda^2 CB/m_1^2)\int d\underset{\sim}{v}\left\{g^{-1}\,\frac{\partial\varphi(\underset{\sim}{v},t)}{\partial v_i}-2g_i g^{-3}\varphi(\underset{\sim}{v},t)\right.$$

$$\left. - g_i g_j g^{-3}\frac{\partial\varphi(\underset{\sim}{v},t)}{\partial v_j}\right\}$$

$$(III.7.3) \qquad = -(16\pi^5\lambda^2 CB/m_1^2)\int d\underset{\sim}{v}\, g_i\, g^{-3}\,\varphi(\underset{\sim}{v},t)$$

$$(III.7;4) \qquad \overline{\Delta v_{1_i}\Delta v_{1_j}/\Delta\tau} = -(16\pi^5\lambda^2 CB/m_1^2)\int d\underset{\sim}{v}\left\{g_i g_j g^{-3}-\delta_{ij}g^{-1}\right\}\varphi(\underset{\sim}{v},t)$$

The transition moments are now functionals of the state of the fluid .

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F. Henin

IV. MICROSCOPIC THEORY OF BROWNIAN MOTION OF A HEAVY PARTICLE IN THE ABSENCE OF EXTERNAL FORCES.

IV.1 - Introduction

In the preceding chapter, we have discussed the brownian motion of a particle which is weakly coupled to a fluid at thermal equilibrium. However, as we have seen, there are no known intermolecular forces corresponding to the weak coupling approximation. Therefore, that problem was rather academic and we shall now consider a more realistic situation. The discussion which will follow will be valid for all cases where the forces are of short range (Coulomb forces can also be included provided the screening effects are taken into account in a phenomenological way). The case of long range forces with no screening (gravitational forces) will be dealt with in chapter VII.

For this model we can use as a starting point the kinetic equation (II.9.3) or (II.9.5) . We shall consider the case where the brownian particle is much heavier than the fluid particles. For the case of a brownian particle moving with thermal velocity in a fluid at equilibrium at temperature T, we shall show that an equation of the Fokker -Planck type is indeed obtained for the velocity distribution function of that particle if one retains only the lowest order terms in the expansion of the kinetic equation in the ratio of the masses of the light and heavy particles . The method we shall follow enables us also to compute the corrections to the Fokker-Planck equation. However , we shall not consider this problem here but we shall rather discuss it in the next chapter where we consider the same problem but with an external force acting on the particle .

IV.2 - Equation for the reduced velocity distribution function of the brownian particle.

Let us start with the kinetic equation in the form (II.9.3). Assuming the fluid to be at equilibrium, we have

$$\rho_o(t) = \varphi(\underset{\sim}{V},t)\,(\rho_o^f)_{equ.} = \varphi(\underset{\sim}{V},t)\prod_{i=1}^{N}(2\pi kT/m)^{3/2}\,4\pi e^{-mv_i^2/2kT} \tag{IV.2;1}$$

where $\underset{\sim}{V}$ is the velocity of the brownian particle (mass: M) while $\underset{\sim}{v}_i$ is the velocity of the i^{th} fluid particle (all fluid particles have the same mass m).

Integrating both sides of (IV.2.1) with respect to the velocities of all the fluid particles, we readily obtain an equation for the reduced velocity distribution function $\varphi(\underset{\sim}{V},t)$ of the brownian particle :

$$\frac{\partial\varphi(\underset{\sim}{V},t)}{\partial t} = \int_o^t d\tau \left\{\int d\underset{\sim}{v}\right\}^N G(t-\tau)\,\varphi(\underset{\sim}{V},\tau)\,(\rho_o^f)_{equ.} \tag{IV.2.2}$$

which is valid only asymptotically.

Let us introduce the operator Γ :

$$\Gamma(t-\tau) = \left\{\int d\underset{\sim}{v}\right\}^N G(t-\tau)\,(\rho_o^f)_{equ.} \tag{IV.2.3}$$

This operator is of course a differential operator with respect to the velocity $\underset{\sim}{V}$ of the brownian particle. (IV.2.2) now becomes :

$$\frac{\partial\varphi(\underset{\sim}{V},t)}{\partial t} = \int_o^t d\tau\,\Gamma(t-\tau)\,\varphi(\underset{\sim}{V},\tau) \tag{IV.2.4}$$

From the very definition of G(t) and (IV.2.3), the Laplace transform of

the operator $\Gamma(t)$ is obviously :

$$\phi(z) = \int \{dv\}^N \psi(z) \; (\rho_o^f)_{equ.} \tag{IV.2.5}$$

Following the same procedure as that used to go from (II.9.3) to (II.9.5) , the equation (IV.2.4) may be written in the pseudomarkovian form :

$$\frac{\partial \varphi(V,t)}{\partial t} = -i\varpi \phi(0) \varphi(V,t) \tag{IV.2.6}$$

where the operator ϖ is given in terms of $\phi(0)$ and its derivatives $\phi'(0)$ by the same relation that holds between Ω and ψ (see (II.9.6) to (II.9.8)) :

$$\varpi = 1 + \phi'(0) + (1/2)\, \phi''(0)\phi(0) + [\phi'(0)]^2 + \ldots \tag{IV.2.7}$$

The equation (IV.2.6) will be our basic equation for a dynamical study of brownian motion. We shall now show how it reduces to an equation of the Fokker-Planck type when only the lowest order terms in the mass ratio m/M are retained .

IV.3 - Expansion in powers of the mass ratio.

As the fluid is at equilibrium at temperature T, we have:

$$\langle v_i \rangle = (2kT/m)^{1/2} \tag{IV.3.1}$$

$$\langle p_i \rangle = (2mkT)^{1/2} \tag{IV.3.2}$$

If the brownian particle moves with thermal velocity , we have:

$$V = 0(2kT/M)^{1/2} = 0(\gamma \langle v_i \rangle) \tag{IV.3.3}$$

$$P = 0(2MkT)^{1/2} = 0(\gamma^{-1} \langle v_i \rangle) \tag{IV.3.4}$$

with

(IV.3.5) $$\gamma = (m/M)^{1/2} \ll 1$$

The unperturbed and perturbed Liouville operators may be written in a way which exhibits their dependence on γ. We have :

(IV.3.6) $$L_o = L_o^f + \gamma L_o^A$$

where L_o^f is the unperturbed Liouville operator for the fluid :

(IV.3.7) $$L_o^f = \sum_{i=1}^{N} \underset{\sim}{v}_i \cdot \frac{\partial}{\partial \underset{\sim}{r}_i}$$

while γL_o^A is that for the brownian particle A :

(IV.3.8) $$\gamma L_o^A = \underset{\sim}{V} \cdot \frac{\partial}{\partial \underset{\sim}{R}}$$

Similarily, we may write :

(IV.3.9) $$\delta L = \delta L^f + \gamma \delta L^A$$

with

$$\delta L^f = \sum_{i<j} \frac{\partial V_{ij}(|\underset{\sim}{r}_i - \underset{\sim}{r}_j|)}{\partial \underset{\sim}{r}_i} \cdot \left(\frac{\partial}{\partial \underset{\sim}{p}_i} - \frac{\partial}{\partial \underset{\sim}{p}_j}\right)$$

(IV.3.10)
$$+ \sum_i \frac{\partial V_{iA}(|\underset{\sim}{r}_i - \underset{\sim}{R}|)}{\partial \underset{\sim}{r}_i} \cdot \frac{\partial}{\partial \underset{\sim}{p}_i}$$

(IV.3.11) $$\gamma \delta L^A = \sum_i \frac{\partial V_{iA}(|\underset{\sim}{r}_i - \underset{\sim}{R}|)}{\partial \underset{\sim}{R}} \cdot \frac{\partial}{\partial \underset{\sim}{P}}$$

With these expressions, we can easily expand the rhs of (IV.2.6) in powers of γ. Using (II.8.7), we have :

(IV.3.12) $$\phi(z) = \int \{d\underset{\sim}{v}\}^N \langle 0 | \delta L \sum_{n=1}^{\infty} \left(\frac{1}{z - L_o} \delta L\right)^n | 0 \rangle_{irr} (\rho_o^f)_{equ.}$$

Taking into account the fact that δL^f is a differential operator with respect to the velocities of the fluid particles, we have :

$$\phi(z) = \int \{dv\}^N \langle 0 | \left(\delta L^f + \gamma \delta L^A \right) \sum_{n=1}^{\infty} \left(\frac{1}{z - L_o} \delta L \right)^n | 0 \rangle_{irr} (\rho_o^f)_{equ.}$$

$$(IV.3.13) \quad = \gamma \sum_{i=1}^{N} \sum_{\underset{\sim}{K}} \langle 0 | \delta L^A | \underset{\sim}{K}, \underset{\sim}{k}_i = -\underset{\sim}{K} \rangle \int \{dv\}^N \langle \underset{\sim}{K}, \underset{\sim}{k}_i = -\underset{\sim}{K} | \sum_{n=1}^{\infty} \left(\frac{1}{z - L_o} \delta L \right)^n | 0 \rangle_{irr} \times$$

$$\times (\rho_o^f)_{equ.}$$

Using (IV.3.6) and (IV.3.9) , we then immediately obtain the expansion:

$$(IV.3.14) \qquad \phi(z) = \gamma \phi_1(z) + \gamma^2 \phi_2(z) + \ldots$$

with

$$\gamma \phi_1(z) = \sum_{i=1}^{N} \sum_{\underset{\sim}{K}} \left\{ \langle 0 | \delta L^A | \underset{\sim}{K}, \underset{\sim}{k}_i = -\underset{\sim}{K} \rangle \int \{dv\}^N \langle \underset{\sim}{K}, \underset{\sim}{k}_i = -\underset{\sim}{K} |$$

$$(IV.3.15) \qquad \sum_{n=1}^{\infty} \left(\frac{1}{z - L_o} \delta L^f \right)^n | 0 \rangle \Big\}_{irr} (\rho_o^f)_{equ.}$$

$$\gamma^2 \phi_2(z) = \sum_{i=1}^{N} \sum_{\underset{\sim}{K}} \langle 0 | \delta L^A | \underset{\sim}{k}_i = -\underset{\sim}{K}, \underset{\sim}{K} \rangle \int \{dv\}^N \langle \underset{\sim}{k}_i = -\underset{\sim}{K}, \underset{\sim}{K} |$$

$$\sum_{n=0}^{\infty} \left(\frac{1}{z - L_o^f} \delta L^f \right)^n \frac{1}{z - L_o^f} L_o^A \sum_{m=0}^{\infty} \left(\frac{1}{z - L_o^f} \delta L^f \right)^m | 0 \rangle_{irr} (\rho_o^f)_{equ.}$$

$$(IV.3.16) \quad + \sum_{i=1}^{N} \sum_{\underset{\sim}{K}} \langle 0 | \delta L^A | \underset{\sim}{k}_i = -\underset{\sim}{K}, \underset{\sim}{K} \rangle \int \{dv\}^N \langle \underset{\sim}{k}_i = -\underset{\sim}{K}, \underset{\sim}{K} \sum_{n=0}^{\infty} \left(\frac{1}{z - L_o^f} \delta L^f \right)^n \times$$

$$\times \frac{1}{z - L_o^f} \delta L^A \sum_{m=0}^{\infty} \left(\frac{1}{z - L_o^f} \delta L^f \right)^m | 0 \rangle_{irr} (\rho_o^f)_{equ.}$$

In principle, in the first term in the rhs of (IV.3.16), the sum over

m shuld go from 1 to infinity instead of from zero to infinity. However, taking into account the fact that L_o^A has no non diagonal elements and irreducible contributions only have to be kept (no intermediate state equal to the vacuum of correlations), we may add the term $m = 0$.

To the expansion (IV.3.14) of $\phi(z)$ corresponds the following expansion of the operator ϖ as given by (IV.2.7):

$$\varpi(z) = 1 + \gamma\phi_1'(z) + \gamma^2\left[\phi_2'(z) + \frac{1}{2}\phi_1''(z)\phi_1(z) + \{\phi_1'(z)\}^2\right] + \ldots \tag{IV.3.17}$$

Hence, if we do not retain terms of higher order than γ^2, we have:

$$\frac{\partial\varphi(\underset{\sim}{V},t)}{\partial t} = -i\gamma\phi_1(0)\varphi(\underset{\sim}{V},t) - i\gamma^2\left[\phi_1'(0)\phi_1(0) + \phi_2(0)\right]\varphi(\underset{\sim}{V},t) \tag{IV.3.18}$$

We shall now discuss in details the various terms which appear in the rhs of (IV.3.18) and show how this equation reduces to a Fokker-Planck equation.

IV.4 - Study of the operator $\phi_1(0)$

This operator is the analytic continuation of the operator $\phi_1(z)$ given by (IV.3.1) for $z \to 0$. Using (II.12.14), for the canonical distribution for the fluid, we have :

$$\lim_{z\to 0} \sum_{m=1}^{\infty} \langle\{\underset{\sim}{k}_i\}\underset{\sim}{K}\left|\left(\frac{1}{z-L_o^f}\delta L^f\right)^m\right|0\rangle(\rho_o^f)_{equ.}$$

$$= (8\pi^3/\Omega)\int d\underset{\sim}{R}\, e^{-i\underset{\sim}{K}.\underset{\sim}{R}} \lim_{z\to 0} \sum_{m=1}^{\infty} \langle\{\underset{\sim}{k}_i\}\left|\left(\frac{1}{z-L_o^f}\delta L^f\right)^m\right|0\rangle(\rho_o^f)_{equ.} \tag{IV.4.1}$$

$$= (8\pi^3/\Omega) \int d\underset{\sim}{R}\ e^{-i\underset{\sim}{K}.\underset{\sim}{R}}\ \rho^{equ.}_{\{\underset{\sim}{k}_i\}}$$

where $\rho^{equ}_{\{\underset{\sim}{k}_i\}}$ is the Fourier coefficient of the complete equilibrium distribution function for the fluid :

$$\rho^{f}_{equ.} = \exp\left[-\frac{1}{kT}\left\{\sum_i \frac{mv_i^2}{2} + \sum_{i<j} V_{ij}(|\underset{\sim}{r}_i - \underset{\sim}{r}_j|) + \sum_i V_{iA}(|\underset{\sim}{R} - \underset{\sim}{r}_i|)\right\}\right] \times$$

(IV.4.2)
$$\left[\int \{d\underset{\sim}{r}\, d\underset{\sim}{p}\}^N \exp\left[-\frac{1}{kT}\left\{\sum_i (mv_i^2/2) + \sum_{i<j} V_{ij}(|\underset{\sim}{r}_i - \underset{\sim}{r}_j|) + \sum_i V_{iA}(|\underset{\sim}{r}_i - \underset{\sim}{R}|)\right\}\right]\right]^{-1}$$
$$= \exp\left[-\frac{1}{kT}\left(\sum_i (mv_i^2/2) + V^f\right)\right]\left[\int \{d\underset{\sim}{r}\, d\underset{\sim}{p}\}^N \exp\left[-\frac{1}{kT}\left(\sum_i \frac{mv_i^2}{2} + V^f\right)\right]\right]^{-1}$$

(IV.4.3)
$$\rho^{equ.}_{\{\underset{\sim}{k}_i\}} = \int \{d\underset{\sim}{r}\}^N \exp\left[-i \sum_i \underset{\sim}{k}_i . \underset{\sim}{r}_i\right] \rho^{f}_{equ.}$$

Introducing (IV.4.1) into (IV.3.6) for $z \to 0$, we obtain :

(IV.4.4)
$$\gamma \phi^{(0)}_I \sim \sum_{i=1} \sum_{\underset{\sim}{K}} \int \{d\underset{\sim}{v}\}^N \langle 0 | \delta L^A | \underset{\sim}{k}_i = -\underset{\sim}{K}, \underset{\sim}{K} \rangle \times$$
$$\times \int d\underset{\sim}{R}\ e^{-i\underset{\sim}{K}.\underset{\sim}{R}}\ \rho^{equ.}_{\underset{\sim}{k}_i = -\underset{\sim}{K}}$$

Now, we have :

(IV.4.5)
$$\langle 0 | \delta L^A | \underset{\sim}{k}_i = -\underset{\sim}{K}, \underset{\sim}{K} \rangle \int d\underset{\sim}{R}\ e^{-i\underset{\sim}{K}.\underset{\sim}{R}}\ \rho^{equ.}_{\underset{\sim}{k}_i}$$
$$= V_{\underset{\sim}{K}} \underset{\sim}{K} \cdot \frac{\partial}{\partial \underset{\sim}{P}} \int d\underset{\sim}{R}\ e^{-i\underset{\sim}{K}.\underset{\sim}{R}} \int \{d\underset{\sim}{r}\}^N\ e^{i\underset{\sim}{K}.\underset{\sim}{r}_i} \rho^{f}_{equ.}$$

Taking into account the fact that V_K is the Fourier transform of V_{iA}, we have :

(IV.4.6)
$$\sum_{\underset{\sim}{K}} V_{\underset{\sim}{K}}\ \underset{\sim}{K}\ e^{i\underset{\sim}{K}.(\underset{\sim}{R} - \underset{\sim}{r}_i)} \sim \frac{\partial V_{iA}(|\underset{\sim}{R} - \underset{\sim}{r}_i|)}{\partial \underset{\sim}{R}}$$

Therefore, we obtain :

$$\gamma \phi_1(0) \sim \int \{d\underset{\sim}{v} d\underset{\sim}{r}\}^N \, d\underset{\sim}{R} \; \frac{\partial \sum_i V_{iA}(|\underset{\sim}{R} - \underset{\sim}{r}_i|)}{\partial \underset{\sim}{R}} \rho^{f}_{equ} \cdot \frac{\partial}{\partial \underset{\sim}{P}}$$

(IV.4.7)
$$\sim \int d\underset{\sim}{R} \; \frac{\partial \int \{d\underset{\sim}{v} d\underset{\sim}{r}\}^N \rho_f^{equ.}}{\partial \underset{\sim}{R}} \cdot \frac{\partial}{\partial \underset{\sim}{P}} = 0$$

and the equation of evolution for the velocity distribution function of the brownian particle (IV.3.19) takes the simple form :

(IV.4.8)
$$\frac{\partial \varphi(\underset{\sim}{V}, t)}{\partial t} = -i\gamma^2 \phi_2(0) \, \varphi(\underset{\sim}{V}, t)$$

The first non vanishing effects are proportional to the mass ratio m/M .

IV.5 - Study of the operator $\phi_2(0)$

From (IV.3.1) and (IV.4.2), we obtain :

$$\gamma^2 \phi_2(0) = \gamma^2 \lim_{z \to 0} \sum_{i=1}^{N} \sum_{\underset{\sim}{K}} \sum_{\underset{\sim}{K}'} \sum_{\{\underset{\sim}{k}'\}} \langle 0 | \delta L^A | \underset{\sim}{k}_i = -\underset{\sim}{K}, \underset{\sim}{K} \rangle \times$$

(IV.5.1)
$$\int \{d\underset{\sim}{v}\}^N \langle \underset{\sim}{k}_i = -\underset{\sim}{K}, \underset{\sim}{K} | \sum_{n=0}^{\infty} \left(\frac{1}{z - L_o^f} \delta L^f \right)^n \frac{1}{z - L_o^f} (L_o^A + \delta L^A) | \{\underset{\sim}{k}'\} \; \underset{\sim}{K}' \rangle \times$$

$$\times \frac{1}{\Omega} \int d\underset{\sim}{R} \; e^{-i\underset{\sim}{K}' . \underset{\sim}{R}} \rho^{equ}_{\{\underset{\sim}{k}'\}}$$

Now, using :

(IV.5.2)
$$\int d\underset{\sim}{R} \; e^{-i\underset{\sim}{K}' . \underset{\sim}{R}} \rho^{equ.}_{\{\underset{\sim}{k}'\}} = \langle \{\underset{\sim}{k}'\} \; \underset{\sim}{K}' | \rho_f^{equ} | 0 \rangle \, \Omega^{N+1} \times$$

(IV.5.3)
$$\times \sum_{n=0}^{\infty} \left(\frac{1}{z - L_o^f} \delta L^f \right)^n \frac{1}{z - L_o^f} = \frac{1}{z - L_o^f - \delta L^f}$$

and performing the summations over $\{\underset{\sim}{k}'\}$, $\underset{\sim}{K}'$, $\underset{\sim}{K}$, we obtain :

$$\gamma^2 \phi_2(0) = \gamma^2 \lim_{z \to 0} (\Omega)^{-1} \int \{d\underset{\sim}{r}\}^N \, d\underset{\sim}{R} \{\delta L^A \int \{d\underset{\sim}{v}\}^N \frac{1}{z - L_o^f - \delta L^f} \times$$

$$\times (L_o^A + \delta L^A)\ \rho^f_{equ.} \tag{IV.5.4}$$

Using the explicit forms of L_o^A and δL^A, this becomes :

$$\gamma^2 \phi_2^{(0)} = (\Omega)^{-1} \lim_{z\to 0} \int \{d\underset{\sim}{r}\}^N d\underset{\sim}{R} \lambda \frac{\partial \sum_i V_{iA}(|\underset{\sim}{R}-\underset{\sim}{r}_i|)}{\partial \underset{\sim}{R}} \cdot \frac{\partial}{\partial \underset{\sim}{P}} \times$$

$$\times \int \{d\underset{\sim}{v}\}^N \frac{1}{z - L_o^f - \delta L^f} \left[-\underset{\sim}{V} \cdot \frac{\partial}{\partial \underset{\sim}{R}} + \lambda \frac{\partial \sum_i V_{iA}(|\underset{\sim}{R}-\underset{\sim}{r}_i|)}{\partial \underset{\sim}{R}} \cdot \frac{\partial}{\partial \underset{\sim}{P}} \right] \rho^f_{equ.} \tag{IV.5.5}$$

Using the explicit form of $\rho^f_{equ.}$ (see IV.2.2), we obtain easily :

$$\gamma^2 \phi_2^{(0)} = \Omega^{-1} \lim_{z\to 0} \int \{d\underset{\sim}{r}\}^N d\underset{\sim}{R} \frac{\partial \sum_i V_{iA}(|\underset{\sim}{R}-\underset{\sim}{r}_i|)}{\partial \underset{\sim}{R}} \cdot \frac{\partial}{\partial \underset{\sim}{P}} \times$$

$$\times \int \{d\underset{\sim}{v}\}^N \frac{1}{z - L_o^f - \delta L^f} \frac{\partial \sum_i V_{iA}(|\underset{\sim}{R}-\underset{\sim}{r}_i|)}{\partial \underset{\sim}{R}} \cdot \left(\frac{\partial}{\partial \underset{\sim}{P}} + \frac{1}{kT} \underset{\sim}{V}\right) \rho^f_{equ.} \tag{IV.5.6}$$

Let us introducing the diffusion coefficient :

$$D_{ij} = \Omega^{-1} \int \{d\underset{\sim}{v}\, d\underset{\sim}{r}\}^N d\underset{\sim}{R}\ F_i(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \times$$

$$\times \lim_{z\to 0} \frac{1}{z - L_o^f - \delta L^f} F_j(\underset{\sim}{R}, \{\underset{\sim}{r}\})\ \rho^f_{equ.} \tag{IV.5.7}$$

where

$$F_1(\underset{\sim}{R}, \{\underset{\sim}{r}\}) = \lambda \frac{\partial \sum_i V_{iA}(|\underset{\sim}{R}-\underset{\sim}{r}_i|)}{\partial R_1} \tag{IV.5.8}$$

is the total force exerted by the fluid on the Brownian particle; the operator $\phi_2^{(0)}$ becomes :

$$\gamma^2 \phi_2^{(0)} = D_{ij} \frac{\partial}{\partial P_i} \left(\frac{\partial}{\partial P_j} + \frac{1}{kT} V_j\right) \tag{IV.5.9}$$

The evolution equation (IV.4.8) may thus be written :

$$\text{(IV.5.10)} \qquad \frac{\partial \varphi(\underset{\sim}{V}, t)}{\partial t} = D_{ij} \frac{\partial}{\partial P_i} \left(\frac{\partial}{\partial P_j} + \frac{1}{kT} V_j \right) \varphi(\underset{\sim}{V}, t)$$

This is indeed an equation of the Fokker-Planck type. An explicit expression in terms of microscopic quantities is now obtained for the diffusion coefficient.

IV.6 - Diffusion coefficient.

