INTERNATIONAL ATOMIC ENERGY AGENCY
UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION

INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
34100 TRIESTE (ITALY) - P.O.B. 586 - MIRAMARE - STRADA COSTIERA 11 - TELEPHONES: 224281/2/3/4/5/6
CABLE: CENTRATOM - TELEX 460392-I

SMR/94-58

SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

14 April - 18 June 1982

ATOMIC MOTIONS IN LIQUIDS

M. GERL

Lab. de Physique du Solide
Université de Nancy - I
Case Officielle n° 140
54037 Nancy Cedex
France

ATOMIC MOTIONS IN LIQUIDS.

Introduction.

1. The self-diffusion in a fluid

1,1. Definition of the diffusion constant D.

1,2. Relation of D with the velocity autocorrelation function $Z(t)$.

1,3. Relation of $Z(t)$ with other correlation functions.

1,4. Measurements of D using neutron diffraction.

2. The Langevin equation.

2,1. The simple Langevin equation.

a) General method

b) Calculation of the friction coefficient.

2,2. Hydrodynamic calculations of the friction coefficient.

2,3. The generalized Langevin equation. The memory function formalism.

2,4. The Mori-Zwanzig formalism.

3. Kinetic theory of atomic transport in liquids.

3,1. The Fokker-Planck equation.

3,2. The Boltzmann and Enskog equations.

3,3. Full kinetic theories.

I. THE SELF-DIFFUSION COEFFICIENT OF A FLUID.

1,1. Definition of D.

Let us consider a number n_o of tagged particles (a radioisotope of the host fluid for instance) which are located at the point $\vec{r} = 0$ at the origin of time. If we let the system evolve, these particles will diffuse in the host fluid and, at time t, we observe a concentration $c(\vec{r},t)$ of tagged particles at the point $\vec{r}$. The flow of particles is given by:

$$\vec{J}(\vec{r},t) = -D\,\vec{\nabla} c(\vec{r},t) \tag{1}$$

where D ($cm^2 . s^{-1}$) is the diffusion constant. On the other hand, the conservation of tagged particles implies that:

$$\frac{\partial c}{\partial t} = -\,\vec{\nabla} . \vec{J} \tag{2}$$

so that the concentration $c(\vec{r},t)$ obeys the well-known diffusion equation:

$$\frac{\partial c}{\partial t} = D\,\nabla^2 c \tag{3}$$

This equation should also be obeyed by the self-correlation function $G_s(\vec{r},t)$ at times much larger than the collision time, for $\frac{c}{n_o}$ can be interpreted as the probability density that a tagged particle be found at the point $\vec{r}$ at time t, given that it was at the origin at $t = 0$:(1)

$$\frac{\partial G_s}{\partial t} = D\,\nabla^2 G_s(\vec{r},t) \qquad (t \gg \tau_c) \tag{4}$$

with the initial condition:

$$G_s(\vec{r},0) = \delta(\vec{r})$$

The equation (4) is most easily solved if we define the self part of the intermediate scattering function:

$$F_s(\vec{k},t) = \int d\vec{r}\, e^{-i\vec{k}.\vec{r}}\, G_s(\vec{r},t) \tag{5}$$

We notice that $F_s(\vec{k},0) = 1$ and it follows immediately from the equation (4) that:

$$F_s(\vec{k},t) = \exp(-k^2 D\,|t|) \tag{6}$$

and, by Fourier inversion of (5):

$$\begin{aligned} G_s(\vec{r},t) &= \int \frac{d\vec{k}}{(2\pi)^3}\, e^{i\vec{k}.\vec{r}}\, F_s(\vec{k},t) \\ &= (4\pi D|t|)^{-3/2} \exp\left(-\frac{r^2}{4D|t|}\right) \end{aligned} \tag{7}$$

Using this form of $G_s(\vec{r},t)$ it is easy to show that the mean-square displacement $\langle r^2(t)\rangle$ of a tagged particle varies linearly with time:

$$\langle r^2(t)\rangle = 6\,D\,t \qquad (t \gg \tau_c) \tag{8}$$

The diffusion coefficient is therefore a measure of the variation with time of the mean square displacement of the particle.

A possible experiment for measuring D is the following. In a capillary initially filled with the host fluid, we insert at $t = 0$ a thin layer of a radioisotope of the element we want to measure the diffusion coefficient. After the time t has elapsed, we measure the concentration along the capillary axis, and we obtain D from the one-dimensional equivalent to the equation (7).