Taking into account :

$$\text{(IV.6.1)} \qquad -i \lim_{z \to 0} \frac{1}{z - L_o^f - \delta L^f} = \lim_{z \to 0} \int_o^\infty dt \exp \left[-i (L_o^f + L^f - z) t \right]$$

the diffusion coefficient may be written as :

$$\text{(IV.6.2)} \qquad D_{ij} = \lim_{z \to 0} \int_o^\infty dt \, (\Omega)^{-1} \int \{ d\underset{\sim}{r} d\underset{\sim}{v} \}^N \, d\underset{\sim}{R} \; F_i(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \times$$
$$\times \exp \left[-i (L_o^f + \delta L^f - z) t \right] F_j(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \, \rho^f_{equ.}$$

Taking into account :

$$\text{(IV.6.3)} \qquad L^f \rho^f_{equ.} = (L_o^f + \delta L^f) \rho^f_{equ.} = 0$$

and the fact that the integrand is a function of relative distances only, we obtain :

$$\text{(IV.6.4)} \qquad D_{\alpha\beta} = \lim_{z \to 0} \int_o^\infty dt \int \{ d\underset{\sim}{v} \, d\underset{\sim}{r} \}^N \, \rho^f_{equ.} \; F_\alpha(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \times$$
$$\times \exp \left[-i (L^f - z) t \right] F_\beta(\underset{\sim}{R}, \{\underset{\sim}{r}\})$$
$$= \lim_{z \to 0} \int_o^\infty dt \left\langle F_\alpha(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \exp \left[-i (L^f - z) t \right] F_\beta(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \right\rangle$$

The diffusion coefficient is thus the average value over the fluid equili-

brium distribution of the time autocorrelation function of the force acting on the brownian particle for a fixed position of the brownian particle.

As an example, let us compute this coefficient in the case of a weakly coupled system. Then we have :

$$L^f \rightarrow L_o^f \tag{IV.6.5}$$

$$\rho^f_{equ.} = (m/2\pi kT)^{3N/2} (4\pi)^{3N} \exp\left[- \sum_1 \frac{mv_1^2}{2kT} \right] \Omega^{-N} \tag{IV.6.6}$$

Expanding the interaction potential in a Fourier series, we obtain :

$$D_{\alpha\beta} = -\lambda^2 (\Omega)^{-N} \sum_{i,j=1}^{N} \lim_{z \to 0} \int_o^\infty dt \int \{ d\underset{\sim}{r} d\underset{\sim}{v} \}^N (m/2\pi kT)^{3N/2}$$

$$(4\pi)^{3N} \exp\left[- \sum_1 mv_1^2/2kT \right] \int d^3k \int d^3k' \, V_k \, V_{k'} k_\alpha k'_\beta \, e^{i\underset{\sim}{k}.(\underset{\sim}{r}_i - \underset{\sim}{R})} \tag{IV.6.7}$$

$$e^{-i(L_o^f - z)t} \, e^{i\underset{\sim}{k}'.(\underset{\sim}{r}_j - \underset{\sim}{R})}$$

Now, we have :

$$e^{-iL_o^f t} \, e^{i\underset{\sim}{k}'.\underset{\sim}{r}_j} = e^{i\underset{\sim}{k}'.(\underset{\sim}{r}_j - \underset{\sim}{v}_j t)} \tag{IV.6.8}$$

With :

$$\int d\underset{\sim}{r}_i \, e^{i\underset{\sim}{k}.\underset{\sim}{r}_i} = 8\pi^3 \delta(\underset{\sim}{k}) \tag{IV.6.9}$$

we verify easily that the only terms which contribute are those for which $i = j$. This result is of course quite obvious . Indeed, the only contributions to the evolution equation are those of diagonal diagrams, in which each particle must appear at least at two vertices. In the weakly coupled case, we only have to consider the cycle and have the-

refore only one fluid particle involved.

Therefore, with $\int d\underset{\sim}{r}_i \; e^{i(\underset{\sim}{k}+\underset{\sim}{k}').\underset{\sim}{r}_i} = 8\pi^3 \delta(\underset{\sim}{k}+\underset{\sim}{k}')$ (IV.ω.10)

we have :

$$D_{\alpha\beta} = 32\pi^4\lambda^2 C(m/2\pi kT)^{3/2} \lim_{z\to 0} \int_0^\infty dt \int d\underset{\sim}{v} \exp(-mv^2/2kT) \times$$

(IV.6.11)

$$\times \int d^3k \, |V_k|^2 \, k_\alpha k_\beta \, e^{i\underset{\sim}{k}.\underset{\sim}{v}t} \, e^{izt}$$

We also have :

$$\lim_{z\to 0} \int_0^\infty dt \; e^{i(\underset{\sim}{k}.\underset{\sim}{v} + z)t} = \pi\delta(\underset{\sim}{k}.\underset{\sim}{v}) + i \, P(1/\underset{\sim}{k}.\underset{\sim}{v}) \qquad \text{(IV.6.12)}$$

As the remaining part of the integrand in (IV.6.11) is an even function of $\underset{\sim}{k}$, the contribution involving the principal part vanishes and we are left with :

$$D_{\alpha\beta} = 32\pi^5\lambda^2 C(m/2\pi kT)^{3/2} \int d\underset{\sim}{v} \exp(-mv^2/2kT) \int d^3k \, |V_k|^2 \, k_\alpha k_\beta \times$$

(IV.6.13)

$$\times \delta(\underset{\sim}{k}.\underset{\sim}{v})$$

One verifies easily that one has :

$$\int d^3k \, |V_k|^2 \, k_\alpha k_\beta \delta(\underset{\sim}{k}.\underset{\sim}{v}) = \delta_{\alpha,\beta} \, (\pi B/v)\left[1 - \frac{(\underset{\sim}{1}.\underset{\sim}{v})^2}{v^2}\right] \qquad \text{(IV.6.14)}$$

where $\underset{\sim}{1} = (1_x, 1_y, 1_z)$ is the unit vector and B is given by (III.4.5) .

Performing the $\underset{\sim}{v}$ integration, one obtains :

$$D_{\alpha\beta} = \delta_{\alpha,\beta} \, 32\pi^6 \lambda^2 C(m/2kT)^{1/2}(4/3\sqrt{\pi}) \qquad \text{(IV.6.15)}$$

One verifies easily that with this value of the diffusion coefficient, the evolution equation (IV.5.10) is indeed identical with the particular Fokker-Planck equation (III.6.14) we obtained for a heavy particle moving with thermal velocity and weakly coupled to the fluid.

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V. BROWNIAN MOTION OF A HEAVY PARTICLE IN AN EXTERNAL FIELD

V.1 - Introduction .

We shall again consider the problem of a heavy particle moving in a fluid at thermal equilibrium. However, now we shall assume that the brownian particle is charged and that at $t = 0$, we switch on an external constant electrical field. The fluid particles are neutral and are not influenced by that field. After a long time, we shall reach a stationary state for the velocity distribution function of the brownian particle, corresponding to a balance between the effect of the external acceleration and the scattering by the fluid particles.

Our starting point for the discussion of this stationary state will be the transport equation (II.14.5). Here again, we shall show that, when only lowest order terms in the mass ratio are kept, the equation for the stationary state is in agreément with that of the stochastic theory. The calculations which have been performed originally by Résibois and Davis[1] will be closely parallel to that of the preceding chapter and we shall go over them very briefly and rather concentrate ourselves on a discussion of higher order corrections. First, we have corrections to the collision terms which are independent of the external field and introduce fourth order differential operators in the equation of evolution. Then , we also have corrections which take into account the effect of the field during a collision. We shall show that these corrections may formally be incorporated in the Fokker-Planck collision operator.

These results are in agreement with those obtained through a rather different method by Lebowitz and Rubin[2] . In order to make connection with this work , we shall show how the transport equation for this parti-

cular problem can be recast in another form, which is precisely that used as a starting point for the m/M expansion in Lebowitz and Rubin. This point has been discussed in great detail in a paper by Lebowitz and Résibois[3].

V.2 - Steady state equation for the velocity distribution function of the brownian particle.

In chapter II, § 14, we have obtained the linearized steady state equation (II.14.5) for the velocity distribution function of a system of charged particles submitted to the action of an external electrical field. We have assumed that at t=0 the system was in equilibrium and that the field was switched on only at t=0. Keeping only terms linear in E and restricting ourselves to the static case, we obtain :

$$(V.2.1)\quad iL_E \rho_o^{equ.} + \sum_{\{k\}} D_{\{k\}}(0)\, iL_E\, C_{\{k\}}(0)\, \rho_o^{equ} = i\psi(0)\Delta\rho_o^{st.}$$

where we have used (II.13.18) to rewrite the second term in the lhs of (II.14.5) as an operator acting on ρ_o .

As the brownian particle is the only charged particle we have here :

$$(V.2.2)\qquad iL_E = e\,\underset{\sim}{E}\cdot\frac{\partial}{\partial \underset{\sim}{P}}$$

instead of (II.13.3) .

In (V.2.1) , ρ_o^{equ} is the velocity equilibrium distribution for the whole system :fluid and brownian particle

$$(V.2.3)\qquad \rho_o^{equ} = \varphi^{equ}(\underset{\sim}{V})\prod_i^N \varphi^{equ}(\underset{\sim}{v}_i)$$

$$(V.2.4) \qquad \varphi^{equ}(\underset{\sim}{v}_i) = 4\pi (m/2\pi kT)^{3/2} \exp(-mv_i^2/2kT)$$

$$(V.2.5) \qquad \varphi^{equ}(\underset{\sim}{V}) = 4\pi (M/2\pi kT)^{3/2} \exp(-MV^2/2kT)$$

$\Delta\rho_o^{st}$ is the linear (in E) correction to ρ_o^{equ} . As previously, we assume molecular chaos for the velocity distribution function. Therefore, we have :

$$\Delta\rho_o^{st} = \delta\varphi(\underset{\sim}{V}) \prod_i^N \varphi^{equ}(\underset{\sim}{v}_i) + \sum_{i=1}^N \delta\varphi(\underset{\sim}{v}_i) \prod_{j\neq i}^N \varphi^{equ}(\underset{\sim}{v}_j)\, \varphi^{equ}(\underset{\sim}{V}) \qquad (V.2.6)$$

Therefore, (V.2.1) becomes :

$$\prod_i^N \varphi^{equ}(\underset{\sim}{v}_i)\, e\underset{\sim}{E}\cdot\frac{\partial\varphi^{equ}(\underset{\sim}{V})}{\partial\underset{\sim}{P}} + \sum_{\{\underset{\sim}{k}\}} D_{\{\underset{\sim}{k}\}}(0) iL_E C_{\{\underset{\sim}{k}\}}(0) \prod_i^N \varphi^{equ}(\underset{\sim}{v}_i)\, \varphi^{equ}(\underset{\sim}{V})$$

$$= i\psi(0)\delta\varphi(\underset{\sim}{V}) \prod_i^N \varphi^{equ}(\underset{\sim}{v}_i) + \sum_{i=1}^N i\psi(0)\delta\varphi(\underset{\sim}{v}_i) \prod_{j\neq i}^N \varphi^{equ}(\underset{\sim}{v}_j)\, \varphi^{equ}(\underset{\sim}{V}) \qquad (V.2.7)$$

Integrating this equation, first over the velocities of all the fluid particles, secondly over the velocity of the brownian particle and the velocities of all but one of the fluid particles, one obtains easily a set of coupled equations for the two unknown functions $\delta\varphi(\underset{\sim}{V})$ and $\delta\varphi(\underset{\sim}{v}_i)$. However, it can be proved [1] that, once terms of order $1/N$ are neglected the velocity distribution function of a fluid particle remains at equilibrium in the stationary case :

$$(V.2.8) \qquad \delta\varphi(\underset{\sim}{v}_i) = 0(1/N) \to 0$$

We shall not prove this here but it is a consequence of the fact that the probability of a given particle to interact with the single heavy par-

cle is quite negligible in the limit of an infinite system. This allows us to neglect all vertices involving A and a fluid particle in the operators $D_{\{k\}}$, $C_{\{k\}}$ and ψ once we integrate over $\underset{\sim}{V}, \underset{\sim}{v}_2 \ldots \underset{\sim}{v}_N$. The equation for $\delta\varphi(\underset{\sim}{v}_1)$ then simplifies a great deal and using arguments similar to those which allowed us to establish the $\mathcal{H}$-theorem in chapter II, § 11 it is easy to show that (V.2.8) is its only solution.

Taking into account (V.2.8), the evolution equation (V.2.7) becomes :

$$\prod_i^N \varphi^{equ}(\underset{\sim}{v}_i)\, e\,\underset{\sim}{E} \cdot \frac{\partial \varphi^{equ}(\underset{\sim}{V})}{\partial \underset{\sim}{P}}$$

$$+ \sum_{\{\underset{\sim}{k}\}} D_{\{\underset{\sim}{k}\}}(0)\; e\underset{\sim}{E} \cdot \frac{\partial}{\partial \underset{\sim}{P}}\, C_{\{\underset{\sim}{k}\}}(0) \prod_i^N \varphi^{equ}(\underset{\sim}{v}_i)\varphi^{equ}(\underset{\sim}{V}) \tag{V.2.9}$$

$$= i\,\psi(0)\,\delta\varphi(\underset{\sim}{V})\; \prod_i^N \varphi^{equ}(\underset{\sim}{v}_i)$$

After integration over the velocities of the fluid particles, we obtain :

$$e\underset{\sim}{E} \cdot \frac{\partial \varphi^{equ}(\underset{\sim}{V})}{\partial P} + \Xi\,(0)\; \varphi^{equ}(\underset{\sim}{V}) = i\phi(0)\delta\varphi(\underset{\sim}{V}) \tag{V.2.10}$$

where

$$\phi(0) = \int \{d\underset{\sim}{v}\}^N \psi(0) \prod_i^N \varphi^{equ}(\underset{\sim}{v}_i) \tag{V.2.11}$$

$$\Xi(0) = \sum_{\{\underset{\sim}{k}\}} \int \{d\underset{\sim}{v}\}^N D_{\{\underset{\sim}{k}\}}(0)\, e\underset{\sim}{E} \cdot \frac{\partial}{\partial \underset{\sim}{P}}\, C_{\{\underset{\sim}{k}\}}(0) \prod_i^N \varphi^{equ}(\underset{\sim}{v}_i) \tag{V.2.12}$$

The operator $\phi(0)$ is identical to the operator $\phi(0)$ given by (IV.2.5)

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V.3 - Expansion in the mass ratio .

Here again, we write :

$$L_o = L_o^f + \gamma L_o^A \tag{V.3.1}$$

$$\delta L = \delta L^f + \gamma \delta L^A \tag{V.3.2}$$

$$e\underset{\sim}{E}.\frac{\partial}{\partial \underset{\sim}{P}} = \gamma L_E \tag{V.3.3}$$

where the fluid operators $L_o^f, \delta L^f$ are given by (IV.3.7) and (IV.3.10) respectively while the particle operators γL_o^A and $\gamma \delta L^A$ are given by (IV.3.8) and (IV.3.11) .

We also expand the operators $\phi(0)$ and $\Xi(0)$:

$$\phi(0) = \gamma \phi^{(1)}(0) + \gamma^2 \phi^{(2)}(0) + \ldots \tag{V.3.4}$$

$$\Xi(0) = \gamma \Xi^{(1)}(0) + \gamma^2 \Xi^{(2)}(0) + \ldots \tag{V.3.5}$$

The zero order term (γ^o) of ϕ vanishes as we have seen in chapter IV. The zero order term of $\Xi(0)$ vanishes because this operator involves the external field operator which is of order γ .

Up to order γ^4, we therefore obtain the following equation of evolution :

$$iL_E \varphi^{equ}(\underset{\sim}{V}) + \left[\gamma \Xi^{(1)}(0) + \gamma^2 \Xi^{(2)}(0) + \gamma^3 \Xi^{(3)}(0) + \gamma^4 \Xi^{(4)}(0)\right] \varphi^{equ}(V) = i\left[\gamma \phi^{(1)}(0) + \gamma^2 \phi^{(2)}(0) + \gamma^3 \phi^{(3)}(0) + \gamma^4 \phi^{(4)}(0)\right] \delta\varphi(\underset{\sim}{V}) . \tag{V.6}$$

In chapter IV, §§ 4 and 5, we have shown :

$$\Phi^{(1)}(0) = 0 \tag{V.3.7}$$

$$i\gamma^2 \Phi^{(2)}(0) = D_{ij} \frac{\partial}{\partial P_i} \left(\frac{\partial}{\partial P_j} + \frac{1}{kT} V_j\right) \tag{V.3.8}$$

where the diffusion coefficient is given by (IV.5.7) . An alternative expression in terms of the average autocorrelation function of the force exerted by the fluid over the fixed brownian particle is given in (IV.6.4) . As to the interference term between the flow and the collision, it is again easy to show that :

$$\Xi^{(1)}(0) = \Xi^{(2)}(0) = 0 \tag{V.3.9}$$

Indeed the term of order γ in the rhs of (V.2.12) is

$$\gamma \Xi^{(1)}(0) = \gamma \sum_{\{k\}} \int \{dv\}^N D^{(0)}_{\{k\}}(0)\ iL_E\ C^{(0)}_{\{k\}}(0) \prod_i^N \varphi^{equ}(v_i) \tag{V.3.10}$$

where $D^{(0)}_{\{k\}}(0)$ and $C^{(0)}_{\{k\}}(0)$ are the terms independent of γ of the destruction and creation operators :

$$D^{(0)}_{\{k\}}(z) = \sum_{n=1}^{\infty} \langle 0 | \left(\delta L^f \frac{1}{z - L^f_o}\right)^n | \{k\} \rangle \tag{V.3.11}$$

$$C^{(0)}_{\{k\}}(z) = \sum_{n=1}^{\infty} \langle \{k\} | \left(\frac{1}{z - L^f_o} \delta L^f\right)^n | 0 \rangle \tag{V.3.12}$$

Taking into account :

$$\int \{dv\}^N \delta L^f \ldots = 0 \tag{V.3.13}$$

we easily verify (V.3.9) for the operator $\Xi^{(1)}(0)$.

As to the operator $\Xi^{(2)}(0)$, we have :

$$\gamma^2 \Xi^{(2)}(0) = \gamma^2 \sum_{\{\underset{\sim}{k}\}} \int \{d\underset{\sim}{v}\}^N D^{(1)}_{\{\underset{\sim}{k}\}}(0)\ iL_E C^{(0)}_{\{\underset{\sim}{k}\}}(0) \prod_i \varphi^{equ}(\underset{\sim}{v}_i)$$

(V.3.14)
$$+ \gamma^2 \sum_{\{\underset{\sim}{k}\}} \int \{d\underset{\sim}{v}\}^N D^{(0)}_{\{\underset{\sim}{k}\}}(0)\ iL_E C^{(1)}_{\{\underset{\sim}{k}\}}(0) \prod_i \varphi^{equ}(\underset{\sim}{v}_i)$$

Using the same argument as above on the structure of $D^{(0)}_{\{\underset{\sim}{k}\}}(0)$, it is easy to show that the second term in the rhs vanishes . As to the first term, we have :

$$\gamma D^{(1)}_{\{\underset{\sim}{k}\}}(z) = \sum_{n=0}^{\infty} \langle 0 | \delta L^A \frac{1}{z - L^f_o} \left(\delta L^f \frac{1}{z - L^f_o} \right)^n | \{\underset{\sim}{k}\} \rangle$$

(V.3.15)
$$+ \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} \langle 0 | \left(\delta L^f \frac{1}{z - L^f_o} \right)^n \left(\delta L^A + L^A_o \right) \frac{1}{z - L^f_o} \left(\delta L^f \frac{1}{z - L^f_o} \right)^m | \{k\} \rangle$$

Again the second term gives a vanishing contribution when we integrate over the velocities. Therefore, we have :

$$\gamma^2 \Xi^{(2)}(z) = \gamma^2 \sum_{n=0}^{\infty} \sum_{m=1}^{\infty} \sum_{\{\underset{\sim}{k}\}} \int \{d\underset{\sim}{v}\}^N \langle 0 | \delta L^A \frac{1}{z - L^f_o} \times$$

(V.3.16)
$$\times \left(\delta L^f \frac{1}{z - L^f_o} \right)^n | \{k\} \rangle\ iL_E \langle \{\underset{\sim}{k}\} | \left(\frac{1}{z - L^f_o} \delta L^f \right)^m | 0 \rangle \prod_i \varphi^{equ}(\underset{\sim}{v}_i)$$

Now, using (IV.4.1) , (IV.5.2) and (IV.5.3) , we easily obtain :

(V.3.17)
$$\gamma^2 \Xi^{(2)}(z) = \gamma^2 \int \{d\underset{\sim}{v}\}^N \langle 0 | \delta L^A \frac{1}{z - L^f_o - \delta L^f} \rho^f_{equ} | 0 \rangle\ iL_E$$

From (IV.3.11) , (IV.6.3) and (IV.4.2) , we easily obtain :

$$(V.3.18)\qquad \gamma^2\,\Xi^{(2)}(z) = \gamma^2\,(1/z)\int dr\,dv\; f^N \frac{\partial \sum_i V_{iA}(|r_i - R|)}{\partial R}\cdot\frac{\partial}{\partial P} f^f_{equ} = 0$$

(see (IV.4.7)).

Therefore, if we restrict ourselves to terms of order m/M, we easily recover the stationary Fokker-Planck equation in presence of an external field acting on the heavy particle :

$$(V.3.19)\qquad eE\cdot\frac{\partial}{\partial P}\,(V) = D_{ij}\frac{\partial}{\partial P_i}\left(\frac{\partial}{\partial P_j} + \frac{1}{kT}\,V_j\right)\delta\varphi(V)$$

The diffusion coefficient is not affected by the presence of the external field.

V.4 - Higher order corrections to the collision operator. Role of the irreducibility condition.

The γ^3 and γ^4 contributions are respectively :

$$\gamma^3\,\phi^{(3)}(0) = \lim_{z\to 0}\gamma^3 \sum_{n=0}^{\infty}\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\int dv\, f^N \langle 0|\,\delta L^A$$

$$(V.4.1)\qquad \frac{1}{z-L_o^f}\left(L^f\,\frac{1}{z-L_o^f}\right)^n (L_A^o + \delta L^A)\,\frac{1}{z-L_o^f}\,(\delta L^f\,\frac{1}{z-L_o^f})^p\,(L_o^A + \delta L^A)$$

$$(\frac{1}{z-L_o^f}\,\delta L^f)^q\,|0\rangle_{irr}\prod_i \varphi^{equ}(v_i)$$

$$\gamma^4\,\phi^{(4)}(0) = \lim_{z\to 0}\gamma^4 \sum_{n=0}^{\infty}\sum_{m=0}^{\infty}\sum_{p=0}^{\infty}\sum_{q=0}^{\infty}\int dv\, f^N \langle 0|\delta L^A$$

$$\frac{1}{z-L_o^f}\,(\delta L^f\,\frac{1}{z-L_o^f})^n\,(L_o^A + \delta L^A)\quad\frac{1}{z-L_o^f}\left(\delta L^f\,\frac{1}{z-L_o^f}\right)^m (L_o^A + \delta L^A)\times$$

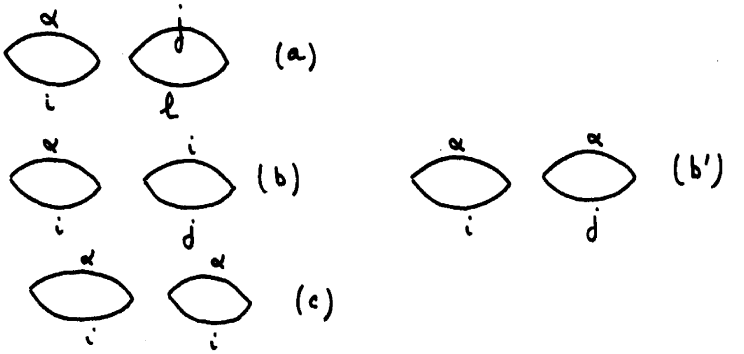
$$(V.4.2)\quad \times \frac{1}{z-L_o^f}\left(\delta L^f \frac{1}{z-L_o^f}\right)^p \left(L_o^A + \delta L^A\right)\left(\frac{1}{z-L_o^f}\delta L^f\right)^q |0\rangle_{irr} \times$$

$$\times \prod_i \varphi^{equ}(v_{\sim i})$$

The first point we want to discuss here is the role played by the irreducibility condition. To do this, we will need a theorem first established by Balescu [4] :

If we have a succession of diagonal fragments, the only contributions to the reduced distribution function of particle α which do not vanish at the limit of an infinite system are those where the diagonal fragments are semi-connected, i.e. where they have a single particle in common with the preceding diagonal fragments.

We shall not prove this theorem in full generality but illustrate it on an example . Let us consider a succession of two cycles: we have three cases (see fig. V.4.1)



Possible connections in a succession of two cycles.

Fig. V.4.1

1) they are disconnected : no particle in common (a)

2) they are semi-connected : one particle in common (b) , (b') .

3) they have two particles in common (c) .

Because of the integration over the velocities of all particles but α, α must necessarily appear at the first vertex on the left. We obtain :

$$(a) = \sum_{ij} \int \{dv\}^{N-1} \langle 0 | \delta L^{\alpha i} | \underset{\sim}{k}_\alpha, \underset{\sim}{k}_i = -\underset{\sim}{k}_\alpha \rangle \langle \underset{\sim}{k}_\alpha, \underset{\sim}{k}_i = -\underset{\sim}{k}_\alpha | \delta L^{\alpha i} | 0 \rangle$$

$$(V.4.1) \quad \langle 0 | \delta L^{jl} | \underset{\sim}{k}_j, \underset{\sim}{k}_l = -\underset{\sim}{k}_j \rangle \langle \underset{\sim}{k}_j, \underset{\sim}{k}_l = -\underset{\sim}{k}_j | \delta L^{jl} | 0 \rangle \rho_o(0)$$

Now, the integrations over $\underset{\sim}{v}_j$ and $\underset{\sim}{v}_l$ commute with the first two matrix elements. Therefore, we have :

$$(a) \sim \int d\underset{\sim}{v}_j \, d\underset{\sim}{v}_l \, \delta L^{jl} \ldots = 0$$

This argument may easily be generalized to more complicated fragments and successions of more than two fragments; whenever there is at least two disconnected fragments, the contribution to the reduced distribution function vanishes.

Let us now consider the case of the semi-connected diagrams (b) and (b'). We have :

$$(b) + (b') = \sum_{ij} \int \{dv\}^{N-1} \langle 0 | \delta L^{i\alpha} | \underset{\sim}{k}_i = -\underset{\sim}{k}_\alpha, \underset{\sim}{k}_\alpha \rangle$$

$$\langle \underset{\sim}{k}_i = -\underset{\sim}{k}_\alpha, \underset{\sim}{k}_\alpha | \delta L^{i\alpha} | 0 \rangle \{ \langle 0 | \delta L^{ij} | \underset{\sim}{k}'_i, \underset{\sim}{k}_j = -\underset{\sim}{k}'_i \rangle$$

$$(V.4.3) \quad \langle \underset{\sim}{k}'_i, \underset{\sim}{k}_j = -\underset{\sim}{k}'_i | \delta L^{ij} | 0 \rangle + \langle 0 | \delta L^{\alpha j} | \underset{\sim}{k}'_\alpha, \underset{\sim}{k}_j = -\underset{\sim}{k}'_\alpha \rangle$$

$$\langle \underset{\sim}{k}'_\alpha, \underset{\sim}{k}_j = -\underset{\sim}{k}'_\alpha | \delta L^{\alpha j} | 0 \rangle$$

It is easily verified that none of these contributions vanishes; indeed, in the first case, the integral over $\underset{\sim}{v}_i$ does no longer commute with the first two matrix elements; in the second case the contribution proportional to $\partial / \partial \underset{\sim}{v}_\alpha$ of $\delta L^{\alpha j}$ in the third matrix element is non vanishing. As we have already seen ((II.6.6)), the contribution of each cycle is proportional to Ω^{-1}; because of the double summation over i and j, we obtain a contribution proportional to C^2. Such diagrams correspond indeed to those described by the above theorem.

As to (c), we may repeat the arguments for (b) or (b'); each cycle is proportional to Ω^{-1}; however, we only have one summation over i; hence we obtain a contribution proportional to C/Ω, which vanishes for $\Omega \to \infty$.

Let us now suppress the irreducibility condition in the operator $\Phi(0)$ and discuss the error introduced in this way. We consider a given contribution to $\Phi(0)$ with m vertices :

$$\Phi^{(m)} = \int |d\underset{\sim}{v}|^N \langle 0 | \delta L^A \left(\frac{1}{z-L_o} \delta L\right)^m | 0 \rangle_{irr} \prod_i \varphi^{equ}(\underset{\sim}{v}_i) \tag{V.4.4}$$

and suppress the irreducibility condition on a given intermediate state (say after r vertices). In this way, we add to $\Phi^{(m)}$ the following contribution :

$$\alpha = \gamma \int |d\underset{\sim}{v}|^N \langle 0 | \delta L^A \left(\frac{1}{z-L_o} \delta L\right)^{m-r} | 0 \rangle_{irr} \times$$
$$\times \langle 0 | \left(\frac{1}{z-L_o} \delta L\right)^r | 0 \rangle_{irr} \prod_i \varphi^{equ}(v_i) \tag{V.4.5}$$

As we have seen such a contribution will be different from zero in the limit of a large system only if the two diagonal fragments are semi-connected. We have two cases :

a) the semi-connection is through one fluid particle; but, then, A does not appear in the last fragment on the right and we have :

$$\langle 0 | \left(\frac{1}{z-L_o} \delta L\right)^r | 0 \rangle \prod_i \varphi^{equ}(v_i)$$
$$= \langle 0 | \left(\frac{1}{z-L_o^f} \delta L^{f,r}\right) | 0 \rangle \prod_i \varphi^{equ}(\underset{\sim}{v}_i) = 0 \tag{V.4.6}$$

if we take into account (II.11.10).

b) the semi connection is through particle A. Then, all the fluid particles in the first fragment are different from those in the last and because of the integration over the velocities of the fluid particles, the first vertex in the second fragment must necessarily involve A ; hence :

$$\alpha = \gamma \int \{dv\}^{N-s} \langle 0 | \delta L^A \left(\frac{1}{z-L_o} \delta L\right)^{m-r} | 0 \rangle_{irr} \frac{1}{z} \times$$

(V.4.7)

$$\times \int \{dv\}^{s} \langle 0 | \delta L^A \left(\frac{1}{z-L_o} \delta L\right)^{r-1} | 0 \rangle_{irr} \prod_i \varphi^{equ}(\underset{\sim}{v}_i)$$

if $\int \{dv\}^s = \int d\underset{\sim}{v}_{i_1} \ldots d\underset{\sim}{v}_{i_s}$, where $i_1 \ldots i_s$ are the fluid particles involved in the second fragment. We easily recognize that the second contribution is a contribution to the operator Φ given by (IV.3.13). As we have seen, the first non-vanishing contribution is of order γ^2 and we have:

$$\alpha = \gamma \int \{dv\}^{N-s} \langle 0 | \delta L^A \left(\frac{1}{z-L_o} \delta L\right)^{m-r} | 0 \rangle_{irr} \left[\varphi^{equ}(\underset{\sim}{v})\right]^{N-s} \times$$

(V.4.8)

$$\times \gamma^2 \frac{1}{z} \int \{dv\}^{s} \langle 0 | \delta L^A \left(\frac{1}{z-L_o} \delta L\right)^{r-1} | 0 \rangle_{irr} \left[\varphi^{equ}(\underset{\sim}{v})\right]^{s}$$

With the same kind of arguments, it is again easy to convince oneself that the fragement on the left is also of order γ^2 at least. Thus, if we supress the irreducibility condition in the operator $\Phi(0)$, we add a contribution of at least order four in γ. The contribution of order γ^4 which we add is:

$$\alpha = \gamma^4 \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \int \{dv\}^{N} \langle 0 | \delta L^A \frac{1}{z-L_f^o} \left(\delta L^f \frac{1}{z-L_f^o}\right)^m \times$$

(V.4.9)

$$\times \left(\delta L^A + L_o^A\right) \frac{1}{z-L_o^f} \left(\delta L^f \frac{1}{z-L_f^o}\right)^n | 0 \rangle_{irr} \langle 0 | \delta L^A \frac{1}{z-L_o^f} \left(\delta L^f \frac{1}{z-L_o^f}\right)^p \times$$

$$\times \left(\delta L^A + L_o^A\right) \left(\frac{1}{z-L_o^f} \delta L^f\right)^q | 0 \rangle_{irr} \prod_i \varphi^{equ}(\underset{\sim}{v}_i)$$

As a conclusion, we may suppress the irreducibility condition in $\Phi^{(3)}(0)$. If we suppress it (which will appear convenient below) in $\Phi^{(4)}(0)$, we have to subtract the contribution (V.4.9). Because of the factor $1/z$, we easily notice that this contribution will diverge at the limit $z \to 0$.

This is easy to understand. Indeed, a product of two irreducible diagonal fragments brings a factor t^2 in the formal solution of the Liouville equation as compared with the single t factor brought by one irreducible fragment. In the long time limit, the first one diverges. The role of the irreducibility condition in $\Psi(z)$ is precisely to suppress such contributions. This is well-known in the discussion of the three-body problem [5]. The operator $\Psi(z)$ brings in the evolution equation only the contributions of genuine three-body collisions, i.e. of those collisions where the three particles interact almost simultaneously (i e. on a time scale of the order of the binary collision time). The suppression of the irreducibility condition would amount to the inclusion of those three body processes which are a succession of 2 two binary collisions and would introduce a divergence. However, it is often convenient to write $\Psi(z)$ as a difference between the reducible contribution (which includes all three-body processes, whatever the time ordering of events) and the reducible term (which describe those processes which are the result of succession of collisions). Both terms diverge but the difference is finite ; the cancellation occurs only for the diverging parts. We shall see an example of this procedure below.

V.5 - Higher order corrections to the collision operator. Explicit evaluation.

The above discussion shows us that we may forget the irreducibility condition in the third order operator ; it is then a simple matter, with the arguments we used in chapter IV, § 5 to compute $\Phi^{(3)}(0)$. We obtain :

$$\gamma^3 \phi^{(3)}(0) = \lim_{z\to 0} \int \{d\underset{\sim}{v}\}^N \langle 0| \delta L^A \frac{1}{z - L_o^f - \delta L^f} (\delta L^A + L_o^A) \times$$

$$\times \frac{1}{z - L_o^f - \delta L^f} (\delta L^A + L_o^A) \rho^f_{equ} |0\rangle$$

$$= \Omega^{-1} \lim_{z\to 0} \int_o^\infty dt_1 \int_o^{t_1} dt_2 \int \{d\underset{\sim}{v}\, d\underset{\sim}{r}\}^N d\underset{\sim}{R}\, \delta L^A e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} \times$$

(V.5.1) $$\times \left[\underset{\sim}{V} \cdot \frac{\partial}{\partial \underset{\sim}{R}} + \underset{\sim}{F} \cdot \frac{\partial}{\partial \underset{\sim}{P}}\right] e^{-i(L_o^f + \delta L^f - z)t_2} \left[\underset{\sim}{V} \cdot \frac{\partial}{\partial \underset{\sim}{R}} + \underset{\sim}{F} \cdot \frac{\partial}{\partial \underset{\sim}{P}}\right] \rho^f_{equ}$$

$$= \lim_{z\to 0} \int_o^\infty dt_1 \int_o^{t_1} dt_2 \int \{d\underset{\sim}{v}\, d\underset{\sim}{r}\}^N F_i(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \frac{\partial}{\partial P_i} e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} \times$$

$$\times \left[V_j \frac{\partial}{\partial R_j} + F_j(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \frac{\partial}{\partial P_j}\right] e^{-i(L_o^f + \delta L^f - z)t_2} F_1(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \rho^f_{equ} \times$$

$$\times \left[\frac{\partial}{\partial P_1} + \frac{1}{kT} V_1\right]$$

where the force $\underset{\sim}{F}$ acting on the fixed brownian particle is given by (I V.5.8).

As the potential is spherically symmetric, one verifies easily that all contributions to the rhs of (V.5.1) vanish for symmetry reasons. Therefore :

(V.5.2) $$\gamma^3 \phi^{(3)}(0) = 0$$

Let us now consider the fourth order contribution. If we denote by $\tilde{\phi}^{(4)}(0)$ the operator $\phi^{(4)}$ in which we suppress the irreducibility condition, we obtain :

(V.5.3) $$\gamma^4 \phi^{(4)}(0) = \gamma^4 \tilde{\phi}^{(4)}(0) - \alpha$$

where α is given by (V.4.9).

Following the same procedure as that used to compute $\phi^{(2)}$ and $\phi^{(3)}$, we have :

$$\gamma^4 \tilde{\phi}^{(4)}(0) = \gamma^4 \lim_{z\to 0} \int_0^\infty dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int \{d\underset{\sim}{v}\, d\underset{\sim}{r}\}^N F_i(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \frac{\partial}{\partial P_i} \times$$

$$\times\ e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} \left[V_j \frac{\partial}{\partial R_j} + F_j(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \frac{\partial}{\partial P_j} \right] \times$$

(V.5.4)

$$\times\ e^{-i(L_o^f + \delta L^f - z)(t_2 - t_3)} \left[V_l \frac{\partial}{\partial R_l} + F_l(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \frac{\partial}{\partial P_l} \right] \times$$

$$\times\ e^{-i(L_o^f + \delta L^f - z)t_3} F_k(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \rho_{equ}^f \left[\frac{\partial}{\partial P_k} + \frac{1}{kT} V_k \right]$$

This is a fourth order differential operator with respect to the velocity of the brownian particle . It diverges as can be easily verified if one keeps only lowest order terms in the coupling constant.

As to the operator α , we easily obtain :

$$\alpha = \gamma^4 \lim_{z\to 0} \sum_{p=0}^{\infty} \sum_{q=0}^{\infty} \int \{d\underset{\sim}{v}\}^N \langle 0 | \delta L^A \frac{1}{z - L_o^f - \delta L^f} (\delta L^A + L_o^A) \times$$

(V.5.5)

$$\times \left(\frac{1}{z - L_o^f} \delta L^f \right)^p |0\rangle_{irr} \frac{1}{z} \langle 0 | \delta L^A \frac{1}{z - L_o^f - \delta L^f} (\delta L^A + L_A^o) \left(\frac{1}{z - L_o^f} \delta L^f \right)^q |0\rangle \times$$

$$\times \prod_i \varphi^{equ}(\underset{\sim}{v}_i)$$

which we can easily rewrite as :

$$\alpha = \gamma^4 \lim_{z\to 0} \int \{d\underset{\sim}{v}\}^N \langle 0 | \delta L^A \frac{1}{z - L_f^o - \delta L^f} (\delta L^A + L_o^A) \frac{1}{z - L_o^f - \delta L^f} |0\rangle_{irr} \times$$

$$(V.5.6)\times \prod_i \varphi^{equ}(\underset{\sim}{v}_i)\int\{d\underset{\sim}{v}\}^N \langle 0|\delta L^A \frac{1}{z-L_o^f-\delta L^f}(\delta L^A+L_o^A)\rho^f_{equ}|0\rangle_{irr}$$

Using

$$\rho^f_{equ}|0\rangle = \sum_{\{\underset{\sim}{k}\}\underset{\sim}{K}} |\{\underset{\sim}{k}\},\underset{\sim}{K}\rangle\langle\{\underset{\sim}{k}\},\underset{\sim}{K}|\rho^{equ}_f|0\rangle$$

$$(V.5.7) \quad = \sum_{\{\underset{\sim}{k}\},\underset{\sim}{K}\neq\{\underset{\sim}{0}\}} |\{\underset{\sim}{k}\},\underset{\sim}{K}\rangle\langle\{\underset{\sim}{k}\},\underset{\sim}{K}|\rho^{equ}_f|0\rangle + |0\rangle\prod_i \varphi^{equ}(\underset{\sim}{v}_i)$$

we have :

$$\sum_{\{\underset{\sim}{k'}\}\underset{\sim}{K'}\neq\{\underset{\sim}{0}\}} \langle\{\underset{\sim}{k'}\},\underset{\sim}{K'}|\frac{1}{z-L_f^o-\delta L^f}|0\rangle\prod_i\varphi^{equ}(v_i)$$

$$(V.5.8)= \sum_{\{\underset{\sim}{k'}\}\underset{\sim}{K'}\neq\{\underset{\sim}{0}\}} \langle\{\underset{\sim}{k'}\},\underset{\sim}{K'}|\frac{1}{z-L_o^f-\delta L^f}\rho^f_{equ}|0\rangle$$

$$-\sum_{\{\underset{\sim}{k'}\}\underset{\sim}{K'}\neq\{\underset{\sim}{0}\}} \langle\{\underset{\sim}{k'}\},\underset{\sim}{K'}|\frac{1}{z-L_o^f-\delta L^f}\rho^f_{equ}|0\rangle_{irr}$$

Therefore, we obtain :

$$(V.5.9) \qquad \alpha = \alpha_1+\alpha_2$$

with

$$\alpha_1 = \gamma^4 \lim_{z\to 0}\int\{d\underset{\sim}{v}\}^N \langle 0|\delta L^A \frac{1}{z-L_o^f-\delta L^f}(\delta L^A+L_o^A)\frac{1}{z-L_o^f-\delta L^f}\rho^f_{equ}|0\rangle :$$

$$(V.5.10) \quad \times\int\{d\underset{\sim}{v}\}^N\langle 0|\delta L^A\frac{1}{z-L_o^f-\delta L^f}(\delta L^A+L_o^A)\rho^f_{equ}|0\rangle_{irr}$$

$$\alpha_2 = -\gamma^4 \lim_{z\to 0}\int\{d\underset{\sim}{v}\}^N \langle 0|\delta L^A \frac{1}{z-L_o^f-\delta L^f}(\delta L^A+L_o^A)\frac{1}{z-L_o^f-\delta L^f}\rho^f_{equ}|0\rangle_{ir}$$

$$(V.5.11) \quad \times\int\{d\underset{\sim}{v}\}^N\langle 0|\delta L^A\frac{1}{z-L_o^f-\delta L^f}(\delta L^A+L_o^A)\rho^f_{equ}|0\rangle_{irr}$$

Using (IV.6.1) and the convolution theorem we easily obtain :

$$\alpha_1 = \gamma^4 \lim_{z\to 0} \int_o^\infty dt_1 \int_o^{t_1} dt_2 \int_o^{t_2} dt_3 \int \{dv_{\sim} dr_{\sim}\}^N F_i(R_{\sim}, \{r_{\sim}\}) \frac{\partial}{\partial P_i} \times$$

$$\times\ e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} F_j(R_{\sim}, \{r_{\sim}\}) \left(\frac{\partial}{\partial P_j} + \frac{1}{kT} V_j\right) \rho_{equ}^f \times$$

(V.5.12)

$$\times \int \{dv_{\sim} dr_{\sim}\}^N F_1(R_{\sim}, \{r_{\sim}\}) \frac{\partial}{\partial P_1}\ e^{-i(L_o + \delta L^f - z)t_3} F_k(R_{\sim}, \{r_{\sim}\}) \left(\frac{\partial}{\partial P_k} + \frac{1}{kT} V_k\right) \times$$

$$\times\ \rho_{equ}^f$$

Again this is a fourth order differential operator with diverging coefficients (this is again easily verified if one takes into account only lowest order terms in the coupling constant) .

In the contribution α_2, because of the irreducibility condition in the diagonal fragment on the left, none of the propagators is identical to z and this contribution is perfectly finite at the limit $z \to 0$.

Introducing the operator :

$$\gamma^2 \overline{\phi}^{(2)}(z) = \gamma^2 \int \{dv_{\sim}\}^N \langle 0 | \delta L^A \frac{1}{z - L_o^f - \delta L^f} (\delta L^A + L_o^A) \frac{1}{z - L_o^f - \delta L^f} \times$$

(V.5.13)

$$\times\ \rho_{equ}^f | 0 \rangle_{irr}$$

we have

(V.5.14)
$$\alpha_2 = -\gamma^4 \overline{\phi}^{(2)}(0) \phi^{(2)}(0)$$

if we take into account (IV.5.6)

The irreducible operator $\phi^{(4)}$, which does not diverge at the limit $z \to 0$, may thus be written (see (V.5.3)) :

(V.5.15)
$$\phi^{(4)}(0) = \widetilde{\phi}^{(4)} - \alpha_1 - \alpha_2$$

The infinite parts in $\tilde{\Phi}^{(4)}$ and α_1 cancel each other. Introducing the fourth order differential operator :

$$\bar{\Phi}^{(4)}(0) = \tilde{\Phi}^{(4)}(0) - \alpha_1$$

$$= \lim_{z \to 0} \int_0^\infty dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \left\{ \left\{ d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^N F_i(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \frac{\partial}{\partial P_i} e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2} \times \right.$$

$$\times \left[V_j \frac{\partial}{\partial R_j} + F_j(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \frac{\partial}{\partial P_j} \right] e^{-i(L_o^f + \delta L^f - z)(t_2 - t_3)} \left[V_l \frac{\partial}{\partial R_l} + \right.$$

$$\left. F_l(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \frac{\partial}{\partial P_l} \right] e^{-i(L_o^f + \delta L^f - z)t_3} F_k(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \rho^f_{equ} \left(\frac{\partial}{\partial P_k} + \frac{1}{kT} V_k \right)$$

(V.5.16)

$$- \left\{ d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^N F_i(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \frac{\partial}{\partial P_i} e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} F_j(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \rho^f_{equ}$$

$$\left(\frac{\partial}{\partial P_j} + \frac{1}{kT} V_j \right) \left\{ \left\{ d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^N F_l(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \frac{\partial}{\partial P_l} e^{-i(L_o^f + \delta L^f - z)t_3} F_k(\underset{\sim}{R}, \{\underset{\sim}{r}\}) \times \right.$$

$$\left. \left. \times \rho^f_{equ} \left(\frac{\partial}{\partial P_k} + \frac{1}{kT} V_k \right) \right\} \right]$$

we see that the fourth order correction to the collision operator is a sum of two finite terms :

$$\Phi^{(4)}(0) \delta\varphi(\underset{\sim}{V}) = \bar{\Phi}^{(4)}(0) \delta\varphi(\underset{\sim}{V}) + \bar{\Phi}^{(2)}(0) \Phi^{(2)}(0) \delta\varphi(\underset{\sim}{V}) \qquad \text{(V.5.17)}$$

The advantage of this form will appear once we calculate the corrections to the flow term. Then shall see that these exactly compensate the effect of the contribution α_2.

One verifies easily that the operator $\bar{\Phi}^{(4)}(0)$ may be written :

$$\overline{\Phi}^{(4)}(0) = \frac{\partial}{\partial P_i}\left\{ a_{ijkl} \frac{\partial^2}{\partial P_j \partial P_l} + b_{ijkl} \frac{\partial}{\partial P_j} V_l + c_{ijkl} V_l \frac{\partial}{\partial P_j} \right.$$

(V.5.18)

$$\left. + d_{ijkl} V_l V_j \left\{ \left\{ \frac{\partial}{\partial P_k} + \frac{1}{kT} V_k \right\} \right.\right.$$

where

$$a_{ijkl} = \lim_{z \to 0} \int_o^\infty dt_1 \int_o^{t_1} dt_2 \int_o^{t_2} dt_3 \left\{ \left\langle F_i \, e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} F_j \times \right.\right.$$

(V.5.19)

$$\left. \times \, e^{-i(L_o^f + \delta L^f - z)(t_2 - t_3)} F_l \, e^{-i(L_o^f + \delta L^f - z)t_3} F_k \right\rangle$$

$$\left. - \left\langle F_i \, e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} F_j \right\rangle \left\langle F_l \, e^{-i(L_o^f + \delta L^f - z)t_3} F_k \right\rangle \right\}$$

$$b_{ijkl} = \lim_{z \to 0} \int_o^\infty dt_1 \int_o^{t_1} dt_2 \int_o^{t_2} dt_3 \left\langle F_i \, e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} F_j \times \right.$$

(V.5.20)

$$\left. \times \, e^{-i(L_o^f + \delta L^f - z)(t_2 - t_3)} \frac{\partial}{\partial R_l} e^{-i(L_o^f + \delta L^f - z)t_3} F_k \right\rangle$$

$$c_{ijkl} = \lim_{z \to 0} \int_o^\infty dt_1 \int_o^{t_1} dt_2 \int_o^{t_2} dt_3 \left\{ \left\langle F_i \, e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} \frac{\partial}{\partial R_l} \times \right.\right.$$

(V.5.21)

$$\left. \times \, e^{-i(L_o^f + \delta L^f - z)(t_2 - t_3)} F_j \, e^{-i(L_o^f + \delta L^f - z)t_3} F_k \right\rangle$$

$$\left. - \left\langle F_i \, e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} F_l (kT)^{-1} \right\rangle \left\langle F_j e^{-i(L_o^f + \delta L^f - z)t_3} F_k \right\rangle \right\}$$

$$d_{ijkl} = \lim_{z \to 0} \int_o^\infty dt_1 \int_o^{t_1} dt_2 \int_o^{t_2} dt_3 \left\langle F_i \, e^{-i(L_o^f + \delta L^f - z)(t_1 - t_2)} \times \right.$$

(V.5.22)

$$\left. \times \frac{\partial}{\partial R_j} e^{-i(L_o^f + \delta L^f - z)(t_2 - t_3)} \frac{\partial}{\partial R_l} e^{-i(L_o^f + \delta L^f - z)t_3} F_k \right\rangle$$

where

$$\langle A \rangle = \int \{ d\underset{\sim}{r}\, d\underset{\sim}{v} \}^N \; A \rho^f_{equ} \tag{V.5.23}$$

The form (V.5.18) may be compared to the results of Lebowitz and Rubin ; it is in complete agreement with their only correction to the lowest order Fokker-Planck equation.

V.6 - Higher order corrections to the flow term.