It is also to be noticed that D can be expressed in terms of $S_s(\vec{k},\omega)$, the self part of the dynamic structure factor. $S_s(\vec{k},\omega)$ is defined as the space-time Fourier transform of $G_s(\vec{r},t)$;

$$(9)\qquad \begin{aligned} S_s(\vec{k},\omega) &= \frac{1}{2\pi}\int d\vec{r}\, e^{-i\vec{k}.\vec{r}}\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, G_s(\vec{r},t) \\ &= \frac{1}{2\pi}\int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, F_s(\vec{k},t) \end{aligned}$$

Using the expression (6) of $F_s(\vec{k},t)$ which is valid for long times and large distances we obtain;

$$(10)\qquad S_s(\vec{k},\omega) = \frac{1}{\pi}\,\frac{Dk^2}{\omega^2+(Dk^2)^2}$$

Therefore, in the long wavelength limit we can write

$$\lim_{k\to 0} k^{-2} S_s(\vec{k},\omega) = \frac{D}{\pi\omega^2}$$

and

$$(11)\qquad \boxed{D = \pi \lim_{\omega\to 0}\omega^2 \lim_{k\to 0}\frac{S_s(k,\omega)}{k^2}}$$

The equation (11) does not actually provides an easy means to determine D because it is rather difficult to accurately measure $S_s(\vec{k},\omega)$ in the limit of small energy and momentum transfers. Any approximate theory of $S_s(\vec{k},\omega)$ should however yield the result (11) in the long time and long wavelength limit, so that (11) should be regarded as a consistency equation.

1,2. Relation of D with the velocity autocorrelation function (V.A.F).

It is more instructive to correlate the diffusion coefficient with the velocity autocorrelation function:

$$Z(t) = \langle u_x(t)\, u_x(0)\rangle$$

where $u_x(t)$ is the x-component of the velocity of the tagged particle at time t. Indeed, the equation (8) can be written, in an isotropic fluid:

$$(12)\qquad D = \lim_{t\to\infty}\frac{1}{2t}\langle x^2(t)\rangle$$

where $\quad x(t) = \int_0^t u_x(s)\, ds$

so that

$$\langle x^2(t)\rangle = \int_0^t dt' \int_0^t dt''\,\langle u_x(t'')\,u_x(t')\rangle$$

In a stationary system we expect the velocity autocorrelation function to depend only on the time interval $t''-t'=s$, not on the choice of the origin of time. Therefore:

$$(13)\qquad \langle x^2(t)\rangle = \int_0^t dt' \int_{-t'}^{t-t'} ds\,\langle u_x(s)\,u_x(0)\rangle$$

and we have to integrate in the domain depicted in the figure 1. In the equation (13) we can now interchange the order of integrations:

$$\langle x^2(t)\rangle = \int_{-t}^{0} ds \int_{-s}^{t} dt'\,\langle u_x(s)u_x(0)\rangle + \int_0^t ds\int_0^{t-s} dt'\,\langle u_x(s)u_x(0)\rangle$$

Putting $s' = -s$ in the first integral and noticing that $\langle u_x(-s') u_x(0) \rangle = \langle u_x(s') u_x(0) \rangle$ we obtain

$$\langle x^2(t) \rangle = \int_0^t ds \, \langle u_x(s) u_x(0) \rangle \left(\int_s^t dt' + \int_0^{t-s} dt' \right)$$

hence:

$$D = \lim_{t \to \infty} \int_0^t ds \, \langle u_x(s) u_x(0) \rangle \left(1 - \frac{s}{t}\right)$$

When s grows to infinity the VAF $\langle u_x(s) u_x(0) \rangle$ is equal to $\langle u_x(s) \rangle \langle u_x(0) \rangle = 0$ and D becomes:

$$(14) \qquad D = \int_0^\infty ds \, \langle u_x(s) u_x(0) \rangle$$

As the diffusion coefficient is the integral of the velocity autocorrelation function it contains much less information than the VAF itself. In what follows we shall be more interested in the behaviour of $Z(t)$ than in the value of the diffusion coefficient which however provides the useful consistency equation (14).