The first correction due to the effect of the field during a collision is given by :

$$\gamma^3 \Xi^{(3)}(0) \varphi^{equ}(\underset{\sim}{V}) = \gamma^3 \int \{ d\underset{\sim}{v} \}^N \sum_{\{\underset{\sim}{k}\}} D^{(2)}_{\{\underset{\sim}{k}\}}(0) iL_E C^{(0)}_{\{\underset{\sim}{k}\}}(0) (\rho^f_o)_{equ} \varphi^{equ}(\underset{\sim}{V})$$

$$+\gamma^3 \int \{ d\underset{\sim}{v} \}^N \sum_{\{\underset{\sim}{k}\}} D^{(1)}_{\{\underset{\sim}{k}\}}(0) iL_E C^{(1)}_{\{\underset{\sim}{k}\}}(0) (\rho^f_o)_{equ} \varphi^{equ}(\underset{\sim}{V}) \tag{V.6.1}$$

$$+\gamma^3 \int \{ d\underset{\sim}{v} \}^N \sum_{\{\underset{\sim}{k}\}} D^{(0)}_{\{\underset{\sim}{k}\}}(0) iL_E C^{(2)}_{\{\underset{\sim}{k}\}}(0) (\rho^f_o)_{equ} \varphi^{equ}(\underset{\sim}{V})$$

The third term vanishes because of the integration over the velocities of the fluid particles.

As to the second term, one verifies easily that one has :

$$C^{(1)}_{\{\underset{\sim}{k}\}}(0) (\rho^f_o)_{equ} \varphi^{equ}(\underset{\sim}{V}) = \langle \{\underset{\sim}{k}\} | \frac{1}{z - L^o_f - \delta L^f} (L^A_o + \delta L^A) \frac{1}{z - L^f_o - \delta L^f}$$

$$| 0 \rangle_{irr} (\rho^f_o)_{equ} \varphi^{equ}(\underset{\sim}{V}) \tag{V.6.2}$$

$$= \langle \{\underset{\sim}{k}\} | \frac{1}{z - L^f_o - \delta L^f} \rho^f_{equ} \; \underset{\sim}{F} \cdot \left(\frac{\partial}{\partial \underset{\sim}{P}} + \frac{1}{kT} \underset{\sim}{V} \right) | 0 \rangle \varphi^{equ}(\underset{\sim}{V}) = 0$$

In the first term, we take into account the fact that L_E commutes with ρ^f_{equ}. We then obtain easily :

$$\gamma^3 \Xi^{(3)}(0)\varphi^{equ}(\underset{\sim}{V}) = \gamma^3 \int \{dv\}^N \langle 0| \delta L^A \frac{1}{z - L_o^f - \delta L^f} (\delta L^A + L_A^o) \times$$

$$(V.6.3) \quad \times \frac{1}{z - L_o^f - \delta L^f} \; iL_E \rho^f_{equ} |0\rangle_{irr} \varphi^{equ}(\underset{\sim}{V})$$

$$= \gamma^3 \bar{\Phi}^{(2)}(0) \; iL_E \varphi^{equ}(\underset{\sim}{V})$$

if we take (V.5.13) into account.

The fourth order correction vanishes for symmetry reasons.

V.7 - Stationary transport equation up to order γ^4.

Summarizing the results of the previous paragraphs, we have:

$$(V.7.1) \qquad \Xi(0)\varphi^{equ}(\underset{\sim}{V}) = \gamma^3 \bar{\Phi}^{(2)}(0) \; iL_E \varphi^{equ}(\underset{\sim}{V})$$

$$(V.7.2) \qquad \Phi(0) = \gamma^2 \Phi^{(2)}(0) + \gamma^4 \bar{\Phi}^{(4)}(0) \qquad + \gamma^4 \bar{\Phi}^{(2)}(0) \Phi^{(2)}(0)$$

where the Fokker-Planck operator $\Phi^{(2)}(0)$ is given by (V.3.8) while the operators $\bar{\Phi}^{(4)}(0)$ and $\bar{\Phi}^{(2)}(0)$ are given by (V.5.18) and (V.5.13) respectively.

Therefore , up to order γ^4, the stationary transport equation becomes :

$$\gamma \left[1 + \gamma^2 \bar{\Phi}^{(2)}(0)\right] iL_E \varphi^{equ}(\underset{\sim}{V}) = \gamma^2 \left[1 + \gamma^2 \bar{\Phi}^{(2)}(0)\right] \Phi^{(2)}(0) \delta\varphi(\underset{\sim}{V})$$

$$(V.(.3) \qquad + \gamma^4 \bar{\Phi}^{(4)}(0) \delta\varphi(\underset{\sim}{V})$$

Expanding $\delta\varphi(\underset{\sim}{V})$ in powers of γ , we have :

$$(V.7.4) \qquad \delta\varphi(\underset{\sim}{V}) = \gamma^{-1}\left[\delta\varphi(\underset{\sim}{V})\right]_0 + \gamma\left[\delta\varphi(\underset{\sim}{V})\right]_1$$

which leads to :

$$(V.7.5) \qquad iL_E\varphi^{equ}(\underset{\sim}{V}) = \phi^{(2)}(0)\left[\delta\varphi(\underset{\sim}{V})\right]_0$$

$$(V.7.6) \qquad 0 = \phi^{(2)}(0)\left[\delta\varphi(\underset{\sim}{V})\right]_1 + \overline{\phi}^{(4)}(0)\left[\delta\varphi(\underset{\sim}{V})\right]_0$$

which we may rewrite as :

$$(V.7.7) \qquad iL_E\varphi^{equ}(\underset{\sim}{V}) = \left[\gamma^2\phi^{(2)}(0) + \gamma^4\overline{\phi}^{(4)}(0)\right]\delta\varphi(V)$$

which shows that the corrections due to the action of the field during a collision can be formally incorporated in a modification of the collision operator. The corrections to the lowest order Fokker-Planck equation are thus entirely given by the operator $\overline{\phi}^{(4)}(0)$. Part of these corrections may of course be incorporated in a modification of the diffusion coefficient D which appears in the lowest order equation. Equation (V.7.7) agrees exactly with the transport equation derived by Lebowitz and Rubin.

V.8 - Alternative form of the transport equation for the brownian motion problem.

Through a rather different method, Lebowitz and Rubin have obtained the following transport equation for the velocity distribution function of the heavy particle :

$$(V.8.1) \qquad \frac{\partial\,\delta\varphi(\underset{\sim}{V},t)}{\partial t} + iL_E\varphi^{equ}(\underset{\sim}{V}) = \int_0^t d\tau\,\mathcal{K}(t-\tau)\,\delta\varphi(\underset{\sim}{V},\tau)$$

The collision operator $\mathcal{K}$ is given by :

$$\mathcal{K}(t) = -(2\pi i)^{-1} \int dz \; e^{-izt} K(z) \tag{V.8.2}$$

$$K(z) = -i\gamma \left\{ \int d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^N \delta L^A \frac{1}{z-(1-\mathcal{P})(L_o+\delta L)} (1-\mathcal{P})(L_o+\delta L) \rho^f_{equ} \tag{V.8.3}$$

where $\mathcal{P}$ is a projection operator :

$$\mathcal{P} \ldots = \rho^f_{equ} \left\{ \int d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^N \ldots \tag{V.8.4}$$

The remarkable feature is that, except for the trivial flow term, all the dynamics of the problem has been incorporated in the collision operator $\mathcal{K}$; at first sight this seems to be in contradiction with our general result of chapter II. However, we have already seen that, up to fourth order in γ , in this brownian motion problem, the corrections to the flow term in (V.2.9) can indeed be taken formally as a modification of the collision operator.

We shall not give here the original derivation of (V.8.1) which can be found in ref. [2], but rather concentrate ourselves on the equivalence between the two transport equations for this problem.

First of all, we shall show that the solutions of (V.8.1) are identical to the solutions of the following equation :

$$\frac{\partial \delta\varphi(\underset{\sim}{V},t)}{\partial t} + iL_E \varphi^{equ}(\underset{\sim}{V}) + \int_o^t d\tau\, \Delta(t-\tau) iL_E \varphi^{equ}(\underset{\sim}{V}) = \int_o^t d\tau \chi(t-\tau) \delta\varphi(\underset{\sim}{V},\tau) \tag{V.8.5}$$

where $\Delta(t)$ and $\chi(t)$ are the inverse Laplace transforms of the operators:

$$(V.8.6)\quad \overline{\chi}(z) = -i\int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \delta L^A \frac{1}{z-(1-I)(L_o+\delta L)} (1-I)(L_o+\delta L) I \rho^f_{equ}$$

$$(V.8.7)\quad \overline{\Delta}(z) = \int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \delta L^A \frac{1}{z-(1-I)(L_o+\delta L)} (1-I)\rho^f_{equ}$$

where I is a projection operator :

$$(V.8.8)\qquad I\ldots = (\Omega)^{-N}(\rho^f_o)_{equ}\int \{d\underset{\sim}{r}d\underset{\sim}{v}\}^N \ldots$$

(I involves the fluid velocity equilibrium distribution function while ρ involves the complete fluid equilibrium distribution function for a fixed position of the brownian particle) .

Using Laplace transforms, one easily obtains the formal solutions of (V.8.1) :

$$(V.8.9)\qquad \overline{\delta\varphi}(z) = \left[-iz-K(z)\right]^{-1} i(z+\omega)^{-1}\ \underset{\sim}{E}.\underset{\sim}{V}\varphi^{equ}(\underset{\sim}{V})$$

and of (V.8.5) :

$$(V.8.10)\qquad \overline{\delta\varphi}(z) = \left[-iz-\overline{\chi}(z)\right]^{-1}\left[1+\overline{\Delta}(z)\right] i(z+\omega)^{-1}\underset{\sim}{E}.\underset{\sim}{V}\varphi^{equ}(\underset{\sim}{V})$$

(We consider here the case of an oscillating field as given by (II.13.12))

In order to establish the identity of these two functions, we have to show that the rhs are identical, or equivalently, that we have :

$$(V.8.11)\quad \left[\overline{\chi}(z) - iz\,\overline{\Delta}(z)\right] f(\underset{\sim}{V}) = \left[1 + \overline{\Delta}(z)\right] K(z)\ f(\underset{\sim}{V})$$

where $f(\underset{\sim}{V})$ is an arbitrary function of $\underset{\sim}{V}$;

Now , using the identity, valid for an arbitrary function $A(\underset{\sim}{V}, \{\underset{\sim}{r}\}, \{\underset{\sim}{v}\})$:

$$(\Gamma - I)A(\underset{\sim}{V}, \{\underset{\sim}{r}\}, \{\underset{\sim}{v}\}) = \left[\rho^{f}_{equ} - (\Omega)^{-N} (\rho^{f}_{o})_{equ}\right] \left\{ \left\{ d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^{N} A \right.$$

(V.8.12)
$$= (1-I)\, \rho^{f}_{equ} \left\{ \left\{ d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^{N} A \right.$$

as well as :

$$\frac{1}{z-(1-\Gamma)(L_o+\delta L)} = \frac{1}{z-(1-I)(L_o+\delta L)+(\Gamma-I)(L_o+\delta L)}$$

$$= \frac{1}{z-(1-I)(L_o+\delta L)} \left\{ 1 + (\Gamma-I)(L_o+\delta L) \frac{1}{z-(1-I)(L_o+\delta L)+(\Gamma-I)(L_o+\delta L)} \right\}$$

(V.8.13)

$$= \frac{1}{z-(1-I)(L_o+\delta L)} \left\{ 1 + (1-I) \rho^{f}_{equ} \left\{ \left\{ d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^{N} (L_o+\delta L) \frac{1}{z-(1-\Gamma)(L_o+\delta L)} \right\} \right.$$

$$= \frac{1}{z-(1-I)(L_o+\delta L)} \left\{ 1 + (1-I) \rho^{f}_{equ} \left\{ \left\{ d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^{N} (L^{A}_{o} + \delta L^{A}) \frac{1}{z-(1-\Gamma)(L_o+\delta L)} \right\} \right.$$

we easily obtain :

$$\left[1 + \tilde{\Delta}(z)\right] K(z) f(\underset{\sim}{V}) = -i\gamma \left\{ \left\{ d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^{N} \delta L^{A} \frac{1}{z-(1-I)(L_o+\delta L)} (1-\Gamma) \times \right.$$

$$\times (L_o+\delta L) \rho^{f}_{equ} \; f(\underset{\sim}{V})$$

(V.8.14)

$$+ i\gamma^{2} \left\{ \left\{ d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^{N} \delta L^{A} \frac{1}{z-(1-I)(L_o+\delta L)} (1-I) \rho^{f}_{equ} \; L^{A}_{o} \times \right.$$

$$\times \left\{ \left\{ d\underset{\sim}{r}\, d\underset{\sim}{v} \right\}^{N} \frac{1}{z-(1-\Gamma)(L_o+\delta L)} (1-\Gamma)(L_o+\delta L) \rho^{f}_{equ} \; f(\underset{\sim}{V}) \right.$$

Now, if :

(V.8.15)
$$\Gamma = \frac{1}{z-(1-\Gamma)(L_o+\delta L)} (1-\Gamma)(L_o+\delta L) \rho^{f}_{equ}$$

we also have :

$$\{z-(1-\mathcal{P})(L_o+\delta L)\}\Gamma=(1-\mathcal{P})(L_o+\delta L)\rho^f_{equ} \tag{V.8.16}$$

Applying the operator $\mathcal{P}$ to both sides , we have :

$$z\mathcal{P}\Gamma\equiv z\rho^f_{equ}\left\{\int dr\,dv\right\}^N\Gamma=0 \tag{V.8.17}$$

which shows us that the second term in the rhs of (V.8.14) vanishes. Hence ,

$$\left[1+\bar{\Delta}(z)\right]K(z)f(V)=-i\gamma\left\{\int dr\,dv\right\}^N\delta L^A\,\frac{1}{z-(1-I)(L_o+\delta L)}(1-\mathcal{P})\times$$

$$\times(L_o+\delta L)\rho^f_{equ}f(V) \tag{V.8.18}$$

The lhs of (V.8.11) can be written , with the definitions (V.8.6) and (V.8.7) :

$$\left[\bar{\chi}(z)-iz\bar{\Delta}(z)\right]f(V)=-i\gamma\left\{\int dr\,dv\right\}^N\delta L^A\,\frac{1}{z-(1-I)(L_o+\delta L)}(1-I)\times$$

$$\times\left\{z+(L_o+\delta L)I\right\}\rho^f_{equ}f(V) \tag{V.8.19}$$

In order to prove identity (V.8.11) , we thus have to show that the quantity α given by :

$$\alpha=\int\left\{dv\,dr\right\}^N\delta L^A\,\frac{1}{z-(1-I)(L_o+\delta L)}\left\{(1-\mathcal{P})\,(L_o+\delta L)\right.$$

$$\left.=(1-I)(L_o+\delta L)\,I-z(1-I)\right\}\rho^f_{equ}\,f(V) \tag{V.8.20}$$

vanishes .

Now, using again (V.8.12) , we have :

$$\left\{(1-\mathcal{P})(L_o+\delta L)-(1-I)(L_o+\delta L)I-z(1-I)\right\}\rho^f_{equ}\,f(V)=$$

$$(1-I)\left\{(L_o+\delta L)(1-I)\rho^f_{equ}-\rho^f_{equ}\left\{\int dr\,dv\right\}^N(L_o+\delta L)\rho^f_{equ}-z\rho^f_{equ}\right\}f(V) \tag{V.8.21}$$

We also have :

$$\int \{d\underset{\sim}{r} d\underset{\sim}{v}\}^N (L_o + \delta L) \rho^f_{equ} = \gamma L_o^A \int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \rho^f_{equ} + \gamma \int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \delta L^A \rho^f_{equ}$$

(V.8.22)

$$= \gamma L_o^A + \gamma \int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \delta L^A \rho^f_{equ}$$

$$\gamma L_o^A f(\underset{\sim}{V}) = 0 \qquad \text{(V.8.23)}$$

If we combine (V.8.20), (V.8.21), (V.8.22) and (V.8.23), we obtain

$$\alpha = \Big[-\int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \delta L^A (1-I) \rho^f_{equ} - \int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \delta L^A \frac{1}{z - (1-I)(L_o + \delta L)} \times$$

(V.8.24)

$$\times (1-I) \rho^f_{equ} \int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \delta L^A \rho^f_{equ} \Big] f(\underset{\sim}{V})$$

Now, we have :

$$\int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \delta L^A \rho^f_{equ} \; f(\underset{\sim}{V}) = 0$$

(see IV.4.7)

and:

$$\text{(V.8.25)} \quad \int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \delta L^A \; I \rho^f_{equ} = \int \{d\underset{\sim}{r}\, d\underset{\sim}{v}\}^N \delta L^A (\rho^f_o)_{equ} (\Omega)^{-N} = 0$$

Therefore, we indeed obtain :

$$\alpha = 0 \qquad \text{(V.8.26)}$$

and the identity of the solutions of (V.8.1) and (V.8.5) is thus established. Equation (V.8.5) has the same structure as the transport equation we obtained in Chapter II, § 13. In the steady state, we obtain :

$$iL_E \varphi^{equ}(\underset{\sim}{V}) + \bar{\Delta}(0)\, iL_E \varphi^{equ}(\underset{\sim}{V}) = \bar{\chi}(0)\, \delta\varphi(\underset{\sim}{V}) \qquad \text{(V.8.27)}$$

To establish the equivalence with (V.2.10), we have to show :

$$\bar{\Delta}(0)\, iL_E \varphi^{equ}(\underset{\sim}{V}) = \sum_{\{\underset{\sim}{k}\}} D_{\{\underset{\sim}{k}\}}(0)\, iL_E C_{\{\underset{\sim}{k}\}}(0)\, \varphi^{equ}(\underset{\sim}{V}) \qquad \text{(V.8.28)}$$

$$\bar{\chi}(0)\delta\varphi(\underset{\sim}{V}) = \phi(0)\,\delta\varphi(\underset{\sim}{V}) \tag{V.8.29}$$

Let us first consider the lhs of (V.8.29) . We have :

$$\bar{\chi}(z)\delta\varphi(\underset{\sim}{V}) = \int\{d\underset{\sim}{v}\}^N \langle 0|\delta L^A \frac{1}{z-L_o^f-(1-I)(L_o^A+\delta L)}\left[L_o^f+(1-I)(L_o^A+\delta L)\right]$$

$$|0\rangle(\rho_o^f)_{equ}\,\delta\varphi(\underset{\sim}{V}) \tag{V.8.30}$$

if we take into account :

$$IL_o^f = 0 \tag{V(8.31)}$$

$$I\rho_{equ}^f\,\delta\varphi(V) = \Omega^{-N}(\rho_o^f)_{equ}\,\delta\varphi(\underset{\sim}{V}) \tag{V.8.32}$$

Through a straightforward expansinn, we obtain :

$$\bar{\chi}(z)\delta\varphi(\underset{\sim}{V}) = \sum_{m=0}^{\infty}\int\{d\underset{\sim}{v}\}^N \langle 0|\delta L^A \frac{1}{z-L_o}\left\{\left[(1-I)\delta L - IL_o^A\right]\frac{1}{z-L_o}\right\}^m \times$$

$$\times\left\{L_o^f + (1-I)(L_o^A+\delta L)\right\}|0\rangle\,(\rho_o^f)_{equ}\,\delta\varphi(\underset{\sim}{V}) \tag{V.8.33}$$

However, we have :

$$\langle\{\underset{\sim}{k}\},\underset{\sim}{K}|I(L_o^A+\delta L)|\{\underset{\sim}{k}'\},\underset{\sim}{K}'\rangle F(\{\underset{\sim}{v}\},\underset{\sim}{V})\delta_{\sum_i \underset{\sim}{k}_i+\underset{\sim}{K},\,0}\,\delta_{\sum_i \underset{\sim}{k}_i'+\underset{\sim}{K}',\,\underset{\sim}{0}}$$

$$= \int\{d\underset{\sim}{r}\}^N d\underset{\sim}{R}\,\exp\left[-i\sum_i \underset{\sim}{k}_i.\underset{\sim}{r}_i\right]e^{-i\underset{\sim}{K}.\underset{\sim}{R}}\,\Omega^{-N}(\rho_o^f)_{equ}\int\{d\underset{\sim}{r}'d\underset{\sim}{v}'\}^N\left[L_o^A(\underset{\sim}{R},\underset{\sim}{V})\right.$$

$$\left.+\delta L(\underset{\sim}{R},\underset{\sim}{V},\{\underset{\sim}{r}'\},\{\underset{\sim}{v}'\})\right]\exp\left[i\sum_i \underset{\sim}{k}_i'.\underset{\sim}{r}_i'\right]e^{i\underset{\sim}{K}'.\underset{\sim}{R}}\,F(\{\underset{\sim}{v}'\},\underset{\sim}{V})\delta_{\sum_i \underset{\sim}{k}_i+\underset{\sim}{K},\,\underset{\sim}{0}}\times$$

$$\times\,\delta_{\sum_i \underset{\sim}{k}_i+\underset{\sim}{K}',\,\underset{\sim}{0}} \tag{V.8.34}$$

$$= \prod_i \delta_{\underset{\sim}{k}_i,\,\underset{\sim}{0}}\,\delta_{\underset{\sim}{K},\,\underset{\sim}{0}}\,\delta_{\sum_i \underset{\sim}{k}_i'+\underset{\sim}{K}',\,\underset{\sim}{0}}\,(\rho_o^f)_{equ}\int\{d\underset{\sim}{v}'\}^N\langle 0|L_o^A(\underset{\sim}{V})+\delta L(\underset{\sim}{V},\{\underset{\sim}{v}'\})$$

$$|\{k'\}, \underset{\sim}{K}'\rangle F\ (\{\underset{\sim}{v}'\}, \underset{\sim}{V})$$

As a consequence all irreducible contributions involving IL_o^A or $I\delta L$ in (V.8.33) vanish (see the product of Kronecker's deltas in the rhs of (V.8.34)).

Let us now consider a reducible contribution made of a product of two irreducible contributions :

$$\beta = \int \{d\underset{\sim}{v}\}^N \langle 0|\delta L^A \frac{1}{z-L_o}\left\{\left[(1-I)\delta L - IL_o^A\right]\frac{1}{z-L_o}\right\}^p |0\rangle \times$$

(V.8.35)
$$\times \langle 0|\left\{\left[(1-I)\delta L - IL_o^A\right]\frac{1}{z-L_o}\right\}^q \left\{L_o^f + (1-I)(L_o^A + \delta L)\right\}|0\rangle_{irr} (\rho_o^f)_{equ} \delta\varphi(\underset{\sim}{V})$$

(V.8.34) shows us that we may drop the operator I every where in the second fragment except at the left. (combine the Kronecker's deltas in (V.8.34) and the irreducibility condition). Let us first consider the case q=0 . Then , using (V.8.34), we have :

(V.8.36)
$$\langle 0 | L_o^f + (1-I)(L_o^A + \delta L) | 0\rangle\ (\rho_o^f)_{equ} \delta\varphi(\underset{\sim}{V}) = 0$$

If q is different from zero, we have :

$$\langle 0|\left\{\left[(1-I)\delta L - IL_o^A\right]\frac{1}{z-L_o}\right\}^q \left\{L_o^f + (1-I)(L_o^A + \delta L)\right\}|0\rangle_{irr} (\rho_o^f)_{equ} \delta\varphi(\underset{\sim}{V})$$

$$= \sum_{\{\underset{\sim}{k}\}\underset{\sim}{K} \neq \{\underset{\sim}{0}\}} \langle 0|(1-I)\delta L - IL_o^A|\{\underset{\sim}{k}\}, \underset{\sim}{K}\rangle\langle\{\underset{\sim}{k}\}, \underset{\sim}{K}|\left(\frac{1}{z-L_o}\delta L\right)^q |0\rangle_{irr} (\rho_o^f)_{equ}(\underset{\sim}{V})$$

(V.8.37)
$$= \langle 0|\delta L \left(\frac{1}{z-L_o}\delta L\right)^q |0\rangle_{irr} (\rho_o^f)_{equ} \delta\varphi(\underset{\sim}{V})$$

$$- (\rho_o^f)_{equ} \int \{d\underset{\sim}{v}\}^N \langle 0|\delta L \left(\frac{1}{z-L_o}\delta L\right)^q |0\rangle_{irr} (\rho_o^f)_{equ} \delta\varphi(\underset{\sim}{V})$$

and we obtain :

$$\beta = \int \{d\underset{\sim}{v}\}^N \langle 0|\delta L^A \frac{1}{z-L_o}\left\{\left[(1-I)\delta L - IL^A_o\right]\frac{1}{z-L_o}\right\}^p |0\rangle\langle 0|\delta L\left(\frac{1}{z-L_o}\delta L\right)^q$$

$$|0\rangle_{irr}\,(\rho^f_o)_{equ}\,\delta\varphi(\underset{\sim}{V})$$

(V.8.38)

$$-\int \{d\underset{\sim}{v}\}^N \langle 0|\delta L^A \frac{1}{z-L_o}\left\{\left[(1-I)\delta L - IL^A_o\right]\frac{1}{z-L_o}\right\}^p |0\rangle(\rho^f_o)_{equ} \times$$

$$\times \int \{d\underset{\sim}{v}\}^N \langle 0|\delta L\left(\frac{1}{z-L_o}\delta L\right)^q |0\rangle_{irr}\,(\rho^f_o)_{equ}\,\delta\varphi(\underset{\sim}{V})$$

If no fluid particle is common to both fragments, the rhs vanishes trivially; now, in our discussion of the role of the irreducibility condition, we have seen that when such a product of fragments has a single semi-connection, it is through particle A; if we have more than a semiconnection, we obtain a contribution of order N^{-1}. Therefore, at the limit of a large system :

(V.8.39) $$\beta = 0$$

This means that all reducible contributions to (V.8.33) vanish. Taking also into account the remark following (V.8.34), we obtain :

$$\bar{\chi}(z)\,\delta\varphi(\underset{\sim}{V}) = \sum_{m=0}^{\infty} \int \{d\underset{\sim}{v}\}^N \langle 0|\delta L^A \left(\frac{1}{z-L_o}\delta L\right)^{m+1} |0\rangle_{irr}\,(\rho^f_o)_{equ} \times$$

(V.8.40)

$$\times\,\delta\varphi(\underset{\sim}{V}) = \phi(z)\delta\varphi(\underset{\sim}{V})$$

which establishes (V.8.29).