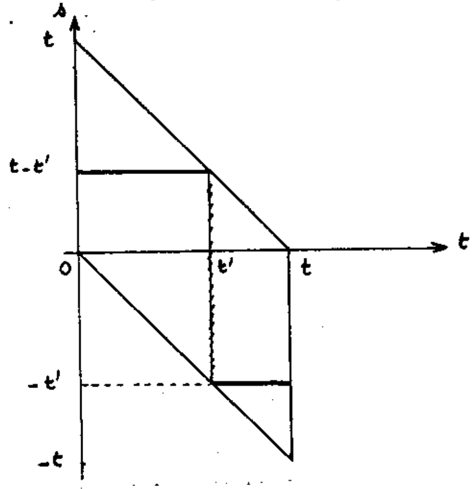

Figure 1. Domain of integration in the Eq. (13)

The short time behaviour of $Z(t)$ is given by the equation (A6) of the Appendix A:

$$(15) \qquad Z(t) = \langle u_x^2 \rangle \left[1 - \frac{t^2}{2!} \frac{\langle a\,a \rangle}{\langle u_x^2 \rangle} + \frac{t^4}{4!} \frac{\langle \dot{a}\,\dot{a} \rangle}{\langle u_x^2 \rangle} - \dots \right]$$

where $a = a_x$ is the x-component of the acceleration $\frac{1}{m} F_x$ of the particle subjected to the force F_x.

It is easy to calculate the mean-square value of the acceleration:

$$(16) \qquad \langle a\,a \rangle = \frac{1}{m^2} \langle F_x^2 \rangle = \frac{1}{m^2} \left\langle \frac{\partial U}{\partial x_0} \frac{\partial U}{\partial x_0} \right\rangle$$

where U is the potential energy of the system and x_0 refers to the position of the tagged particle along the x-axis.

The configurational average (16) can be written:

$$(17) \qquad \langle F_x^2 \rangle = \frac{1}{A} \int dr^{(N)} \, e^{-U/k_B T} \, \frac{\partial U}{\partial x_0} \frac{\partial U}{\partial x_0}$$

where $\qquad A = \int dr^{(N)} \, e^{-U/k_B T}$

The expression (17) can be integrated by parts to give:

$$\langle F_x^2 \rangle = \frac{k_B T}{A} \int dr^{(N)} \, e^{-U/k_B T} \, \frac{\partial^2 U}{\partial x_0^2}$$

so that:

$$(18) \qquad \langle F_x^2 \rangle = k_B T \left\langle \frac{\partial^2 U}{\partial x_0^2} \right\rangle = k_B T \, \frac{n}{3} \int d\vec{r} \, g(\vec{r}) \, \nabla^2 v(r)$$

if $v(|\vec{r} - \vec{r}_0|)$ denotes the two body interatomic potential and n is the number density of the fluid.

Bearing in mind that $\langle u_x^2 \rangle = k_B T / m$, it follows therefore that:

$$Z(t) = \frac{k_B T}{m}\left(1 - \Omega_0^2 \frac{t^2}{2!} + \cdots\right) \tag{19}$$

with

$$\boxed{\Omega_0^2 = \frac{n}{3m}\int d\vec{r}\; g(\vec{r})\, \nabla^2 v(r)} \tag{20}$$

It is straightforward to show that Ω_0 is the frequency of vibration of the tagged particle if all the atoms in the liquid were maintained fixed at their average equilibrium position. Let us imagine that the system is in equilibrium with the tagged particle located at $\vec{r}_0 = 0$. If we expand the potential energy around $\vec{r}_0$ we obtain:

$$U(\vec{r}, \vec{r}_1, \dots \vec{r}_N) = U(\vec{r}_0, \vec{r}_1, \dots, \vec{r}_N) + (\vec{r} - \vec{r}_0) . \vec{\nabla}_0 U$$

$$+ \frac{1}{2} \sum_{\alpha,\beta} \frac{\partial^2 U}{\partial x_0^\alpha \partial x_0^\beta} (x^\alpha - x_0^\alpha)(x^\beta - x_0^\beta)$$

We now take the configurational average to obtain:

$$\langle U(\vec{r}) \rangle = \langle U(\vec{r}_0) \rangle + \frac{1}{6} \langle \nabla^2 U \rangle (\vec{r} - \vec{r}_0)^2$$

and we see that the restoring force on the tagged particle is

$$- \frac{1}{3} \langle \nabla^2 U \rangle (\vec{r} - \vec{r}_0) = - m \Omega_0^2 (\vec{r} - \vec{r}_0)$$

1,3. Relation of Z(t) with other correlation functions

As we are mainly interested in the motion of a given atom, which we label "i", we shall concentrate on the self-correlation function:

$$G_s(\vec{r}, t) = \langle \delta [\vec{r} - (r_i(t) - r_i(0))] \rangle \tag{21}$$

which is the average probability density of finding the particle i at the position $\vec{r}_i(t) = \vec{r} + \vec{r}_i(0)$ when we know that it was located at the point $\vec{r}_i(0)$ at $t = 0$. The law of conservation of the tagged particle leads of course to the normalization:

$$\int G_s(\vec{r}, t)\, d\vec{r} = 1$$

and

$$\lim_{t \to \infty} G_s(\vec{r}, t) = \frac{1}{V}$$

We can alternatively define the density of the particle i at the point $\vec{r}$ and time t by:

$$\rho_i(\vec{r}, t) = \delta [\vec{r} - \vec{r}_i(t)]$$

and rewrite the equation (21) as:

$$G_s(\vec{r} - \vec{r}', t) = V \langle \delta(\vec{r} - \vec{r}_i(t))\, \delta(\vec{r}' - \vec{r}_i(0)) \rangle$$

$$= V \langle \rho_i(\vec{r}, t)\, \rho_i(\vec{r}', 0) \rangle$$

If we define the spatial Fourier transform $\rho_{ki}(t)$ of $\rho_i(\vec{r}, t)$ by:

$$\rho_{ki}(t) = \int d\vec{r}\, e^{-i\vec{k}.\vec{r}} \rho_i(\vec{r}, t) = e^{-i\vec{k}.\vec{r}_i(t)}$$

we obtain:

$$F_s(\vec{k}, t) = \int d\vec{r}\, e^{-i\vec{k}.\vec{r}} G_s(\vec{r}, t) = \langle e^{-i\vec{k}.(\vec{r}_i(t) - \vec{r}_i(0))} \rangle$$

or

$$F_s(\vec{k}, t) = \langle \rho_{ki}(t)\, \rho_{-ki}(0) \rangle \tag{22}$$

This shows that the intermediate scattering function $F_s(\vec{k}, t)$ is the time correlation function of the $\vec{k}$ Fourier component of the particle density.

In the same way, the current of the particle i is given by:

$$\vec{j}_i(\vec{r}, t) = \vec{u}_i(t)\, \rho_i(\vec{r}, t)$$

and the equation of continuity:

$$\frac{\partial \rho_i}{\partial t} + \vec{\nabla} \cdot \vec{j}_i = 0$$

can be written in Fourier transform as:

$$\dot{\rho}_{ki}(t) + i\vec{k} \cdot \vec{j}_{ki}(t) = 0$$

The self current autocorrelation function:

$$C_s(k,t) = \langle [\vec{k} \cdot \vec{j}_{ki}(t)][\vec{k} \cdot \vec{j}_{-ki}] \rangle$$

can therefore be written:

$$C_s(k,t) = \langle \dot{\rho}_{ki}(t)\, \dot{\rho}_{-ki} \rangle = -\langle \ddot{\rho}_{ki}(t)\, \rho_{-ki} \rangle$$

$$= -\frac{d^2 F_s(k,t)}{dt^2}$$

From this equation it follows that the time Fourier transforms of C_s and $F_s(k,t)$ are related by the equation:

$$C_s(k,\omega) = \omega^2 S_s(k,\omega) \qquad (23)$$

This result emphasizes the close relationship between the self part of the dynamic structure factor and the self current autocorrelation function.

The motion of the single particle is determined by $F_s(\vec{k},t)$ or its Fourier transform $S_s(\vec{k},\omega)$. The long time behaviour of $F_s(\vec{k},t)$ is given by the equation (6). It is also interesting to study the short time expansion of $F_s(\vec{k},t)$:

$$F_s(\vec{k},t) = 1 + \frac{t^2}{2!} \frac{d^2F_s}{dt^2}\Big|_{t=0} + \frac{t^4}{4!} \frac{d^4F_s}{dt^4}\Big|_{t=0} + \cdots \qquad (24)$$

where

$$\frac{d^2F_s}{dt^2}\Big|_{t=0} = -\langle \dot{\rho}_{ki}(t)\, \dot{\rho}_{-ki} \rangle_{t=0} = -k^2 \langle u_{ix}^2 \rangle = -k^2 \left(\frac{k_B T}{m} \right) = -\omega_0^2$$

if we define:

$$\omega_0^2 = k^2 \left(\frac{k_B T}{m} \right)$$

We therefore notice that the parabolic shape of $F_s(\vec{k},t)$ at short times is only determined by the mean-square value of the velocity of the tagged particle. This can be traced to the fact that, at very short times, the particle behaves as in an ideal gas. If we assume that the particle retains at time t the velocity it had at $t=0$, we obtain:

$$F_s(\vec{k},t) = \langle e^{-i\vec{k}\cdot\vec{u}_i t} \rangle = 1 - \frac{k^2}{2!} \langle u_{ix}^2 \rangle t^2 + \cdots$$