(V.8.28) can be established in a similar way, if one takes into account:

$$\langle \{\underset{\sim}{k}\},\ \underset{\sim}{K}|(1-I)\rho^f_{equ}|0\rangle iL_E = 0 \quad \text{if } |\{\underset{\sim}{k}\},\ \underset{\sim}{K}\rangle = |0\rangle$$

$$= \langle \{\underset{\sim}{k}\},\ \underset{\sim}{K}|\rho^f_{equ}|0\rangle iL_E$$

(V.8.41)

$$= iL_E \langle \{\underset{\sim}{k}\},\ \underset{\sim}{K}|\rho^f_{equ}|0\rangle$$

$$= iL_E C_{\{\underset{\sim}{k}\}\underset{\sim}{K}} (\rho_o^f)_{equ} \quad \text{if} \quad |\{\underset{\sim}{k}\}, \underset{\sim}{K}\rangle \neq |0\rangle$$

This completes the proof of the equivalence between our starting point and that of Lebowitz and Rubin. This equivalence shows us that quite generally all corrections due to the effect of the field during a collision can, in this brownian motion problem, be incorporated formally in a modification of the collision operator ($\phi \to \mathcal{K}$).

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F. Henin

VI. BROWNIAN MOTION IN AN EXTERNAL FIELD. QUANTUM CASE

VI. - Introduction

We shall now consider the problem of brownian motion of of a heavy particle in a quantum system. Our starting point for a microscopic discussion of the evolution equation of quantum systems will be the Von Neuman equation for the density matrix. As we shall see, provided we choose suitable variables, this equation can be written in a form which is very similar to the Liouville equation. The main difference will be the replacement of differential operators by displacement operators. This corresponds to the physical fact that energy transfers are infinitesimal in the classical case while they are finite in the quantum case. The similarity between the quantum equation for the density matrix and the Liouville equation for the distribution function enables us to extend the whole formalism very easily to quantum systems.

However, the problem of brownian motion in quantum systems presents features which are quite different from those of the classical problem. In the classical case, we performed an expansion in powers of the mass ratio and showed that, to lowest order, the velocity distribution function of the heavy particle obeys a Fokker-Planck equation. At first sight, we might expect this to be true also for the quantum case, the quantum effects appearing in the diffusion coefficient. However, if we go back for a while to the classical problem, we easily notice that, what we did, was to assume that we were dealing with a particle moving with thermal velocity (i. e. a velocity of the order of its equilibrium velocity) in a fluid at equilibrium. We then had:

$$\langle p \rangle / P = 0(m/M)^{1/2} = 0(\gamma) \ll 1 \qquad \text{(VI. 1. 1)}$$

Our expansion in a power series of γ was actually an expansion in $\langle p \rangle / P$.

It is easy to convince oneself that (VI. 1.1.) does not necessarily hold in the quantum case. Let us for instance consider the case of a heavy particle moving in a weakly coupled Fermi fluid. At very low temperature, the particle collides with fermions whose energy is very close to the Fermi energy ϵ_F. Then we have:

$$\langle p \rangle / P = O(m\epsilon_F/MkT)^{1/2} = O(\gamma \xi) \qquad \text{(VI. 1. 2.)}$$

where

$$\xi = (\epsilon_F/kT)^{1/2} \qquad \text{(VI. 3. 3)}$$

and we may expect to find a Fokker-plank equation only in the region where

$$\gamma \xi << 1 \qquad \text{(VI. 1. 4)}$$

This condition is much more restrictive than the condition we met in the classical problem.

With this example, one might think that such difficulties will appear only if we consider fermions, because of the exclusion principle and the existence of the Fermi energy. However, we shall see that it is not the case and that the difficulty is more general. At very low temperatures, we must always expect that the Fokker-Planck equation will not be valid.

We shall first show how the Von Neumann equation may be written in a form very similar to the Liouville equation[1]. Then, assuming that an expansion in $\langle p \rangle / P$ is valid, we shall easily obtain a Fokker-Planck equation. We shall discuss the quantum corrections to the diffusion

coefficient in some simple cases [2)3)] and compare briefly the theoretical results with the results obtained in experiments on heavy ions moving in liquid helium. Finally, we shall discuss on somewhat more general grounds than above the validity of expansions in powers of $\langle p \rangle / P$. [4)]

VI. 2 - Von Neumann - Liouville equation.

Let us consider one heavy charged particle acted upon by a constant external field moving in a fluid of light neutral particles. If we use a second quantization representation for free fluid particles and a plane wave representation for the heavy particle, the hamiltonian operator is (we take $\hbar = 1$):

$$H = H_o + \lambda V + H_E \tag{VI. 2. 1}$$

The unperturbed hamiltonian is a sum over the kinetic energies of the fluid particles and the brownian particles :

$$H_o = \sum_{\underset{\sim}{k}} (k^2/2m)\, a^+_{\underset{\sim}{k}}\, a_{\underset{\sim}{k}} + K^2/2M \tag{VI. 2. 2}$$

where $a^+_{\underset{\sim}{k}}$, $a_{\underset{\sim}{k}}$ are the creation and destruction operators for a fluid particle of momentum $\underset{\sim}{k}$.

As in the classical case, the interaction is a sum of two terms : one which describes the interactions of the fluid particles among themselves and a second one which describes the interactions of the heavy particle with the fluid particles :

$$V = (\lambda/2\Omega) \sum_{\underset{\sim}{klpr}} v(\underset{\sim}{k}, \underset{\sim}{l}, \underset{\sim}{p}, \underset{\sim}{r})\; a^+_{\underset{\sim}{k}}\, a^+_{\underset{\sim}{l}}\, a_{\underset{\sim}{p}}\, a_{\underset{\sim}{r}}\, \delta_{\underset{\sim}{k+l-p-r}, \underset{\sim}{0}}$$

$$+ (\lambda/\Omega) \sum_{\underset{\sim}{kl}} u(\underset{\sim}{k}-\underset{\sim}{l})\, e^{-i(\underset{\sim}{k}-\underset{\sim}{l}).\underset{\sim}{R}}\, a^+_{\underset{\sim}{k}}\, a_{\underset{\sim}{l}} \tag{VI. 2. 3}$$

The contribution due to the action of the external field on the heavy particle is :

$$H_E = e\,\underset{\sim}{E}.\underset{\sim}{R} \qquad \text{(VI.2.4)}$$

In the mixed representation $|\underset{\sim}{K}, \{n\}\rangle$ of the eigenstates of H_o :

$$H_o\,|\underset{\sim}{K}, \{\underset{\sim}{n}\}\rangle = \left\{K^2/2M + \sum_{\underset{\sim}{k}} (k^2/2m)n_{\underset{\sim}{k}}\right\}|\underset{\sim}{K}, \{n\}\rangle \qquad \text{(VI.2.4)}$$

the Von Neumann equation for the density matrix is :

$$i\frac{\partial\langle \underset{\sim}{K}, \{n\}|\rho|\underset{\sim}{K'}, \{n'\}\rangle}{\partial t} = \langle \underset{\sim}{K}, \{n\}|[H,\rho]|\underset{\sim}{K'}, \{n'\}\rangle \qquad \text{(VI.2.5)}$$

where $[H, \rho]$ is the commutator of the two operators H and ρ .

Let us now perform the following change of variables: for the heavy particle :

$$\underset{\sim}{\mathcal{K}} = \underset{\sim}{K} - \underset{\sim}{K'}$$
$$\underset{\sim}{P} = (\underset{\sim}{K}+\underset{\sim}{K'})/2 \qquad \text{(VI.2.6)}$$

for the fluid particles :

$$\nu_{\underset{\sim}{k}} = n_{\underset{\sim}{k}} - n'_{\underset{\sim}{k}}$$
$$N_{\underset{\sim}{k}} = (n_{\underset{\sim}{k}} + n'_{\underset{\sim}{k}})/2 \qquad \text{(VI.2.7)}$$

We also write any matrix element of an operator A in the following form :

$$\langle \underset{\sim}{K}, \{n\}|A|\underset{\sim}{K'}, \{n'\}\rangle = A_{\underset{\sim}{K}-\underset{\sim}{K'}, \{n-n'\}}\left((\underset{\sim}{K}+\underset{\sim}{K'})/2, \{(n+n')/2\}\right)$$
$$= A_{\underset{\sim}{\mathcal{K}}, \{\nu\}}(\underset{\sim}{P}, \{N\}) \qquad \text{(VI.2.8)}$$

To the operator A, we associate an operator $\mathcal{A}$, which we define through the relation :

$$\langle \underset{\sim}{\kappa}, \{\nu\} | \mathcal{H}(\underset{\sim}{P}, \{N\}) | \underset{\sim}{\kappa}', \{\nu'\} \rangle = \zeta^{\underset{\sim}{\kappa}'} \eta^{\sum_{\underset{\sim}{k}} \underset{\sim}{\nu}_{\underset{\sim}{k}}'} A_{\underset{\sim}{\kappa}, \{\nu\}}(\underset{\sim}{P}, \{N\}) \zeta^{-\underset{\sim}{\kappa}}$$

(VI. 2. 9)

$$\times \eta^{-\sum_{\underset{\sim}{k}} \underset{\sim}{\nu}_{\underset{\sim}{k}}} - \zeta^{-\underset{\sim}{\kappa}'} \eta^{-\sum_{\underset{\sim}{k}} \underset{\sim}{\nu}_{\underset{\sim}{k}}'} A_{\underset{\sim}{\kappa}, \{\nu\}}(\underset{\sim}{P}, \{N\}) \zeta^{\underset{\sim}{\kappa}} \eta^{\sum_{\underset{\sim}{k}} \underset{\sim}{\nu}_{\underset{\sim}{k}}}$$

where the ζ and η 's are displacement operators acting on the variables P and N respectively :

$$\zeta^{\pm \underset{\sim}{\kappa}} f(\underset{\sim}{P}) = \exp\left[\pm \frac{\underset{\sim}{\kappa}}{2} \cdot \frac{\partial}{\partial \underset{\sim}{P}}\right] f(\underset{\sim}{P}) = f\left(\underset{\sim}{P} \pm \frac{\underset{\sim}{\kappa}}{2}\right) \qquad \text{(VI. 2. 10)}$$

$$\eta^{\pm \sum_{\underset{\sim}{k}} \underset{\sim}{\nu}_{\underset{\sim}{k}}} f(\{N\}) = \exp\left[\pm \frac{1}{2} \sum_{\underset{\sim}{k}} \underset{\sim}{\nu}_{\underset{\sim}{k}} \frac{\partial}{\partial \underset{\sim}{N}_{\underset{\sim}{k}}}\right] f(\{N\}) = f\left(\left\{N \pm \frac{\nu}{2}\right\}\right) \qquad \text{(VI. 2. 11)}$$

One can then easily write the Von Neumann equation as :

$$i \frac{\partial \rho_{\underset{\sim}{\kappa}, \{\nu\}}(\underset{\sim}{P}, \{N\})}{\partial t} = \sum_{\underset{\sim}{\kappa}', \{\nu'\}} \langle \underset{\sim}{\kappa}, \{\nu\} | \mathcal{H}(\underset{\sim}{P}, \{N\}) | \underset{\sim}{\kappa}', \{\nu'\} \rangle \times$$

(VI. 2. 12)

$$\times \rho_{\underset{\sim}{\kappa}', \{\nu'\}}(\underset{\sim}{P}, \{N\})$$

which is formally analogous to the classical Liouville equation. The Von Neumann-Liouville operator $\mathcal{H}$ can be split into three terms :

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{W} + \mathcal{H}_E \qquad \text{(VI. 2. 13)}$$

The unperturbed operator $\mathcal{H}_0$ is given by :

$$\langle \underset{\sim}{\kappa}, \{\nu\} | \mathcal{H}_0 | \underset{\sim}{\kappa}', \{\nu'\} \rangle = \delta_{\underset{\sim}{\kappa}, \underset{\sim}{\kappa}'} \prod_{\underset{\sim}{k}} \delta_{\underset{\sim}{\nu}_{\underset{\sim}{k}}, \underset{\sim}{\nu}_{\underset{\sim}{k}}'} \times$$

(VI. 2. 14)

$$\times \left[\frac{\underset{\sim}{\kappa} \cdot \underset{\sim}{P}}{M} + \sum_{\underset{\sim}{k}} (k^2/2m) \nu_{\underset{\sim}{k}} \right]$$

The interaction operator is given by :

$$\langle \underset{\sim}{\kappa}, \{\nu\} | \lambda \mathcal{W} | \underset{\sim}{\kappa}', \{\nu'\} \rangle = (\lambda / 2\Omega) \sum_{\underset{\sim}{k} \underset{\sim}{l} \underset{\sim}{p} \underset{\sim}{r}} v(\underset{\sim}{k}; \underset{\sim}{l}, \underset{\sim}{p}, \underset{\sim}{r}) \delta_{\underset{\sim}{k}+\underset{\sim}{l}-\underset{\sim}{p}-\underset{\sim}{r}, \underset{\sim}{l}} \times$$

$$\Big\{\eta^{\nu'_k+\nu'_l+\nu'_p+\nu'_r}\Big[(N_k+\tfrac{1}{2})(N_l+\tfrac{1}{2})\,(N_p+\tfrac{1}{2})(N_r+\tfrac{1}{2})\Big]^{1/2}\times$$

$$\times\,\eta^{-\nu_k-\nu_l-\nu_p-\nu_r}-\eta^{-\nu'_k-\nu'_l-\nu'_r-\nu'_p}\Big[(N_k+\tfrac{1}{2})(N_l+\tfrac{1}{2})$$

$$(N_p+\tfrac{1}{2})(N_r+\tfrac{1}{2})\Big]^{1/2}\eta^{\nu_k+\nu_l+\nu_p+\nu_r}\Big\}\delta_{\nu'_k,\,\nu_k-1}\,\delta_{\nu'_l,\,\nu_l-1}\times$$

$$\text{(V.2.15)}\quad\times\,\delta_{\nu'_p,\,\nu_p+1}\,\delta_{\nu'_r,\,\nu_r+1}\prod_{i\neq klpr}\delta_{\nu'_i,\,\nu_i}\,\delta_{\underset{\sim}{\kappa}',\,\underset{\sim}{\kappa}}$$

$$+(\lambda/\Omega)\sum_{kl}u(k-l)\Big\{\eta^{\nu'_k+\nu'_l}\zeta^{\underset{\sim}{\kappa}'}\Big[(N_k+\tfrac{1}{2})(N_l+\tfrac{1}{2})\Big]^{1/2}\times$$

$$\times\,\eta^{-\nu_k-\nu_l}\zeta^{-\underset{\sim}{\kappa}}-\eta^{-\nu'_k-\nu'_l}\zeta^{-\underset{\sim}{\kappa}'}\Big[(N_k+\tfrac{1}{2})(N_l+\tfrac{1}{2})\Big]^{1/2}\times$$

$$\times\,\eta^{\nu_k+\nu_l}\zeta^{\underset{\sim}{\kappa}}\Big\{\delta_{\nu_k,\,\nu_k-1}\,\delta_{\nu'_l,\,\nu_l+1}\prod_{i\neq kl}\delta_{\nu'_i,\,\nu_i}\times$$

$$\times\,\delta_{\underset{\sim}{k}-\underset{\sim}{l},\,\underset{\sim}{\kappa}-\underset{\sim}{\kappa}'}$$

The external hamiltonian is given by :

$$\langle\underset{\sim}{\kappa},\{\nu\}|\mathcal{H}_E|\underset{\sim}{\kappa}',\{\nu'\}\rangle = ieE\cdot\frac{\partial}{\partial\underset{\sim}{P}}\times$$

$$\text{(V.2.16)}\qquad\times\,\delta_{\underset{\sim}{\kappa},\,\underset{\sim}{\kappa}'}\prod_k\delta_{\nu_k,\,\nu'_k}$$

The algebra which leads to these results is very simple. We give examples in Appendix VI.1.

The equation (VI.2.12) can be treated in the same way as the Liouville equation. Whenever we had a matrix element of the classical Liouville operator, we must now replace it by a matrix element of the Von Neumann Liouville operator . If we compare those matrix elements,

we notice that the main difference between quantum and classical matrix elements is the appearance of displacements operators in the former while we had differential operators in the latter. This is specially striking for the operators acting on the heavy particle variables: the classical operator $\partial / \partial P$ is now replaced by the displacement operator $\xi^{\pm \underset{\sim}{\kappa}}$; this is due to the fact that we used a plane wave representation in the quantum case which is the analog of the Fourier expansion in the position variables in the classical case. For the fluid particles, the similarity is also very striking when one compares the quantum equation to the Liouville equation for a system of oscillators in action (J) - angle (α) variables). The displacement operators acting on the N variables are the analog of the differential operators acting on the action variables in the classical problem (for more details see [5)6)]).

VI.3 - Stationary transport equation.

The quantum analog of the stationary transport equation (II.14.5) in a static field will be :

$$(VI.3.1) \quad i \underset{\sim}{\kappa}_E \rho_o^{equ}(P, \{N\}) + i \sum_{\underset{\sim}{\kappa} \{\nu\}} D_{\underset{\sim}{\kappa} \{\nu\}}(0) \underset{\sim}{\kappa}_E C_{\{\nu\} \underset{\sim}{\kappa}}(0) \rho_o^{equ}(\underset{\sim}{P}, \{N\})$$

$$(V.3.1) \quad = i \psi(0) \Delta \rho_o(\underset{\sim}{P}, \{N\})$$

Here $\rho_o(P, \{N\})$ represents the diagonal elements of the Von Neumann matrix. At equilibrium, we have in the $|\{n\}, \underset{\sim}{K}\rangle$ representation:

$$(VI.3.2) \quad \langle \{n\}, \underset{\sim}{K} | \rho^{equ} | \{n\}, \underset{\sim}{K} \rangle = \langle \{n\}, \underset{\sim}{K} | e^{-(H_o + \lambda V)/kT} | \{n\}, \underset{\sim}{K} \rangle \times$$

$$\times \left[\sum_{\{n'\}, \underset{\sim}{K}'} \langle \{n'\}, \underset{\sim}{K}' | e^{-(H_o + \lambda V)/kT} | \{n'\}, \underset{\sim}{K}' \rangle \right]^{-1}$$

Because of the non commutativity of H_o and V, this expression is much less simple, if all orders in λ are kept, than the corresponding classical expression. It is only in the weak coupling case, where we can neglect the interaction that we obtain :

$$\langle \{n\}\, \underset{\sim}{K} | \rho^{equ}_{\lambda \to 0} | \{n\}, K \rangle = \exp\left\{ -\left[\sum_{\underset{\sim}{k}} \frac{k^2}{2m}\, n_{\underset{\sim}{k}} + \frac{K^2}{2M} \right] \Big/ k\, T \right\} \times$$

(VI. 3. 3)
$$\times \left[\sum_{\{n\}\, \underset{\sim}{K}} \exp\left\{ -\left[\sum_{\underset{\sim}{k}} \frac{k^2}{2m} n_{\underset{\sim}{k}} + \frac{K^2}{2M} \right] \Big/ k\, T \right\} \right]^{-1}$$

$$\text{or } \rho^{equ}_{o\ \lambda \to o}(\underset{\sim}{P}, \{N\}) = \exp\left\{ -\left[\sum_{\underset{\sim}{k}} \frac{k^2}{2m}\, N_{\underset{\sim}{k}} + \frac{P^2}{2M} \right] \Big/ kT \right\} \times$$

(VI. 3. 4)
$$\times \left[\sum_{\{N\}\, \underset{\sim}{P}} \exp\left\{ -\left[\sum_{\underset{\sim}{k}} \frac{k^2}{2m}\, N_{\underset{\sim}{k}} + \frac{P^2}{2M} \right] \Big/ kT \right\} \right]^{-1}$$

This will play an important role in our discussion of the validity of the Fokker-Planck equation in the quantum case .

The collision operator ψ is given by :

(VI. 3. 5)
$$\psi(0) = \lim_{z \to 0} \langle 0 | W \sum_{n=1}^{\infty} \left(\frac{1}{z - \chi_o} W \right)^n | 0 \rangle_{irr}$$

while for the operators of creation or destruction of correlations we have :

(VI. 3. 6)
$$C_{\underset{\sim}{k}\{\nu\}}(0) = \lim_{z \to 0} \langle \underset{\sim}{k}\{\nu\} | \sum_{n=1}^{\infty} \left(\frac{W}{z - \chi_o} \right)^n | 0 \rangle_{irr}$$

(VI. 3. 7)
$$D_{\underset{\sim}{k}\{\nu\}}(0) = \lim_{z \to 0} \langle 0 | \sum_{n=1}^{\infty} \left(W \frac{}{z - \chi_o} \right)^n | \underset{\sim}{k}\{\nu\} \rangle_{irr}$$

The index irr means that only irreducible contributions have to be kept, i.e. contributions such that no intermediate state is identical to the vacuum of correlations (diagonal elements of the Von Neumann matrix).

As in the classical problem , we assume molecular chaos ; hence :

(VI.3.8) $$\rho_o^{equ}(\underset{\sim}{P},\{N\}) = \varphi^{equ}(\underset{\sim}{P})\{\rho_o^f(N)\}_{equ}$$

(VI.3.9) $$\Delta\rho_o(\underset{\sim}{P},\{N\}) = \delta\varphi(\underset{\sim}{P})\{\rho_o^f(N)\}_{equ}$$

if we take into account the fact that the modification of the density matrix of a fluid particle is of order N^{-1}, hence negligible in the limit of a large system.

VI.4 - Expansion in the mass ratio.

Whenever the ratio $\langle p\rangle/P$ satisfies the relation

(VI.4.1) $$\langle p\rangle/P = 0\,(m/M)^{1/2} = 0(\gamma)$$

we easily obtain an expansion in the mass ratio if we follow the same procedure as in the classical case. We decompose the unperturbed operator $\mathcal{H}_o$:

(VI.4.2) $$\mathcal{H}_o = \mathcal{H}_o^f + \gamma\mathcal{H}_o^A$$

with (VI.4.3) $$\langle\{\nu\}\underset{\sim}{x}|\mathcal{H}_o^f|\{\nu'\}\underset{\sim}{x}'\rangle = \sum_{\underset{\sim}{k}}(k^2/2m)\nu_{\underset{\sim}{k}}\prod_{\underset{\sim}{k}}\delta_{\nu_{\underset{\sim}{k}},\nu'_{\underset{\sim}{k}}}\,\delta_{\underset{\sim}{x},\underset{\sim}{x}'}$$

(VI.4.4) $$\langle\{\nu\},\underset{\sim}{x}|\gamma\mathcal{H}_o^A|\{\nu'\},\underset{\sim}{x}'\rangle = (\underset{\sim}{x}.\underset{\sim}{P})/M\prod_{\underset{\sim}{k}}\delta_{\nu_{\underset{\sim}{k}},\nu'_{\underset{\sim}{k}}}\,\delta_{\underset{\sim}{x},\underset{\sim}{x}'}$$

Similarily :

(VI.4.5) $$\mathcal{W} = \mathcal{W}^f + \gamma\mathcal{V}_1^A + \gamma^2\mathcal{V}_2^A + \ldots$$

where

(VI.4.6) $$\mathcal{W}^f = \mathcal{V} + \mathcal{V}_o^A$$

where $\mathcal{V}$ represents the fluid-fluid interaction (first term in the rhs

of (VI. 2. 15) . $\mathcal{U}^A$ is the fluid-particle interaction (second term in the rhs of (VI. 2. 15) . If one expands the displacement operators $\zeta^{\pm\frac{\varkappa}{2}}$ in a power series, one easily obtains an expansion of $\mathcal{U}^A$ in a power series of γ . For instance, $\mathcal{U}^A_o$ is obtained by the mere replacement of the displacement operators by unity :

$$\left\langle \{\nu\}, \frac{\varkappa}{2} \middle| \mathcal{U}^A_o \middle| \frac{\varkappa'}{2}, \{\nu'\} \right\rangle = \left\langle \left\{N + \frac{\nu}{2}\right\}, \frac{\varkappa}{2} \middle| U \middle| \left\{N - \frac{\nu}{2} + \nu'\right\}, -\frac{\varkappa}{2} + \varkappa' \right\rangle \eta^{\sum_k (\nu'_k - \nu_k)}$$

(VI. 4. 7)
$$- \left\langle \left\{N + \frac{\nu}{2} - \nu'\right\}, \frac{\varkappa}{2} - \varkappa' \middle| U \middle| \left\{N - \frac{\nu}{2}\right\}, -\frac{\varkappa}{2} \right\rangle \eta^{\sum_k (-\nu'_k + \nu_k)}$$

while

$$\left\langle \{\nu\}, \frac{\varkappa}{2} \middle| \mathcal{U}^A_1 \middle| \frac{\varkappa'}{2}, \{\nu'\} \right\rangle = (\lambda/\Omega) \sum_{kl} u\left(\frac{k}{2} - \frac{l}{2}\right) \left\{ \eta^{\nu'_k + \nu'_l} \times \right.$$

$$\times \left[\left(N_k + \frac{1}{2}\right)\left(N_l + \frac{1}{2}\right) \right]^{1/2} \eta^{-\nu_k - \nu_l} + \eta^{-\nu'_k - \nu'_l} \left[\left(N_k + \frac{1}{2}\right)\left(N_l + \frac{1}{2}\right) \right]^{1/2} \times$$

$$\left. \eta^{\nu_k + \nu_l} \right\} \delta_{\nu'_k, \nu_k - 1} \delta_{\nu'_l, \nu_l + 1} \prod_{i \neq kl} \delta_{\nu'_i, \nu_i} \delta_{k-l, \varkappa - \varkappa'} \times$$

(VI. 4. 8)
$$\times \frac{1}{2} (\varkappa - \varkappa') \cdot \frac{\partial}{\partial P}$$

$$= \left\{ \left\langle \left\{N + \frac{\nu}{2}\right\}, \frac{\varkappa}{2} \middle| U \middle| \left\{N - \frac{\nu}{2} + \nu'\right\}, \varkappa' - \frac{\varkappa}{2} \right\rangle \eta^{\sum_k (\nu'_k - \nu_k)} \right.$$

$$\left. + \left\langle \left\{N + \frac{\nu}{2} - \nu'\right\}, \frac{\varkappa}{2} - \varkappa' \middle| U \middle| \left\{N - \frac{\nu}{2}\right\}, -\frac{\varkappa}{2} \right\rangle \eta^{\sum_k (\nu_k - \nu'_k)} \right\} \frac{1}{2} (\varkappa' - \varkappa) \cdot \frac{\partial}{\partial P}$$

The external field contribution is, as in the classical case, of order γ . The main difference with the classical case is the appearance of higher order terms in the expansion of $\mathcal{U}^A$. However, one verifies easily again , that, to lowest order in γ , the equation may be written ;

$$i\gamma \langle 0|\mathcal{H}_E|0\rangle \varphi^{equ}(\underset{\sim}{P}) = \lim_{z\to 0} \gamma^2 \int_o^\infty dt \sum_{\{N\}} \langle 0|\mathcal{V}_1^A \; e^{-i(\mathcal{H}^f - z)t} \; \times$$

(VI.4.9)

$$\times \; (\mathcal{V}_1^A + \mathcal{H}_o^A) \rho^f_{equ} |0\rangle \delta\varphi(\underset{\sim}{P})$$

where

$$\mathcal{H}^f = \mathcal{H}^f_o + \mathcal{W}^f \qquad \text{(VI.4.10)}$$

Moreover, at this order, we can restrict ourselves to the lowest order term $\varphi^{equ}_o(\underset{\sim}{P})$ in the equilibrium distribution function.

Hence , we have :

$$i\gamma \langle 0|\mathcal{H}_E|0\rangle \varphi^{equ}_o(\underset{\sim}{P}) = \lim_{z\to 0} \gamma^2 \int_o^\infty dt \sum_{\underset{\sim}{\{N\}}\{\nu\}} \langle 0|\mathcal{V}_1^A \; \times$$

(VI.4.11)

$$\times \; e^{-i(\mathcal{H}^f - z)t} \; (\mathcal{V}_1^A + \mathcal{H}_o^A)|\{\nu\}, \underset{\sim}{\kappa}\rangle (\rho^f_{\{\nu\}\underset{\sim}{\kappa}})_{equ} \delta\varphi(\underset{\sim}{P})$$

where

$$(\rho^f_{\{\nu\}\underset{\sim}{\kappa}})_{equ} = \frac{\int d\underset{\sim}{R} \; e^{-i\underset{\sim}{\kappa}.\underset{\sim}{R}} \langle \{N + \nu/2\}|e^{-H^f/kT}|\{N - \nu/2\}\rangle}{\sum_{\{N\}} \langle \{N\}|e^{-H^f/kT}|\{N\}\rangle} \qquad \text{(VI.4.12)}$$

where

$$H^f = H^o_f + V$$

is the fluid hamiltonian operator

VI.5 - Fokker-Planck equation.

Let us consider the rhs of (VI.4.11) at t=0 (the calculation of the contribution involving twice $\mathcal{V}_1^A$ at a time t different from zero is given in appendix VI.2). For the contribution involving twice $\mathcal{V}_1^A$, we have*:

$$\alpha = \sum_{\{N\}} \sum_{\{\nu\}\{\nu'\}} \sum_{\underset{\sim}{\kappa}\underset{\sim}{\kappa}'} \langle 0|\mathcal{V}_1^A|\underset{\sim}{\kappa}, \{\nu\}\rangle \langle \{\nu\}, \underset{\sim}{\kappa}|\mathcal{V}_1^A|\underset{\sim}{\kappa}', \{\nu'\}\rangle \; \times$$

(VI.5.1)

$$\times \left[\rho^f_{\underset{\sim}{\kappa}', \{\nu'\}}(\{N\})\right]_{equ}$$

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*When no confusion is possible , we do no longer use a special notation for vectors.

Using (VI.4.8) , we obtain :

$$\sum_{\{\nu'\}\varkappa'} \langle \varkappa,\{\nu\}\,|\,U_1^A\,|\varkappa'\{\nu'\}\rangle \left[\rho^f_{\varkappa',\{\nu'\}}(\{N\})\right]_{equ}$$

$$= (\lambda/\Omega) \sum_{kl} u(k-\ell) \Big\{ \Big[(N_k + \nu'_k/2)\,(N_l+1+\nu'_l/2) \Big]^{1/2} \times$$

$$\text{(VI.5.2)} \times \Big[\rho^f_{\{\nu'\},\nu'_k-1,\,\nu'_l+1,\,\varkappa'-k+\ell}\,(\{N\}',\,N_k-1,\,N_l+1) \Big]_{equ} + (N_k+1-\nu'_k/2) \times$$

$$\times\,(N_l - \nu'_l/2)\Big]^{1/2} \Big[\rho^f_{\{\nu'\},\nu'_k-1,\,\nu'_l+1,\,\varkappa'-k+1}(\{N\}',\,N_k+1,\,N_l-1)\Big] \Big\} \times$$

$$(1/2)(1-k)\cdot \frac{\partial}{\partial P}$$

Going back to the occupation number-plane wave representation we obtain :

$$\sum_{\{\nu'\}\varkappa'} \langle \varkappa\{\nu\}\,|\,U_1^A\,|\varkappa'\{\nu'\}\rangle \left[\rho^f_{\varkappa'\{\nu'\}}(\{N\})\right]_{equ} =$$

$$\text{(VI.5.3)} \qquad \sum_{i=x,y,z} \sum_K \langle \{N+\nu/2\}\,|\,F_i(K)\,\rho^f_{\varkappa-K} + \rho^f_{\varkappa-K}\,F_i(K)\,|\,\{N-\nu/2\}\rangle \frac{\partial}{\partial P_i}$$

where the force operator is given by :

$$\text{(VI.5.4)} \qquad F_i(K) = \sum_k u(K)\,K_i\,a_k^+\,a_{K-k}$$

Therefore, we have :

$$\alpha = \sum_{\{N\}} \sum_{\{\nu\}} \sum_{\varkappa} \langle 0\,|\,U_1^A\,|\varkappa\{\nu\}\rangle \sum_i \sum_K \langle \{N+\nu/2\}\,|\,F_i(K)\,\rho^f_{\varkappa-K}$$

$$+ \rho^f_{\varkappa-K} F_i(K)\,|\,\{N-\nu/2\}\rangle (1/2) \frac{\partial}{\partial P_i}$$

$$= \sum_{\{N\}} \sum_{ij} \sum_{K} \sum_{\varkappa} \Big\{ \langle \{N\} | U | \{N+\nu\}, \varkappa \rangle \langle \{N+\nu\} | F_i(K) \rho^f_{\varkappa - K} + \rho^f_{\varkappa - K} F_i(K) | \{N\} \rangle$$

$$+ \langle \{N-\nu\}, -\varkappa | U | \{N\} \rangle \langle \{N\} | F_i(K) \rho^f_{\varkappa - K} + \rho^f_{\varkappa - K} F_i(K) | \{N - \tfrac{\nu}{2}\} \rangle \Big\} \times$$

$$\times (1/4) \frac{\partial^2}{\partial P_i \partial P_j} \varkappa_j$$

(VI.5.5)

$$= \sum_{\{N\}} \sum_{ij} \sum_{\varkappa K} \langle \{N\} | F^\dagger_j(\varkappa) F_i(K) \rho^f_{\varkappa - K} + F^\dagger_j(\varkappa) \rho^f_{\varkappa - K} F_i(K)$$

$$+ F_i(K) \rho^f_{\varkappa - K} F^\dagger_j(\varkappa) + \rho^f_{\varkappa - K} F_i(K) F^\dagger_j(\varkappa) | \{N\} \rangle \frac{1}{4} \frac{\partial^2}{\partial P_i \partial P_j}$$

Taking into account the fact that we can interchange $\varkappa, K$ and i and j, and that the trace of a product of operators the invariance for cyclic permutations of the operators, as well as the hermiticity properties of the operators, we obtain :

$$\alpha = \sum_{\{N\}} \sum_{ij} \sum_{K} \sum_{\varkappa} \langle \{N\} | F^\dagger_i(K) F_j(\varkappa) \rho^f_{\varkappa - K} | \{N\} \rangle \frac{\partial^2}{\partial P_i \partial P_j}$$

(VI.5.6)

$$= \langle F^\dagger_i F_j \rangle \frac{\partial^2}{\partial P_i \partial P_j}$$

As in the classical case, we see that we have here the average over the fluid equilibrium distribution of the tensor operator FF.

As to the second term, at $t = 0$, we have :

$$\beta = \sum_{\{N\}} \sum_{\{\nu\}} \sum_{\varkappa} \langle 0 | U^A_1 | \varkappa + \nu \rangle \langle \varkappa + \nu | \chi^0_A | \varkappa + \nu \rangle \left[\rho^f_{\varkappa + \nu} \right]_{\text{équ.}}$$

(VI.5.7)

$$= \sum_{\{N\}} \sum_{ij} \sum_{\varkappa} \langle \{N\} | F^\dagger_i(\varkappa) \varkappa_j \rho^f_{\varkappa} + \varkappa_j \rho^f_{\varkappa} F^\dagger_i(\varkappa) | \{N\} \rangle \frac{\partial}{\partial P_i} (P_j / M)$$

Now we have , performing an integration by parts in the second step,

$$\langle \{n'\}| k_j \rho^f_k |\{n\}\rangle = \int d\underset{\sim}{R}\ k_j\ e^{-ik\underset{\sim}{R}} \langle \{n'\}|\ e^{-H^f/kT}\ |\{n\}\rangle \times$$

$$\times \left[\sum_n \langle \{n\}|\ e^{-H^f/kT}\ |\{n\}\rangle\right]^{-1}$$

$$(VI.5.8) = \sum_{\{n''\}} \sum_{\underset{\sim}{k}'} \int d\underset{\sim}{R}\ e^{-i(k+k')R} \langle \{n'\}|\ F_j(k')\ |\{n''\}\rangle (kT)^{-1} \langle \{n''\}|\ e^{-H^f/kT}\ |\{n\}\rangle \times$$

$$\times \left[\sum_{\{n\}} \langle \{n\}|\ e^{-H^f/kT}\ |\{n\}\rangle\right]^{-1}$$

$$= \sum_{k'} \langle \{n'\}|\ F_j(k')\ \rho^f_{k+k'}\ |\{n\}\rangle$$

and therefore :

$$(VI.5.9) \quad \sum_{\{N\}} \langle 0|\mathcal{U}^A_1\ \mathcal{K}^A_o\ \rho^f_{equ}\ |0\rangle = \langle F^+_i\ F_j\rangle \frac{\partial}{\partial P_i}\ (P_j/kTM)$$

Therefore, at $t = 0$, the integrand in the rhs of (VI.4.11) becomes :

$$(VI.5.10) \qquad \langle F^+_i\ F_j\rangle \frac{\partial}{\partial P_i}\left[\frac{\partial}{\partial P_j} + \frac{1}{kTM}\ P_j\right]$$

In appendix VI.2, we show that the first term, at a time t different from zero, is identical to (VI.5.6) but with F_i replaced by $F_i(t)$ where $F_i(t)$ is the Heisenberg representation of the force operator:

$$(VI.5.11) \qquad F_i(t) = e^{-iH^f t}\ F_i\ e^{iH^f t}$$

A similar proof can be given for the second term and we obtain finally the Fokker-Planck form of (VI.4.11) :

$$(VI.5.12) \quad i\gamma \langle 0|\mathcal{K}_E\ |0\rangle \varphi^{equ}_o(P) = \zeta_{ij} \frac{\partial}{\partial P_i}\left[\frac{\partial}{\partial P_j} + \frac{1}{MkT}\ P_j\right] \delta\varphi(P)$$

where the diffusion coefficient in terms of microscopic quantities is given by

$$\zeta_{ij} = \int_0^\infty dt \, \langle F_i(t) \, F_j^+ \rangle \tag{VI.5.13}$$

As it can also be shown that, to first order in γ, we have*:

$$\varphi_o^{equ}(P) = (M/2\pi kT)^{3/2} \, 4\pi \exp(-P^2/2MkT) \tag{VI.5.14}$$

we have :

$$-(1/MkT) \, \underset{\sim}{E}.\underset{\sim}{P} \, \varphi_o^{equ}(P) = \zeta_{ij} \frac{\partial}{\partial P_i}\left[\frac{\partial}{\partial P_j} + \frac{1}{MkT} P_j\right]\varphi(P) \tag{VI.5.15}$$

This completes our outline of the derivation of the Fokker-Planck equation in the quantum case. Let us stress that this equation is valid whenever the condition :

$$\langle p \rangle / P \ll 1 \tag{VI.5.16}$$

is satisfied.

VI.6 - Diffusion coefficient for a heavy ion in a slightly imperfect Bose fluid.

In a weakly coupled Bose gas, the condition (VI.5.16) for the validity of the Fokker-Planck equation would always be fulfilled. When strong interactions are present, the zero point motion of both kind of particles starts to play a role and it is difficult to make general assertions.

We shall assume that the interaction between the fluid and the

*One can for instance use an expansion of φ^{equ} in powers of γ. As we must have : $\phi(0)\varphi^{equ} = 0$, we have $\phi^{(2)}(0) \, \varphi_o^{equ} = 0$. But as we have just seen, $\phi^{(2)}(0)$ is the Fokker - Planck operator : hence φ_o^{equ} must be the Boltzmann distribution.

heavy ion is very weak and that we can neglect it in H^f. We shall also restrict ourselves to a slightly imperfect Bose fluid and assume that the temperature is sufficiently low to insure that the Bose-Einstein condensation has already occurred to a large extend. Then most of the bosons are in the ground state and we have :

$$n_o \simeq N \tag{VI.6.1}$$

where n_o is the number of particles in the ground state. Then we can apply the well-known assumption :

$$a_o \simeq a_o^+ \simeq (n_o)^{1/2} \tag{VI.6.2}$$

The force operator becomes :

$$\begin{aligned} \underset{\sim}{F}(k) = {} & \Omega^{-1} \sum_{\underset{\sim}{k}} u(k) \sqrt{n_o}\, (a_k^+ - a_k) \\ & + \Omega^{-1} \sum_{l \neq 0} \underset{\sim}{k}\, u(k)\, a_l^+ a_{l-k} \end{aligned} \tag{VI.6.3}$$

while , if we use a pseudopotential (see ref. [4]) with $U \simeq 4\pi a/m$ (a: radius of the particles) :

$$\begin{aligned} V = (U/2\Omega) \Big[& n_o^2 + 2n_o \sum_{p \neq 0} (a_{-p}^+ a_p + a_p^+ a_{-p}) \\ & + n_o \sum_{p=0} (a_p^+ a_{-p}^+ + a_p^+ a_{-p}) \Big] \end{aligned} \tag{VI.6.4}$$

We shall use the Bogoliubov transformation to phonons operators b_k and b_k^+. (see for instance ref [4]) :

$$a_k = g_k b_k + f_k b_{-k}^+ \tag{VI.6.5}$$

$$a_k^+ = g_k b_k^+ + f_k b_{-k} \tag{VI.6.6}$$

$$g_k = (1 - \alpha_k^2)^{1/2} \tag{VI.6.7}$$

(VI.7.8) $$f_k = \alpha_k (1 - \alpha_k^2)^{-1/2}$$

(VI.6.9) $$\alpha_k = 1 + x^2 - x(x^2+2)$$

(VI.6.10) $$x^2 = k^2 \Omega / 8\pi a n_o = k^2/c^2$$

This transformation does not change the commutation rules and we have

(VI.6.11) $$b_k^+ |n_k\rangle = \sqrt{n_k+1}\, |n_k+1\rangle \; ; \; b_k |n_k\rangle = \sqrt{n_k}\, |n_k-1\rangle$$

(VI.6.12) $$H^f = E_o + \sum_k \omega_k b_k^+ b_k$$

(VI.6.13) $$\omega_k = (k/2M)(k^2 + 16\pi a n_o \Omega^{-1})^{1/2}$$

Similarly, the force operator can be written in the phonon representation b_k, b_k^+. In this representation, it is a matter of algebra to compute the diffusion coefficient (see an example of computation in the next paragraph for Fermi systems). One obtains [2], if one restricts oneself to small wave numbers (i.e. to the linear term in the dispersion relation (VI.6.13)):

$$\zeta_{ij} = (\pi/\Omega^2) \sum_{kl} k_i k_j \, (f_l^2 f_{l-k}^2 + g_l^2 g_{l-k}^2) \, m_l^o (m_{l-k}^o + 1)$$

(VI.6.14) $$\delta(|l-k| - l)$$

m_l^o is the distribution function in a slightly imperfect Bose gas in the limit of small momentum :

(VI.6.15) $$m_l^o = \left[\exp(\omega_l/kT) - 1\right]^{-1} = \left[\exp(cl/kT) - 1\right]^{-1}$$

The integrations can be performed and one obtains, if one reintroduces

explicitly Planck's constant :

$$\zeta = (2\pi^3/45(kT)^5\ a^2\ \hbar^{-3}\ c^{-4} \qquad \text{(VI.6.16)}$$

The mobility of a heavy ion is given by [5]:

$$\mu = eD/kT \qquad \text{(VI.6.18)}$$

where D is the diffusion coefficient in ordinary space. As we have seen in chapter I, we have :

$$D = (kT/M\beta) = (kT/M)^2(M/kT\beta) = (kT/M)^2(M^2/\zeta) \qquad \text{(VI.6.19)}$$

(note that D is the coefficient appearing in the diffusion equation in ordinary space, $(M/kT\beta)^{-1}$ that appearing in the Fokker-Planck equation in velocity space, ζ that appearing in the Fokker-Planck equation in momentum space).

Therefore we obtain :

$$\mu = (45/2\pi^3)\, e\, \hbar^3\ c^4\ a^{-2}(KT)^{-4} \sim T^{-4} \qquad \text{(VI.6.20)}$$

In a measure of the static mobility of $(He^+)_n$ in liquid He^4 at low temperature, Meyer and Reif [5] have found :

$$\mu \sim T^k \quad \text{with} \quad k = -3.3 \pm 0.3 \qquad \text{(VI.6.21)}$$

which is in good agreement with the above result if one takes into account the fact that our model is quite rough .

VI.7 - Diffusion of a heavy ion in a weakly coupled Fermi fluid.

We have seen in the introduction that in a Fermi fluid, at low temperature, the Fokker-Planck equation is valid only if the condition (VI.1.4) is satisfied. We shall discuss again this problem in the next paragraph but presently we consider a situation where this condition is

satisfied and compute the diffusion coefficient, assuming the fluid to be weakly coupled.

As well known, in a Fermi system, the creation and destruction operators anticommute

$$\left[a_k^+ \ , a_k\right]_+ = 1 \tag{VI.7.1}$$

and the only possible values of the occupation numbers are :

$$n_k = 0 \quad \text{or} \quad 1 \tag{VI.7.2}$$

In order to avoid difficulties with the subsidiary condition

$$\sum_k n_k = N \tag{VI.7.2}$$

we shall consider the grand canonical ensemble . Then the equilibrium distribution for a weakly coupled system is given by :

$$\langle \{n\} | \rho^f_{\varkappa - K} | \{n'\} \rangle = \prod_k \delta_{n_k, n'_k} \exp\left[- \sum_k n_k (k^2/2m - \varepsilon_F)/kT \right] \times$$

$$\times \prod_k \left\{ 1 + \exp\left[- (k^2/2m - \varepsilon_F)/kT \right] \right\}^{-1} \delta_{\varkappa, K} \tag{VI.7.4}$$

where ε_F is the Fermi energy .

Thus, going back to the occupation number representation we have :

$$\langle F_i(t) F_j^+ \rangle = \sum_{\{n\}} \sum_{\{n'\}} \sum_{\{n''\}} \sum_{\{n'''\}} \sum_{\{n''''\}} \sum_k \sum_l \sum_{l'} |u(k)|^2 \times$$

$$\times \ k_i k_j \langle \{n\} | \exp\left[-i \sum_k (k^2/2m) a_k^+ a_k t \right] | \{n'\} \rangle \langle \{n'\} | a_k^+ a_{k-l} | \{n''\} \rangle \times$$

$$(VI.7.5)\quad \times \langle \{n''\} | \exp\left[i \sum_k (k^2/2m) a_k^+ a_k t\right] | \{n'''\} \rangle \langle \{n'''\} | a_k a_{k-1'}^+ | \{n''''\} \rangle \times$$

$$\times \langle \{n''''\} | \rho_o^f | \{n\} \rangle$$

Using

$$(VI.7.6)\qquad a_k^+ | n_k \rangle = | n_k + 1 \rangle \, \delta_{n_k\, 0}$$

$$(VI.7.7)\qquad a_k | n_k \rangle = n_k - 1 \, \delta_{n_k,\, 1}$$

one easily verifies that one must have :

$$(VI.7.8)\qquad 1 = 1'$$

and one obtains :

$$\langle F_i(t) F_j^+ \rangle = (\lambda^2/\Omega^2) \sum_{\{n\}} \sum_k \sum_l |u(k)|^2 \, k_i k_j \, \delta_{n_k,\, 1} \, \delta_{n_{k-1},\, 0} \times$$

$$\times \exp\left[-i \{k^2 - (k-1)^2\} t/2m\right] \exp\left[- \sum_k n_k (k^2/2m - \varepsilon_F)/kT\right] \times$$

$$\times \prod_k \left\{1 \exp\left[- (k^2/2m - \varepsilon_F)/kT\right]\right\}^{-1}$$

$$(VI.7.9)\qquad = (\lambda^2/\Omega^2) \sum_k \sum_{k'} |u(k)|^2 \, k_i k_j \exp\left[-i (k^2 - k'^2) t/2m\right] \times$$

$$\times \exp\left[- (k^2/2m - \varepsilon_F)/kT\right] \left\{1 + \exp\left[- (k^2/2m - \varepsilon_F)/kT\right]\right\}^{-1} \times$$

$$\times \left\{1 + \exp\left[-(k'^2/2m - \varepsilon_F)/kT\right]\right\}^{-1}$$

At the limit of a large system, the summations over k and l become integrals. If we also perform the asymptotic time integration in (VI.5.13) , we obtain

$$\zeta_{ij} = 2m \pi \lambda^2 \int d^3k \int d^3k' \, |u(k)|^2 \, k_i k_j \, \delta(k^2 - k'^2) \exp\left[+ (k^2/2m - \varepsilon_F)/kT\right] \times$$

$$(VI.7.10)\qquad \times \left\{1 + \exp\left[(k^2/2m - \varepsilon_F)/kT\right]\right\}^{-1} \left\{1 + \exp\left[(k'^2/2m - \varepsilon_F)/kT\right]\right\}^{-1}$$

One easily verifies that this tensor is diagonal and that one has :

$$\underline{\underline{\zeta}} = \frac{1}{3}\,\zeta \tag{VI.7.11}$$

with

$$\zeta = (16\pi^3 m/3)\int_0^\infty dk k^3 \int_0^\infty dk' k'^2 |u(k)|^2 \left[\delta(k-k') + \delta(k+k')\right] \times$$

$$\times \exp\left[(k'^2/2m - \varepsilon_F)/kT\right]\left\{1 + \exp\left[(k^2/2m - \varepsilon_F)/kT\right]\right\}^{-1} \times \tag{VI.7.12}$$

$$\times \left\{1 + \exp\left[(k'^2/2m - \varepsilon_F)/kT\right]\right\}^{-1}$$

We integrate over k' and approximate the potential by a constant; we then have :

$$\zeta = (128/3)\pi^3 (kT)^3 m^4 u^2 \int_0^\infty d\varepsilon\, \varepsilon^2 e^{(\varepsilon - \xi^2)}\left\{1 + e^{(\varepsilon - \xi^2)}\right\}^{-2}$$

$$= -(128/3)\pi^3 m^4 u^2 (kT)^3 \int_0^\infty d\varepsilon\, \varepsilon^2 \frac{d}{d\varepsilon}\left\{1 + e^{(\varepsilon - \xi^2)}\right\}^{-1} \tag{VI.7.13}$$

$$= (256/3)\pi^3 m^4 (kT)^3 u^2 \int_0^\infty d\varepsilon\varepsilon\left[1 + e^{(\varepsilon - \xi^2)}\right]^{-1}$$

where

$$\xi = (\varepsilon_F/kT)^{1/2} \tag{VI.7.14}$$

At sufficiently low T, we have :

$$\xi \gg 1 \tag{VI.7.15}$$

and we may write :

$$\int_0^\infty d\varepsilon\,\varepsilon\left[1 + e^{(\varepsilon - \xi^2)}\right]^{-1} = \int_{-\xi^2}^\infty dy\,(y+\xi^2)(1+e^y)^{-1}$$

$$= \xi^2 \int_{-\xi^2}^\infty dy\,(1+e^y)^{-1} + \int_{-\xi^2}^0 dy\,y + 2\int_0^\infty dy\,y\,(1+e^y)^{-1}$$

$$- \int_{\xi^2}^\infty dy\,y\,(1+e^y)^{-1} \tag{VI.7.16}$$

$$= \xi^4/2 + \pi^2/6$$

where we have neglected exponentially decreasing contributions in the first integral as well as the last one whose integrand is exponentially small.