The next term in the expansion of $F_s(\vec{k},t)$ however involves the structure of the liquid. We have:

$$\frac{d^4F_s}{dt^4}\Big|_{t=0} = k^2 \langle \dot{j}^x_{ki}(t)\, \dot{j}^x_{-ki} \rangle_{t=0} = k^2 \langle \dot{u}_{ix}^2 + k^2 u_{ix}^4 \rangle$$

It is easy to show that $\langle u_{ix}^4 \rangle = 3 \left(\frac{k_B T}{m} \right)^2$ and we know from the equation (18) that $\langle \dot{u}_{ix}^2 \rangle = \frac{k_B T}{m} \Omega_0^2$. Hence:

$$\frac{d^4F_s}{dt^4}\Big|_{t=0} = \omega_0^2 \left(3\omega_0^2 + \Omega_0^2 \right)$$

where Ω_0 is related to $g(r)$ and to the interatomic potential. The short time expansion of $F_s(\vec{k},t)$ is then given by:

$$\boxed{F_s(\vec{k},t) = 1 - \omega_0^2 \frac{t^2}{2!} + \omega_0^2 \left(3\omega_0^2 + \Omega_0^2 \right) \frac{t^4}{4!} - \cdots} \qquad (25)$$

From this we can determine the first moments of $S_s(\vec{k},\omega)$. From the definition of the equation (9) we have:

$$F_s(\vec{k},t) = \int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t} S_s(\vec{k},\omega)$$

so that

$$\frac{d^n}{dt^n} F_s(\vec{k},t) = (-i)^n \langle \omega^n \rangle$$

where

$$\langle \omega^n \rangle = \int_{-\infty}^{+\infty} d\omega\, \omega^n S_s(\vec{k},\omega)$$

is the n frequency moment of $S_s(\vec{k},\omega)$. According to the expansion (25) we therefore obtain:

$$\begin{aligned} \langle \omega^0 \rangle &= \int_{-\infty}^{+\infty} S_s(\vec{k},\omega)\, d\omega = 1 \\ \langle \omega^2 \rangle &= \omega_0^2 \\ \langle \omega^4 \rangle &= \omega_0^2 \left(3\omega_0^2 + \Omega_0^2 \right) \end{aligned} \tag{26}$$

Let us also notice that:

$$- \lim_{k \to 0} \frac{1}{k^2} \frac{d^2 F_s(\vec{k},t)}{dt^2} = \langle u_{ix}(t)\, u_{ix} \rangle = Z(t)$$

so that we could expect to obtain $Z(t)$ from measurements of $F_s(\vec{k},t)$ at very small momentum transfers. The experiment is difficult however because one needs large incident energies ($\omega \sim 10^{13}\, s^{-1}$) and therefore small scattering angles. In these conditions it is difficult to extract $S_s(\vec{k},\omega)$ from the total dynamic structure factor $S(\vec{k},\omega)$.

1,4. Measurements of D using neutron diffraction (5)

It is in principle possible to measure the diffusion coefficient through neutron inelastic scattering experiments. It is well known that the double-differential scattering cross section for neutron scattering is given by:

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \left(\frac{k_1}{k_0}\right) \left[\langle b \rangle^2 S(\vec{k},\omega) + \left(\langle b^2 \rangle - \langle b \rangle^2 \right) S_s(k,\omega) \right] \tag{27}$$

where b is the scattering length of neutrons by a nucleus. The first term in (27) describes the coherent scattering of neutrons by the "average nucleus" of scattering length $\langle b \rangle$.

The second term describes the incoherent scattering. The incoherent scattering law provides very useful information about the average motion of a given atom among the other atoms in the fluid, but to obtain it requires the separation of the scattered intensity according to (27). From this point of view the ideal situation would be met if we could work on an element for which $\langle b \rangle$ happens to be small or vanishes. Unfortunately only two elements, Hydrogen and Vanadium, exhibit such a property; the first forms a molecular system whose theoretical analysis is difficult, and Vanadium has an inconvenient high melting point temperature. In order to obtain separately the coherent and incoherent parts of the scattering law it is therefore necessary to work with mixtures of different isotopic compositions. We shall take as an example the work of Sköld et al.(4) on liquid Argon at $T = 85.2$ K. They have made scattering experiments with neutrons of 15 and 20 meV on a sample of almost pure ^{36}A, an isotope for which the scattering is coherent, and on a mixture of ^{36}A and ^{40}A with the composition adjusted so that the ratio of incoherent to coherent scattering was close to the maximum value possible ($\sigma_{inc} / \sigma_{coh} \simeq 2.9$). We shall not dwell on experimental details but let us notice that the experimental corrections are very important in the analysis. In particular the data must be corrected for energy resolution broadening, scattering by the container and multiple scattering.