Therefore, we obtain :

$$(VI.7.17) \qquad \zeta = (128/3)\,\pi^3\, m^4\, kT\, u^2 \left\{ \varepsilon_F^2 + (\pi^2/3)(kT)^2 \right\}$$

From this, we easily obtain the mobility (see VI.6.18). Introducing $\hbar$ and the collision cross section σ in the Born approximation ($\sigma = 2m\,\pi\,u^2$), we obtain :

$$(VI.7.18) \qquad \mu = \frac{3\,\pi\, e\hbar^3}{8m^2\sigma \left\{ \varepsilon_F^2 + (\pi^2/3)\,(kT)^2 \right\}}$$

Davis and Dagonnier[1] compared this result with the experimental mobility for a heavy ion in liquid He^3 at 1.2 °K measured by Meyer and al.[6]. However, the comparison is not very easy because of the lack of information about the collision cross section (radius of the ion) and the effective mass of the ion. With reasonable estimates for these quantities, they find a good agreement.

VI.8 - Validity of the Fokker-Planck equation for brownian motion in quantum systems.

Let us first consider again the case of motion in a weakly coupled Fermi fluid. We may distinguish three temperature regions:

a) the temperature is so high that both the fluid and the particle behave classically. Then, if the particle moves with thermal velocity, we have:

$$(VI.8.1) \qquad \langle p \rangle / P = 0\,(m/M)^{1/2} = 0\,(\gamma)$$

and the classical Fokker-Planck equation is valid.

At lower temperature, quantum effects become important for the fluid. Only those fluid particles near the Fermi surface interact with the particle and we obtain :

(VI.8.2) $\langle p \rangle / P = 0 \ (m \varepsilon_F / MkT)^{1/2} = 0 \ (\gamma \xi)$

We may now distinguish two cases :

b) an intermediate temperature range where the more restrictive condition :

(VI.8.3) $\gamma \xi << 1$

is satisfied and the quantum Fokker-Planck equation (VI.4.11) is valid .

c) the case of very low temperature where

$$\gamma \xi > 1$$

and where the Fokker-Planck description does no longer hold.

In a discussion of the possibility of convergence of the $\langle p \rangle / P$ development presented here, Résibois and Dagonnier [3)8)] have shown that, in general, one must not expect this convergence to be realized at very low temperature, whatever the statistics. A very simple argument is the fact that at very low temperature, the average momentum P is independent of the mass ratio. It is essentially determined by the interactions with the fluid molecules and momentum transfers can become very large; the Fokker-Planck description is then no longer valid.

Let us show briefly how this conclusion about the independence of the average momentum at very low temperature can be obtained. For simplicity, we consider the case of Boltzmann statistics. The equilibrium distribution function for the brownian particle is :

$$\varphi^{equ}(P) = \frac{Tr_{fluid}\ \rho_{equ}}{Tr_{fluid,A}\ \rho_{equ}}$$

(VI.8.5)
$$= \frac{tr_{fluid}\ \exp\left[-\beta(H_o^f + H_o^A + V + U)\right]}{tr_{fluid,A}\ \exp\left[-\beta(H_o^f + H_o^A + V + U)\right]}$$

where

(VI.8.6) $$\beta = (kT)^{-1}$$

Let us write :

(VI.8.7) $$\rho(\beta) = e^{-\beta H_o}\omega(\beta) = e^{-\beta H}$$

Then:

(VI.8.8) $$\omega(\beta) = \exp\left[\beta(H_o^f + H_o^A)\right]\exp\left[-\beta(H_o^A + H_o^f + V + U)\right]$$

One verifies easily that this quantity satisfies the Bloch equation :

(VI.8.9) $$\frac{\partial\omega(\beta)}{\partial\beta} = \left\{\exp\left[\beta(H_o^A + H_o^F)\right](V + U)\exp\left[-\beta(H_o^A + H_o^f)\right]\right\}\omega(\beta)$$

Taking into account the commutation relations

(VI.8.10) $$\left[V,\ e^{-\beta H_o^A}\right] = 0$$

(VI.8.11) $$\left[H_o^f,\ H_o^A\right] = 0$$

and introducing

(VI.8.12) $$\tilde{V} = \exp(\beta H_o^f)\ V \exp(-\beta H_o^f)$$

(VI.8.13) $$\tilde{U} = \exp(\beta H_o^f)\ U \exp(-\beta H_o^f)$$

this equation can be rewritten :

(VI.8.14) $$\frac{\partial\omega(\beta)}{\partial\beta} = \left\{\tilde{V} + \exp(\beta H_o^A)\,\tilde{U}\exp(-\beta H_o^A)\right\}\omega(\beta)$$

Expanding the rhs in powers of H_o^A, we obtain :

$$(VI.8.15)\quad \frac{\partial \omega(\beta)}{\partial \beta} = \left\{ \tilde{V} + \tilde{U} + \beta \left[H_0^A , \tilde{U} \right] + \beta^2 \left[H_0^A , \left[H_0^A , \tilde{U} \right] \right] + \ldots \right\} \omega(\beta)$$

After a rather lengthy calculation [8], one can finally obtain the γ^2 (=m/M) correction to the maxwellian $\varphi_0^{equ}(P)$:

$$(VI.8.16)\quad \varphi^{equ}(P) = \varphi_0^{equ}(P) + \gamma^2 \left[(P^2/2MkT)(kT_Q/kT) + \alpha \right] \varphi_0^{equ}(P) + 0(\gamma^4)$$

where α is a factor which guarantees the normalization of φ^{equ} to unity. T_Q is a characteristic quantum temperature which expression is quite compicated but can be shown to have the following properties:

$$(VI.8.17)\quad \lim_{T \to 0} T_Q(\hbar, T) = \text{constant}$$

$$(VI.8.18)\quad \lim_{\substack{\hbar \to 0 \\ T \to \infty}} T_Q(\hbar, T) = 0$$

From the above equilibrium distribution, we obtain easily :

$$(VI.8.19)\quad \langle P^2 \rangle = 3m \gamma^{-2} \left[(kT + \gamma^2 kT_Q) + 0(\gamma^4) \right]$$

At sufficiently high temperature, we have

$$(VI.8.19)\quad kT \gg \gamma^2 kT_Q$$

$$(VI.8.20)\quad \langle P^2 \rangle \simeq \frac{3m}{\gamma^2} kT$$

However, at sufficiently low temperature, we may reach a regime where:

$$(VI.8.21)\quad \gamma^2 kT_Q/kT \gg 1$$

In that case :

$$(VI.8.22)\quad \langle P^2 \rangle \simeq 3m\, kT_Q$$

does no longer depend on γ .

A more rigorous mathematical analysis is of course quite difficult in general because of the complexity of dense systems. A more elaborate discussion can be found in [3)8)].

Appendix VI.1 - Examples of the algebra leading to the Von Neumann - Liouville equation (VI.2.12)

In the mixed occupation numbers-plane wave representation the Von Neumann equation is :

$$i\frac{\partial \langle K\{n\}|\rho|K'\{n'\}\rangle}{\partial t} = \sum_{K''\{n''\}} \{\langle K\{n\}|H|K''\{n''\}\rangle\langle K''\{n''\}|K'\{n'\}\rangle$$

(AVI.1.1)

$$-\langle K\{n\}|\rho|K''\{n''\}\rangle\langle K''\{n''\}|H|K'\{n'\}\rangle\}$$

Let us consider in the first term in the rhs one contribution to the fluid-fluid interaction :

$$(AVI.1.2)\quad \alpha = \sum_{K''\{n''\}} \langle K\{n\}|\bar{V}|K''\{n''\}\rangle\langle K''\{n''\}|\rho|K'\{n'\}\rangle$$

with

$$(AV1.1.3)\quad \bar{V} = v(k,l,p,r)\,\delta_{k+l-p-r,0}\; a_k^+ \; a_l^+ \; a_p \; a_r$$

We perform the following change of variables :

$$(AVI.1.4)\qquad \begin{aligned} K-K' &= \varkappa & n_k - n'_k &= \nu_k \\ K''-K' &= \varkappa' & n''_k - n'_k &= \nu'_k \\ \frac{K+K'}{2} &= P & \frac{n_k+n'_k}{2} &= N_k \end{aligned}$$

Then, we have

$$\alpha = \sum_{\varkappa' \{\nu'_k\}} \sum \left\langle P + \frac{\varkappa}{2}, \{N + \frac{\nu}{2}\} \middle| \bar{V} \middle| P - \frac{\varkappa}{2} + \frac{\varkappa'}{2}, \{N - \frac{\nu}{2} + \frac{\nu'}{2}\} \right\rangle \times$$

(AVI.1.5)

$$\times \left\langle P - \frac{\varkappa}{2} + \frac{\varkappa'}{2}, \{N - \frac{\nu}{2} + \frac{\nu'}{2}\} \middle| \rho \middle| P - \frac{\varkappa}{2}, \{N - \frac{\nu}{2}\} \right\rangle$$

Using the notation (VI.2.8) , this becomes :

$$\alpha = \sum_{\varkappa' \{\nu'_k\}} \sum \bar{V}_{\varkappa - \varkappa', \{\nu - \nu'\}} (P + \frac{\varkappa'}{2}, \{N + \frac{\nu'}{2}\}) \times$$

(AVI.1.6)

$$\times \rho_{\varkappa' \{\nu'\}} (P - \frac{\varkappa}{2} + \frac{\varkappa'}{2}, \{N - \frac{\nu}{2} + \frac{\nu'}{2}\})$$

Introducing the displacement operators defined by (VI.2.10) and (VI.2.11) we may write :

$$\alpha = \sum_{\varkappa' \{\nu'_k\}} \sum \xi^{\varkappa'} \eta^{\sum_k \nu'_k} \bar{V}_{\varkappa - \varkappa', \{\nu - \nu'\}} (P, \{N\}) \xi^{-\varkappa} \eta^{-\sum_k \nu_k} \times$$

(AVI.1.7)

$$\times \rho_{\varkappa' \{\nu'\}} (P, \{N\})$$

(the displacement operators act on everything that stands at their right.)

Now, using again (VI.2.8) and (AVI.1.3) , we have :

$$\bar{V}_{\varkappa - \varkappa', \{\nu - \nu'\}} (P, \{N\}) = v(k, l, p, r) \delta_{k+l-p-r, 0} \times$$

$$\times \left\langle P + \frac{\varkappa - \varkappa'}{2}, \{N + \frac{\nu - \nu'}{2}\} \middle| a_k^+ a_l^+ a_p a_r \middle| P - \frac{\varkappa - \varkappa'}{2}, \{N + \frac{\nu - \nu'}{2}\} \right\rangle$$

(AVI.1.8)

$$= v(l, lp, r) \delta_{k+l-p-r, 0} \delta_{\varkappa, \varkappa'} \prod_{i \neq klpr} \delta_{\nu_i, \nu'_i} \delta_{\nu'_k, \nu_k - 1} \times$$

$$\times \delta_{\nu'_l, \nu_l - 1} \delta_{\nu'_p, \nu_p + 1} \delta_{\nu'_r, \nu_r + 1} \left[(N_k + 1/2)(N_l + 1/2) \times \right.$$

$$\left. \times (N_p + 1/2)(N_r + 1/2) \right]^{1/2}$$

If we combine (AVI.1.7) and (AVI.1.8), we readily obtain the first term in the rhs of (VI.2.12) .

As another example, let us consider the external field term. One can also very easily obtain the following contribution to the Von Neumann - Liouville equation :

$$\sum_{\kappa'} \sum_{\{\nu'\}} \langle \kappa \{\nu\} | \mathcal{H}_E | \{\nu'\} \kappa' \rangle \rho_{\kappa' \{\nu'\}} (P, \{N\})$$

$$= \sum_{\kappa'} \sum_{\{\nu'\}} \left\{ \xi^{\kappa'} \eta^{\sum_k \nu_k} H^E_{\kappa - \kappa', \{\nu - \nu'\}} (P, \{N\}) \xi^{-\kappa} \eta^{-\sum_k \nu_k} \right.$$

$$\left. - \xi^{-\kappa'} \eta^{-\sum_k \nu_k} H^E_{\kappa - \kappa', \{\nu - \nu'\}} (P, \{N\}) \xi^{\kappa} \eta^{\sum_k \nu_k} \right\} \rho_{\kappa' \{\nu'\}} (P, \{N\})$$

$$= \sum_{\kappa'} \sum_{\{\nu'\}} \left\{ \exp \left(\frac{\kappa'}{2} \frac{\partial}{\partial P} \right) \exp \left[\frac{1}{2} \sum_k \nu'_k \frac{\partial}{\partial N_k} \right] \left\langle P + \frac{\kappa - \kappa'}{2}, \{N + \frac{\nu - \nu'}{2}\} \right| \right.$$

$$\underset{\sim}{E}.\underset{\sim}{R} \left| P - \frac{\kappa - \kappa'}{2}, \{N - \frac{\nu - \nu'}{2}\} \right\rangle \exp \left(- \frac{\kappa}{2} \frac{\partial}{\partial P} \right) \exp \left[- \frac{1}{2} \sum_k \nu_k \frac{\partial}{\partial N_k} \right]$$

(AVI.1.9)

$$- \exp \left(- \frac{\kappa'}{2} \frac{\partial}{\partial P} \right) \exp \left[- \frac{1}{2} \sum_k \nu'_k \frac{\partial}{\partial N_k} \right] \left\langle P + \frac{\kappa - \kappa'}{2}, \{N + \frac{\nu - \nu'}{2}\} \right|$$

$$\left. \underset{\sim}{E}.\underset{\sim}{R} \left| P - \frac{\kappa - \kappa'}{2}, \{N - \frac{\nu - \nu'}{2}\} \right\rangle \exp \left(\frac{\kappa}{2} \frac{\partial}{\partial P} \right) \exp \left[\frac{1}{2} \sum_k \nu_k \frac{\partial}{\partial N_k} \right] \right\} \times$$

$$\times \rho_{\kappa' \{\nu'\}} (P, \{N\})$$

$$= \sum_{\kappa'} \sum_{\{\nu'\}} \prod_k \delta_{\nu_k, \nu'_k} \int d\underset{\sim}{R}\, \underset{\sim}{E}.\underset{\sim}{R}.\, e^{i(\kappa' - \kappa).R} \times$$

$$\times \left\{ \rho_{\kappa' \{\nu'\}} (P + \frac{\kappa' - \kappa}{2}, \{N\}) - \rho_{\kappa' \{\nu'\}} (P - \frac{\kappa' - \kappa}{2}, \{N\}) \right\}$$

$$= \sum_{\kappa'} \sum_{\{\nu'\}} \prod_k \delta_{\nu_k, \nu'_k}\, \delta_{\kappa', \kappa}\, iE. \frac{\partial}{\partial (\kappa' - \kappa)} \times$$

$$\times \left\{ \rho_{\kappa' \{\nu'\}} (P + \frac{\kappa' - \kappa}{2}, \{N\}) - \rho_{\kappa' \{\nu'\}} (P - \frac{\kappa' - \kappa}{2}, \{N\}) \right\}$$

$$= i E. \frac{\partial}{\partial P} \sum_{\kappa'} \sum_{\{\nu'\}} \prod_{k} \delta_{\nu_k, \nu'_k} \delta_{\kappa'} , \kappa \rho_{\kappa' \{\nu'\}} (P , \{N\})$$

which agrees with (VI. 2. 16)

Appendix VI. 2 - Equivalence between (VI. 4. 11) and (VI. 5. 6)

Let us discuss the contribution involving twice U_1^A :

$$\alpha (t) = \sum_{\{N\}} \sum_{\{\nu\} \kappa} \sum_{\{\nu'\} \kappa'} \sum_{\{\nu''\} \kappa''} \langle 0 | U_1^A | \{\nu\} \kappa \rangle \times$$

$$\text{(AVI. 2. 1)} \times \langle \{\nu\} \kappa | \exp \left[- i \left(\mathcal{H}^f - z \right) t \right] | \kappa' \{\nu'\} \rangle \langle \kappa' \{\nu'\} | U_1^A | \kappa'' \{\nu''\} \rangle \times$$

$$\times \rho^f_{\kappa'' \{\nu''\}} (\{N\})$$

Using (VI. 5. 6), we have (see § 5) :

$$\sum_{\{\nu''\}} \sum_{\kappa''} \langle \kappa' \{\nu'\} | U_1^A | \kappa'' \{\nu''\} \rangle \rho^f_{\kappa'' \{\nu''\}} (\{N\})$$

$$\text{(AVI. 2. 2)} \quad = \sum_i \sum_K \langle \{N + \frac{\nu'}{2}\} | F_i(K) \rho^f_{\kappa' - K} + \rho^f_{\kappa' - K} F_i(K) | \{N - \frac{\nu'}{2}\} \rangle \frac{\partial}{\partial P_i}$$

$$= \sum_i \sum_K \langle \{N + \frac{\nu'}{2}\} \kappa' | F_i(K) \rho^f + \rho^f F_i(K) | K \{N - \frac{\nu'}{2}\} \rangle \frac{\partial}{\partial P_i}$$

where the force operator is given by (VI. 5. 4). Hence , we obtain :

$$\alpha (t) = \sum_i \sum_K \sum_{\{N\}} \sum_{\{\nu\} \kappa} \sum_{\{\nu'\} \kappa'} \langle 0 | U_1^A | \{\nu\} \kappa \rangle \times$$

$$\text{(AVI. 2. 3)} \times \langle \{\nu\} \kappa | \exp (-i \mathcal{H}^f t) | \{\nu'\} \kappa' \rangle \langle \{N + \frac{\nu'}{2}\} , \kappa' | F_i(K) \rho^f$$

$$+ \rho^f F_i(K) | \{N - \frac{\nu'}{2}\} , K \rangle \frac{\partial}{\partial P_i}$$

Now, let us differentiate with respect to t the quantity :

$$\beta_{\nu,\varkappa\,-K}(\{N\},t) = \sum_{\{\nu'\}\,\varkappa'} \langle \{\nu\}\varkappa | \exp(-i\varkappa^f t) | \{\nu'\}\varkappa' \rangle \times$$

(AVI. 2. 4)

$$\times \langle \varkappa' , \{N + \frac{\nu'}{2}\} | F_i(K) \rho^f | \{N - \frac{\nu'}{2}\}, K \rangle$$

with

(AVI. 2. 5) $$\beta_{\nu,\varkappa\,-K}(\{N\}, 0) = \langle \varkappa, \{N + \frac{\nu}{2}\} | F_i(K) \rho^f | \{N - \frac{\nu}{2}\}, K \rangle$$

hence

(AVI. 2. 6) $$\beta(0) = F_i(K) \rho^f$$

We have :

(AVI. 2. 7) $$\frac{\partial \beta_{\nu,\varkappa\,-K}(\{N\}, t)}{\partial t} = -i \sum_{\{\nu'\}\,\varkappa'} \langle \{\nu\}\varkappa | \beta^f | \{\nu'\}\varkappa' \rangle \beta_{\nu',\varkappa'\,-K}(\{N\}, t)$$

or , going back to the occupation numbers-plane wave representation;

$$\frac{\partial \langle \{N + \frac{\nu}{2}\}, \varkappa | \beta(t) | \{N - \frac{\nu}{2}\}, K \rangle}{\partial t} = -i \langle \{N + \frac{\nu}{2}\}, \varkappa | [H_f , \beta(t)] |$$

(AVI. 2. 8)

$$\{N - \frac{\nu}{2}\}, K \rangle$$

where

(AVI. 2. 9) $$H_f = H_o^f + V$$

(To obtain this result, we take into account the fact that, in the term involving V_o^A , we have :

$$\sum_{\varkappa'} \int dR\ e^{-i(\varkappa - k + l - \varkappa').R} \int dR'\ e^{-i(\varkappa' - K).R'}\ \beta^f(R, t)$$

(AVI. 2. 10)

$$= \int dR\ e^{-i\varkappa R}\ e^{i(k-l).R} \beta^f(R, t)\ e^{iKR} = \langle \varkappa | e^{i(k-l).R} \beta^f | K \rangle$$

Therefore, we have

(AVI. 2. 11) $$\beta(t) = e^{-iH^f t} \beta(K)\, e^{iH^f t} = e^{-iH^f t}\ F_i(K)\, e^{iH^f t}\, \rho^f = F_i(K, t)\, \rho^f$$

where $F_i(K, t)$ is the force operator in Heisenberg representation.

Therefore :

$$\alpha(t) = \sum_i \sum_K \sum_{\{N\}} \sum_{\nu\varkappa} \langle 0 | U_1^A | \{\nu\varkappa\} \rangle \langle \varkappa, \{N + \frac{\nu}{2}\} | F_i(K,t) \rho^f$$

(AVI.2.12)

$$+ \rho^f F_i(K,t) | \{N - \frac{\nu}{2}\}, K \rangle \frac{\partial}{\partial P_i}$$

From now, on , the derivation goes on as in the text and leads to the second order differential contribution in (VI.6.12) .

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VII. GRAVITATIONAL PLASMAS.

VII.1 - Introduction.

In all the preceding chapters on brownian motion, we have used the kinetic equation (II.9.5) as the starting point . However, when we derived this equation, we stressed the importance of time scales. This equation fails to describe correctly the asymptotic behavior of a system where there is no net separation between the collision time and the relaxation time, or where the initial correlations are over long distances. Now, long collision times or long range correlations must obviously be expected in systems interacting through long range forces. As examples of such systems, we have immediatly in mind, on the one hand, systems interacting through electrostatic forces and, on the other hand, systems interacting through gravitational forces. In both cases, the interaction between two particles is inversely proportional to their relative distance.

A great deal of effort has been done to understand the situation in the case of electrostatic forces. If we consider a charged test particle moving in a plasma, it polarizes the medium : the charge distribution around the particle is no longer uniform. The medium screens the interaction between two particles and we are no longer dealing with a pure Coulomb force. This idea, in its simplest form leads to the Debye Huckel theory. Out of equilibrium, it has been shown that, if one sums in the operator Ψ all contributions proportional to $(e^2C)^m$, the result of this summation is to introduce a dynamical screening. This screening introduces a short time scale :

$$t_p = (m/e^2 c)^{1/2} = (k_D v)^{-1} \qquad \text{(VII.1.1)}$$

and a long time scale

$$t_r = (e^4 c)^{-1} m^{1/2} (kT)^{3/2} \sim c^{-1} \qquad \text{(VII.1.2)}$$

We are again in the conditions where an asymptotic kinetic equation may be written (Balescu-Lenard equation).