The appropriate scattering functions for the two samples are:

$$S^{36}(k,\omega) = \frac{1}{\left(b_c^{36}\right)^2+\left(b_i^{36}\right)^2}\left[\left(b_c^{36}\right)^2 S_{coh}(k,\omega) + \left(b_i^{36}\right)^2 S_{inc}(k,\omega)\right] \quad (28)$$

$$S^{m}(k,\omega) = \frac{1}{\left(b_c^{m}\right)^2+\left(b_i^{m}\right)^2}\left[\left(b_c^{m}\right)^2 S_{coh}(k,\omega) + \left(b_i^{m}\right)^2 S_{inc}(k,\omega)\right] \quad (29)$$

where the supercript "m" stands for "mixture" and b_c^m denotes for instance the coherent scattering length of the mixture. The equation (28) is solved for $S_{coh}(k,\omega)$ which is substituted in Eq. (29). This provides $S_{inc}(k,\omega)$ in terms of S^{36} and S^m; then S_{coh} can be obtain from the Eq. (28).

Let us notice that in a fluid, as in any system which possesses inversion symmetry, $S(\vec{k},\omega)$ should be invariant in the change $\vec{k} \to -\vec{k}$. Moreover in a classical fluid, $S(\vec{k},-\omega) = S(\vec{k},\omega)$. On the other hand the cross-sections for neutron scattering from an equilibrium system must obey the principle of detailed balance: the cross-section $S'(\vec{k},\omega)$ for the event where the system absorbs the energy $\hbar\omega$ from the incident neutron is larger, by the factor $\exp\left(\frac{\hbar\omega}{k_B T}\right)$ than $S'(\vec{k},-\omega)$, which describes the emission of a quantum $\hbar\omega$ by the system:

$$S'(\vec{k},\omega) = \exp\left(\frac{\hbar\omega}{k_B T}\right) S'(\vec{k},-\omega) \quad (30)$$

From this equation it is possible to construct a symmetrized form $\bar{S}(\vec{k},\omega)$ which has even parity with respect to ω:

$$\bar{S}(\vec{k},\omega) = \exp\left(-\frac{\hbar\omega}{2k_B T}\right) S'(k,\omega) \quad (31)$$

and it is $\bar{S}(\vec{k},\omega)$ which is to be used for comparison with the Fourier transform of density fluctuations in a classical fluid. In particular:

$$F_s(\vec{k},t) = \int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t}\, \bar{S}_{inc}(\vec{k},\omega)$$

$$= 2\int_0^{\infty} d\omega \cos\omega t\, \bar{S}_{inc}(\vec{k},\omega)$$

The experimental values for $\bar{S}_{inc}(\vec{k},\omega)$ obtained by Sköld et al. are shown in the figure (2). In order to interpret the data, and explain the overall shape observed, it is useful to consider two limits:

a) In an ideal gas there is no correlations between particles so that $G_d(\vec{r},t) = n$. The calculation of $G_s(\vec{r},t)$ is straightforward. If the tagged particle was located at the point $\vec{r} = 0$ at time $t = 0$, it is found at the point $\vec{r} = \vec{v}t$ at time t with the probability $f(\vec{v})$ given by the Maxwell distribution function of velocities. Therefore:

$$4\pi r^2 dr\, G_s(r,t) = 4\pi v^2 dv\, f(\vec{v})$$

with

$$f(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(-\frac{m v^2}{2k_B T}\right)$$

From this we obtain:

$$G_s(r,t) = \left(\frac{m}{2\pi k_B T t^2}\right)^{3/2} \exp\left(-\frac{r^2}{2\langle u_x^2\rangle t^2}\right) \quad (32)$$

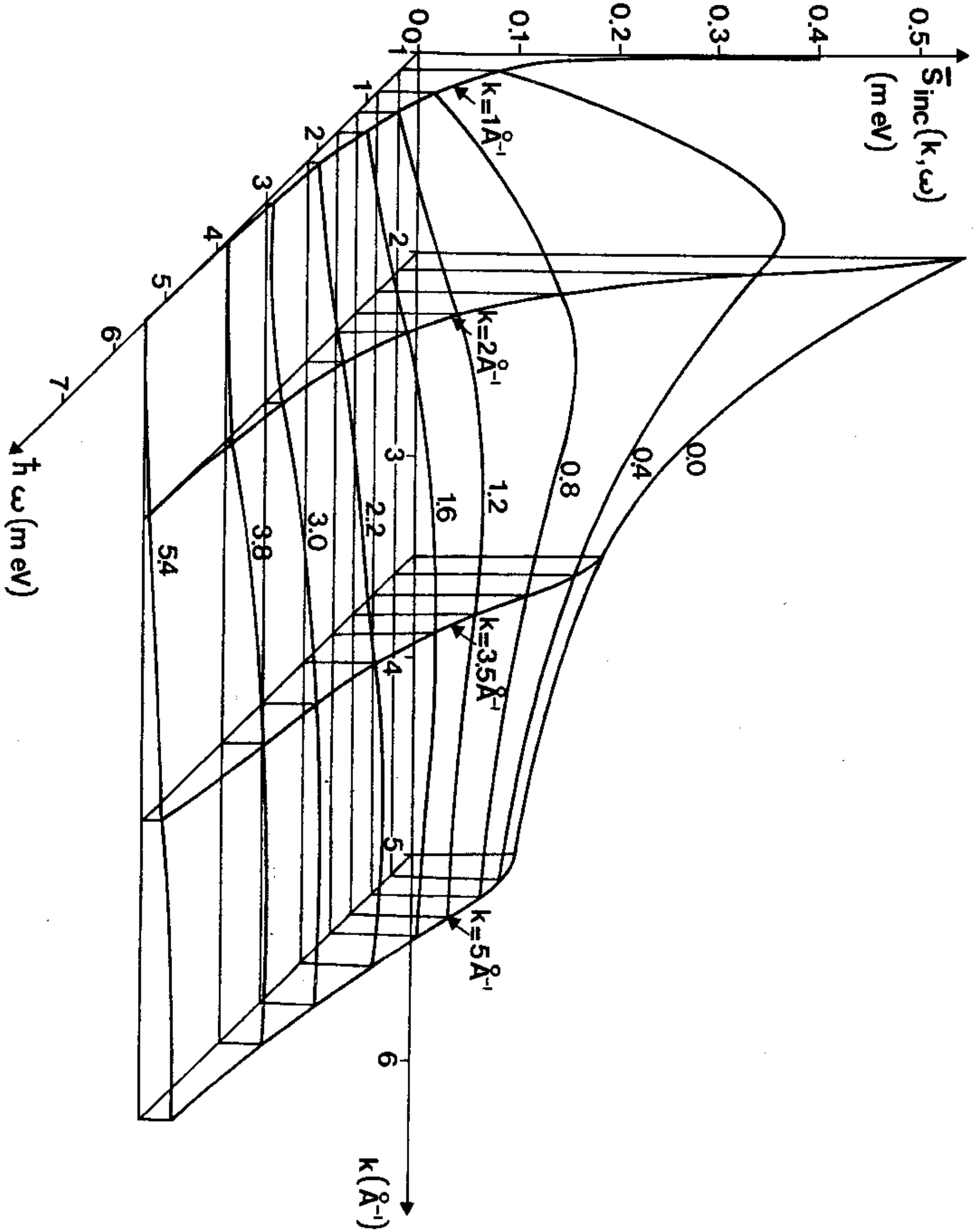

Fig.2. Incoherent scattering law from liquid argon at 85.2 K (after corrections). After Sköld et al.⁽⁴⁾

from which it follows that:

$$(33)\quad \begin{cases} F_s(k,t) = \exp\left(-\frac{1}{2}\langle u_x^2\rangle k^2 t^2\right) = \exp\left(-\frac{\omega_0^2 t^2}{2}\right) \\ S_s(k,\omega) = \left(\frac{m}{2\pi k_B T h^2}\right)^{3/2} \exp\left(-\frac{\omega^2}{2\omega_0^2}\right) \end{cases}$$

In this ideal gas limit $S_s(k,\omega)$ is a gaussian function of ω, with half width at half maximum:

$$(34)\qquad W(k) = k\left(2\ln 2\,\langle u_x^2\rangle\right)^{1/2}$$

$W(k)$ varies linearly with k. In a liquid this limit is interesting as $(t,\vec{r}) \to 0$ that is, as long as the tagged particle has not had the time to feel the presence of the other particles in the fluid. In practise the ideal gas limit is useful for $k \gtrsim 10$ Å^{-1} (see fig. 2).

b) At large $\vec{r}$ and t i.e. when the tagged particle has undergone a large number of collisions, the diffusion approximation becomes valid. The correlation functions are given by the Equations (6) and (7) and the self part of the dynamic structure factor is now a Lorentzian:

$$(35)\qquad S_s(k,\omega) = \frac{1}{\pi}\,\frac{Dk^2}{\omega^2 + (Dk^2)^2}$$

with a half width at half maximum $W(k) = Dk^2$, which varies parabolically with k. (See the fig. 3 for an illustration of the validity of the two limits).