What is now the situation with gravitational forces? The essential feature is that the interaction is now purely, attractive, whereas when we deal with electrostatic forces we have a mixture of attractive and repulsive forces (with a condition of overall neutrality). In a discussion of equilibrium properties in the framework of Mayer's cluster integrals, one notices very easily the importance of this difference. Indeed, there it appears clearly that the most divergent contributions can be eliminated because of the electroneutrality condition; the next dominant terms (which diverge also) can then be summed and lead to the screening. This problem arises always as soon as one computes average quantities, but, in the derivation of the Balescu-Lenard equation, one can restrict oneself to an electron plasma with a positive background; one notices then that the background plays no role in the derivation. In this case , we are dealing with purely repulsive forces. The first idea is then to perform in the case of purely attractive gravitational forces, the same summation that worked for purely electrostatic repulsive forces, or for a mixture of both attractive and repulsive electrostatic forces. In simple models, which leads for electrostatic potentials to the Debye potential :

$$V_D = e^{-\kappa r}/r \qquad \text{(VII.1.3)}$$

one obtains, for gravitational systems an effective potential of the form :

$$V_G = e^{i\kappa r}/r \qquad \text{(VII.1.4)}$$

This partial summation does not lead to a screening; the "effective interaction " has the same range as the gravitational interaction.

The intuitive ideas which lead to the Debye potential for an elec-

trostatic plasma can obviously not be extended to the gravitational systems. As we have seen, more elaborate techniques did not succeed to bring anything which ressembles whatsoever to an effective short range interaction. In view of the failure of all those attemps to justify the use of the kinetic equation for such systems, one may try to use a completely different starting point . If we cannot use the kinetic equation, we must go back to the exact equation, the generalized master equation (II. 8. 9) . One can then try to discuss the new features introduced by the long range character of the interaction. This is what Prigogine and Severne [1] attempted very recently. They considered a very idealized model of a gravitational system: a weakly coupled, homogeneous system, with no correlations at t=0. Although the first condition can be justified with the conditions prevailing at present in our galaxy [1)2)], the other conditions of the model are certainly not realistic. A real gravitational system is an inhomogeneous system. However, the finding of a proper treatment for this idealized model , which is the simplest model of a gravitational system one can find, is certainly the first obvious step one has to take if one wants to achieve an understanding of the much more complex actual systems (or at least of realistic simplifications of the actual systems) .

We shall first show on a very simplified collision operator what is the basic difference between systems with a very short collision time (as compared to the relaxation time) and systems where the collision time is infinite . This will enable us to convince ourselves that, even if we require only an understanding of the asymptotic behavior of the latter systems, it is necessary to start with the generalized master equation . We shall then discuss the characteristics of the long time evolution as described by this equation in the limit of infinite collision times.

More details as well as general considerations about the following discussion can be found in the paper by Prigogine and Severne[1] as well as in a paper by Prigogine [5].

VII.2 - Simple model for the collision operator.

In order to see what are the difficulties which arise when one deals with long range forces, i.e. long collision times, let us investigate a simple model for the collision operator [3)4)] :

$$\psi(z) = \frac{\alpha}{z + i\beta} \qquad (\alpha, \beta > 0) \tag{VII.2.1}$$

The collision time in this model is given by β^{-1} while the relaxation time is given by $\alpha^{-1}\beta$.

The non markovian equation for this case, if we do not take into account the destruction term, is :

$$\begin{aligned} \frac{\partial \rho_o}{\partial t} &= \int_o^t d\tau\, G(t-\tau)\, \rho_o(\tau) \\ &= (2\pi i)^{-1} \int_o^t d\tau \int_C dz\, e^{-iz(t-\tau)} \psi(z) \rho_o(\tau) \end{aligned} \tag{VII.2.2}$$

Provided that we can neglect terms of the form $\exp(-t/\tau_{coll})$, an expansion of (VII.2.3) in powers of $(\tau_{coll}/\tau_{rel}) = \alpha\beta^{-2}$, leads to the pseudo-markovian equation (see chapter II, § 9) :

$$\begin{aligned} \frac{\partial \rho_o}{\partial t} &= -i\,\Omega(0)\psi(0)\rho_o^{(t)} = -i\left\{\psi(0) + \psi'(0)\psi(0) + \left[\frac{1}{2}\psi''(0)\psi(0) \right.\right. \\ &\quad \left.\left. + \psi'^2(0)\right]\psi(0) + \ldots\right\}\rho_o(t) \\ &= -\left\{1 + \alpha\beta^{-2} + 2\,(\alpha\beta^{-2})^2 + \ldots\right\}(\alpha/\beta)\,\rho_o(t) \end{aligned} \tag{VII.2.3}$$

This expansion has a simple meaning for small values of τ_{coll}/τ_{rel}. On the other hand, if we take the extreme case of infinite collision times ($\beta \to 0$), it is meaningless; the operator $\psi(0)$ is no longer defined. However, in any case the non markovian equation predicts a well defined behavior of the distribution function. Indeed, from (VII. 2. 1) and (VII. 2. 2) we have

$$\frac{\partial \rho_o}{\partial t} = -\alpha \int_o^t d\tau e^{-\beta(t-\tau)} \rho_o(\tau) \tag{VII. 2. 4}$$

and we easily obtain the second order differential equation :

$$\frac{\partial^2 \rho_o}{\partial t^2} + \beta \frac{\partial \rho_o}{\partial t} + \alpha \rho_o = 0 \tag{VII. 2. 5}$$

The solution of this equation is very simple and perfectly well defined whatever β (note that $[\partial \rho_o / \partial t]_{t=0} = 0$) :

$$\begin{aligned} \rho_o(t) = &(1/2)\rho_o(0)\left[1 - \beta(\beta^2-4\alpha)^{-1/2}\right]\exp\left[-\left(\frac{\beta}{2} + \frac{(\beta^2-4\alpha)^{1/2}}{2}\right)t\right] \\ &+(1/2)\rho_o(0)\left[1+\beta(\beta^2-4\alpha)^{-1/2}\right]\exp\left[-\left(\frac{\beta}{2} - \frac{(\beta^2-4\alpha)^{1/2}}{2}\right)t\right] \end{aligned} \tag{VII. 2. 6}$$

When

$$\tau_{coll}/\tau_{rel} = \alpha\beta^{-2} \leq 4 \tag{VII. 2. 7}$$

we have a monotonic decay of $\rho_o(t)$.
If $\alpha\beta^{-2} \ll 1$, neglecting terms proportional to $e^{-t/\tau_{coll}}$ ($e^{-\beta t}$), we obtain :

$$\rho_o(t) \simeq \rho(0) \exp(-\alpha\beta^{-1} t) \tag{VII. 2. 8}$$

which is the behavior that is given by the pseudomarkovian equation if we restrict ourselves to the first term in the rhs of (VII. 2. 3)

For

(VII. 2. 9) $$\alpha \beta^{-2} > 4$$

i.e. for large collision times, we obtain damped oscillations . In the extreme case of infinite collision time, we obtain a purely oscillating behavior :

(VII. 2. 10) $$\rho_o(t) = (1/2)\, \rho_o(0)(e^{-i\sqrt{\alpha}\, t} + e^{i\sqrt{\alpha}\, t})$$

In other words, for long range interactions (small β), the corrections due to the non markovian character of the equation are quite important.

VII. 3 - Non markovian equation in the weak coupling approximation.

Let us consider a gravitational plasma :

(VII. 3. 1) $$H = \sum_{i=1}^{N} (1/2) m v_i^2 + \lambda \sum_{i<j} | \underset{\sim}{r}_i - \underset{\sim}{r}_j |^{-1}$$

where

(VII. 3. 2) $$\lambda = - Gm^2$$

where G is the constant of gravitation .

The characteristic parameters of such a system are (numerical values correspond to conditions prevailing now in our galaxy and in the vicinity of the sun [2]) :

(VII. 3. 3)

$G = 6,7.10^{-8}$ cgs (constant of gravitation)

$m = 10^{33}$ g (average mass)

$\bar{v} = 3.10^{6}$ cm/sec (mean star velocity)

$C = 3,4.10^{-57}$ cm^{-3} (number density)

With these parameters we can form one non dimensional quantity proportional to G:

$$\Gamma = C^{1/3} \lambda (m\bar{v}^2)^{-1} = 0\,(10^{-6}) \qquad \text{(VII.3.4)}$$

The smallness of this parameter justifies a weak coupling approximation.

In our discussion in chapter III, § 6, we have seen that the asymptotic weak coupling operator $\psi(0)$ for a potential in $1/r$ presents a double divergence. We shall show here that the non-markovian corrections, even in the weak coupling approximation, permits to remove the long distance divergence. The short distance divergence, due to the close collisions cannot be removed in this way; however as close encounters are not very frequent, we shall neglect them in the evolution equation; in other words, we shall cut-off the potential at some short distance R.

In the following analysis, we shall find-two time scales : :
the "nominal" relaxation time :

$$\tau_r = C^{-1} \lambda^{-2} m^2 \bar{v}^3 = C^{-1/3} \Gamma^{-2} \bar{v}^{-1} \simeq 7.10^{16} \text{ years} \qquad \text{(VII.3.5)}$$

the duration of close encounters :

$$\tau_c = R\bar{v}^{-1} = C^{-1/3} \Gamma \bar{v}^{-1} \simeq 7.10^{-2} \text{ years} \qquad \text{(VII.3.6)}$$

if one takes for R the distance corresponding to a mean 90° deflection in the two body scattering problem.

We shall, as usual , consider the limiting case

$$N \to \infty \ , \ \Omega \to \infty \ , \ C \text{ finite} \qquad \text{(VII.3.7)}$$

We shall also neglect all time variations occuring on the close collisions time scale τ_c .

We shall assume that we are dealing with an homogeneous system in which there are no spatial correlations at t=0. Then , the destruction term in the non markovian equation vanishes identically and this equation has the form (VII. 2. 2) .

In the weak coupling approximation, the collision operator $\psi(z)$ is given by (see III. 2. 3) :

$$\psi(z) = (8i\pi^3\lambda^2 C/m^2)\int d^3k \left|V_k\right|^2 \underset{\sim}{k}\cdot\left(\frac{\partial}{\partial \underset{\sim}{v}_1} - \frac{\partial}{\partial \underset{\sim}{v}_2}\right)\frac{1}{\underset{\sim}{k}\cdot(\underset{\sim}{v}_1 - \underset{\sim}{v}_2) - z} \times$$

(VII. 3. 8)

$$\times\ \underset{\sim}{k}\cdot\left(\frac{\partial}{\partial \underset{\sim}{v}_1} - \frac{\partial}{\partial \underset{\sim}{v}_2}\right)$$

In order to treat in a proper way the divergence, we shall consider the gravific potential as the limit of a screened potential:

$$V_k = \lim_{K\to 0} (2\pi^2)^{-1}(k^2 + K^2)^{-1} \qquad \text{(VII. 3. 9)}$$

Following the technique of chapter III, § 4 , one obtains easily :

$$\psi(z) = (32i\pi^3\lambda^2 C/m^2)\ \frac{\partial}{\partial g_r}\ T_{rs}\ \frac{\partial}{\partial g_s} \qquad \text{(VII. 3. 10)}$$

with

$$T_{rs} = T_{/\!/}\ g_r g_s g^{-2} + T_{\perp}(g^2 \delta_{r,s} - g_r g_s) g^{-2} \qquad \text{(VII. 3. 11)}$$

where

$$\underset{\sim}{g} = \underset{\sim}{v}_1 - \underset{\sim}{v}_2 \qquad \text{(VII. 3. 12)}$$

is the relative velocity. $T_{/\!/}$ and $T_{\perp}$ are the parallel and transverse components :

$$T_{/\!/} = \lim_{K\to 0} (4\pi^2)^{-1}\left\{\frac{K}{z+iKg} - \frac{\mu}{z+i\mu g}\right\} \qquad \text{(VII. 3. 13)}$$

$$(VII.3.14)\quad T_{\perp} = \lim_{K \to 0} (4\pi^2)^{-1} \left\{ \frac{i}{g} \ln \frac{z+iKg}{z+i\mu g} - \frac{1}{2} \frac{1}{\mu R^2} \frac{1}{z+i\mu g} \right\}$$

where R is the short distance cut-off and

$$(VII.3.15)\quad \mu = (R^{-2} + K^2)^{1/2}$$

For instance, in a reference frame where the z axis is along $\underset{\sim}{g}$, using cylindrical coordinates, we have :

$$T_{//} = (2\pi^3)^{-1} \lim_{K \to 0} \int_{-\infty}^{+\infty} dk_z \int_0^R dk_{\perp}\, k_{\perp}\, k_z^2 (k_z^2 + k_{\perp}^2 + K^2)^{-2} (k_z g - z)^{-1}$$

$$(VII.3.16)\quad = (4\pi^2)^{-1} \lim_{K \to 0} \int_{-\infty}^{+\infty} dk_z\, k_z^2 (k_z g - z)^{-1} \left\{ (k_z^2 + K^2)^{-1} - (k_z^2 + K^2 + R^{-2})^{-1} \right\}$$

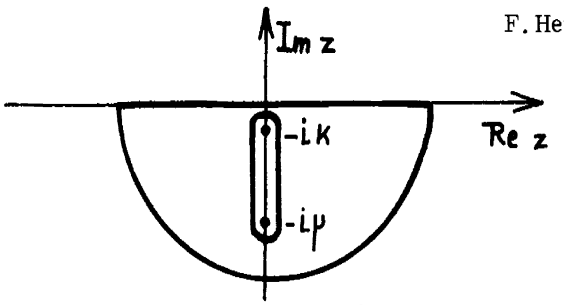
The last integration is easily performed by the method of residues ($z \in S^+$) and leads to (VII.3.13).

Also :

$$T_{\perp} = (4\pi^3)^{-1} \lim_{K \to 0} \int_{-\infty}^{+\infty} dk_z \int_0^R dk_{\perp}\, k_{\perp}^3 (k_z^2 + k_{\perp}^2 + K^2)^{-2} (k_z g - 1)^{-1}$$

$$(VII.3.17)\quad = (8\pi^3)^{-1} \lim_{K \to 0} \int_{-\infty}^{+\infty} dk_z \left\{ \ln \frac{k_z^2 + \mu^2}{k_z^2 + K^2} - \frac{1}{R^2 (k_z^2 + \mu^2)} \right\} (k_z g - z)^{-1}$$

The second term is easily computed, using, the method of residues and gives the second contribution in the rhs of (VII.3.14). As to the first contribution, we complete the real axis with a half circle at infinity in S^- and avoid the two branch points at $-i\mu$ and $-iK$ by making a cut. (see fig. VII.3.1)



Integration contour for log. term in (VII. 3. 17)

Fig. VII. 3. 1

One can then easily obtain the first contribution in the rhs of (VII. 3. 14).

The most important feature of the operator $\Psi(z)$ is that, at the limit $K \to 0$, the transverse part $T_\perp$ has a logarithmic singularity at $z = 0$. The collision operator may be rewritten :

$$(VII.2.18) \qquad -i\Psi(z) = \Phi(z) + \left\{ \frac{R^{-2}\, g}{2i\mu\,(z+i\mu g)} \ln \frac{z+iKg}{z+i\mu g} \right\} \hat{\Psi}$$

with

$$(VII.3.19) \qquad \Phi(z) = (8\pi\lambda^2 C/m^2) \frac{\partial}{\partial g_r} \frac{g_r g_s}{g^3} \left[\frac{Kg}{z+iKg} - \frac{\mu g}{z+i\mu g} \right] \frac{\partial}{\partial g_s}$$

$$(VII.3.20) \qquad \hat{\Psi} = (8\pi\lambda^2 C/m^2) \frac{\partial}{\partial g_r} \frac{g^2 \delta_{r,s} - g_r g_s}{g^3} \frac{\partial}{\partial g_s}$$

if one takes into account the fact that any function of g commutes with the differential operator $\hat{\Psi}$.

We have singularities both at $z = -iKg$ and $z = -i\mu g$. The singularities at $z = -i\mu g$ are related to the close collisions and are at a finite distance from the real axis. As the time scale for the close collisions is much shorter than any time scale we shall meet, we treat the close collisions as instantaneous. This means that we consider values of z such that :

$$(VII.3.21) \qquad z \ll -i\mu g$$

We then obtain the approximate form :

$$-i\psi(z) = \phi(z) + \left[\frac{R^{-2}}{2\mu^2} + \ln\left(\frac{K}{\mu} + \frac{z}{i\mu g}\right)\right]\hat{\psi} \tag{VII.3.22}$$

$$\phi(z) = (8\pi\lambda^2 C/m^2)\frac{\partial}{\partial g_r}\frac{g_r g_s}{g^3}\left[\frac{Kg}{z+iKg} + i\right]\frac{\partial}{\partial g_s} \tag{VII.3.23}$$

Now, in the case of electrostatic plasmas , K is finite and if we neglect effects proportional to $(Kgt)^{-1}$, we obtain the asymptotic form :

$$-i\psi(0) = -\left[\frac{1}{2(1+K^2R^2)} + \ln\frac{KR}{(1+K^2R^2)^{1/2}}\right]\hat{\psi} \tag{VII.3.24}$$

$$= \int_0^{R^{-1}} dk k^3 (k^2+K^2)^{-2}\,\hat{\psi} \tag{VII.3.24}$$

which is easily verified to be identical to (III.3.5) when one takes as the interaction the screened Coulomb potential. However, in the limit $K \to 0$, this procedure is meaningless and we obtain :

$$-i\psi(z) = \phi - \{(1/2) + \ln(-izRg^{-1})\}\hat{\psi} \tag{VII.3.25}$$

with

$$= (8\pi\lambda^2 C/m^2)\frac{\partial}{\partial g_r}\frac{g_r g_s}{g^3}\frac{\partial}{\partial g_s} \tag{VII.3.26}$$

The solution of the non markovian equation (VII.2.2) may be written (see II.9.4) :

$$\rho_o(t) = -(2\pi i)^{-1}\int dz\; e^{-izt}\sum_{n=0}^{\infty}\frac{1}{z^{n+1}}\left[\psi(z)\right]^n \rho_o(0)$$

$$= -(2\pi i)^{-1}\int dz\; e^{-izt}\,\frac{1}{z-\psi(z)}\,\rho_o(0) \tag{VII.3.27}$$

VII.4 - Time evolution of the velocity distribution function.

The operators $\hat{\psi}$ and ϕ do not commute; hence they do not have a common set of eigenfunctions and the analysis of the time evolution is not very easy. However, the problem will be considerably simplified if one of the contributions turns out to be dominant. Let us first investigate the type of behavior determined by the second term.

The characteristic time involved in $\hat{\psi}$ is the nominal relaxation time τ_r given by (VII.3.5) . The operator $-i\hat{\psi}$, as we have already seen (see the discussion of the $\mathcal{H}$ -theorem, chapter III, § 2) has real, negative or zero eigenvalues which define a spectrum of relaxation times. We may in a qualitative discussion introduce the following approximation :

$$-i\hat{\psi}\rho_o = -\rho_o/\tau_r \qquad \text{(VII.4.1)}$$

Also , we replace Rg^{-1} by its average value, the collision time for close encounters τ_c . Then , we obtain :

$$\rho_o(t) = -(2\pi i)^{-1} \int dz\ e^{-izt} \left[z-\chi(z)\right]^{-1} \rho_o(0) \qquad \text{(VII.4.2)}$$

where

$$\chi(z) = -\left\{(1/2) + \ln(-iz/\tau_c)\right\}(i\tau_r)^{-1} \qquad \text{(VII.4.3)}$$

In order to understand the evolution of $\rho_o(t)$, we have to discuss the singularities of the integrand, i.e. find out the roots of the equation :

$$z - \chi(z) = 0 \qquad \text{(VII.4.4)}$$

Let us introduce :

$$z = -\omega - i\varkappa \qquad \text{(VII.4.5)}$$

Then (VII. 4. 4) and (VII. 4. 4) give us :

(VII. 4. 6) $$-x+iy = (1/2) + \ln \Gamma^{-1}(-x+iy)$$

with

(VII. 4. 7) $$x = \alpha\tau_r \qquad y = \omega\tau_r \qquad \Gamma = \tau_r/\tau_c = 10^{18}$$

A detailed discussion of the dispersion equation (VII. 4. 6) can be found in ref.[1)]. The main point is that the equation can be very much simplified if one takes into account the largeness of Γ . A whole spectrum of solutions is found . For consistency, the range of the spectrum is restricted to frequencies such that :

(VII. 4. 8) $$\omega \ll \omega_{max} \simeq \tau_c^{-1}$$

The frequencies ω_n are essentially the odd harmonics of $\omega_o = \tau_r^{-1}$

(VII. 4. 9) $$\omega_n \simeq (2n+1)\pi/\tau_r$$

In the useful part of the spectrum (frequencies less than $10^{-2}\omega_{max}$), the damping is such that :

(VII. 4. 10) $$\alpha_n > 4\tau_r^{-1}$$

In fact, in the major part of the spectrum, the damping is found to be of order :

(VII. 4. 11) $$\alpha_o = \tau_r^{-1} \ln \Gamma^{-3} = 40\tau_r^{-1}$$

The time scale for the oscillations is of the order of the nominal relaxation time τ_r^{-1} while for the damping it is much shorter (at least by a factor 4) . The essential feature is that we have now an oscillatory relaxation of $\rho_o(t)$ on a time scale much shorter than the nominal relaxation time and given by :

$$t_{rel} = \tau_r \Big/ \ln(\tau_r/\tau_c) \tag{VII.4.12}$$

The consideration of the complete spectrum of eigenfunctions and eigenvalues of Ψ, avoided in the approximation (VII.4.1), would only lead to further complications of detail.

However, we still have to examine the effect of the operator Φ which appears in the complete equation (VII.3.27). The time scale for the effects due to Φ is again the nominal relaxation time τ_r, while the term involving $\hat{\Psi}$ has a much shorter time scale t_{rel}. Therefore, the system will first reach a quasiequilibrium distribution, which will be further modified by the action of the Φ contribution. One verifies easily that, if the $\hat{\Psi}$ contribution conserves the kinetic energy, this is not true for the Φ contribution. One obtains easily for the variation of the kinetic energy per star:

$$\begin{aligned}
\frac{\partial E_{kin}}{\partial t} &= N^{-1}\int\{d\underset{\sim}{v}\}^N \sum_{i=1}^{N} (mv_i^2/2)\,(\partial \rho_o/\partial t) \\
&= -(2\pi i)^{-1}N^{-1}\int\{d\underset{\sim}{v}\}^N \sum_{i=1}^{N} (mv_i^2/2)\int dz\, e^{-izt}\Psi(z)\overline{z-\Psi(z)}\,\rho_o(o) \\
&= -(2\pi i)^{-1}N^{-1}\int\{d\underset{\sim}{v}\}^N \sum_{i=1}^{N} (mv_i^2/2)\,\Phi\,\rho_o(t) \\
&= 4\pi\lambda^2 Cm^{-1}\int d\underset{\sim}{g}\, d\underset{\sim}{w}\; g^{-1}\,\rho_o(\underset{\sim}{v}_1, \underset{\sim}{v}_2; t) > 0
\end{aligned} \tag{VII.4.13}$$

where

$$\underset{\sim}{g} = \underset{\sim}{v}_1 - \underset{\sim}{v}_2 \tag{VII.4.14}$$

$$\underset{\sim}{w} = (\underset{\sim}{v}_1 + \underset{\sim}{v}_2)/2 \tag{VII.4.15}$$

are respectively the relative and center of mass velocities.

Therefore, the Φ contribution plays the role of a source term

and leads to a continuous increase of the kinetic energy. In other words, we have the following picture of the time evolution of ρ_0: first, a quasiequilibrium distribution will be reached on a time scale t_{rel}; the aged system then remains in the quasiequilibrium state but with a time dependent temperature.

VII. 5 - Role of the initial correlations.

In this whole discussion, we have assumed that there were no initial correlations. Then, we have seen that there is a continuous increase of kinetic energy. Because of total energy conservation, we have at the same time a decrease of potential energy (the complete energy balance can be verified in detail but requires the evaluation of binary correlation Fourier coefficient and will not be considered here). This continuous exchange between kinetic and potential energy of course occurs for any system when the non markovian description is retained. The particularity of the gravitational plasma is that it occurs at lowest order, which finally is due to the fact that there exists no approximation corresponding to instantaneous collisions. However, we may wonder whether this picture could not be affected if initial correlations were present. As we are dealing with long range forces, once initial correlations are present, there is no mechanism by which the system can loose the memory of these conditions in a short time as it happens for systems interacting through short range forces. The fact that the true collision time for such a system is very long on the time scale over which we discuss the behavior of the system, has the consequence that neither can we consider the collisions as complete nor can we assume that the system has forgotten its initial conditions. Therefore, we have to retain both the non markovian character of the collision term and the destruc-

tion term in the master equation.

We can easily see that the presence of initial correlations will indeed modify our results. Let us take as the initial condition a function of the hamiltonian :

(VII.5.1) $\rho(0) = f(H)$

If one adds to (VII.2.2), the destruction term and computes it for this initial situation with the same assumptions as the collision term, one verifies easily that the increase of the kinetic energy which results from the ϕ contribution is completely cancelled by the destruction contribution.

This example clearly shows us the important role played by the initial correlations in the description of systems interacting through long range forces. It would therefore be of great importance to have realistic models of non equilibrium correlations.

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