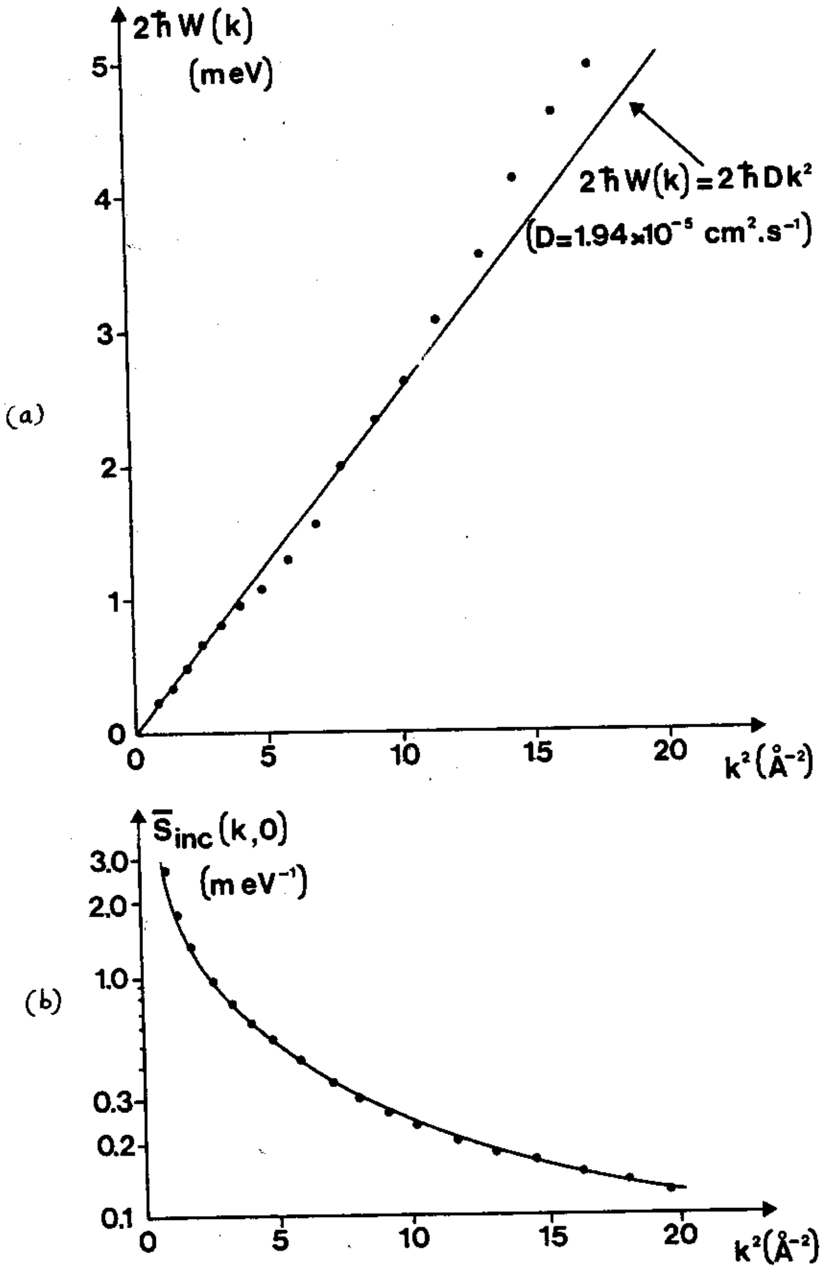

Fig 3. (a) Full width at half maximum $2\hbar W(k)$ of $\bar{S}_{inc}(k,\omega)$
- experimental points after correction (after Sköld et al (4)).

(b) — : simple diffusion result.
- experimental data after the resolution correction (4).

c) It is interesting to notice that in both limits of large and small $\vec{k}$ the intermediate scattering function $F_s(k,t)$ depends on k in a gaussian manner. It is therefore reasonable to assume that, for intermediate values of $\vec{r}$ and t, $G_s(r,t)$ varies according to the law:

$$G_s(r,t) = \left(\frac{1}{2\pi\alpha(t)}\right)^{3/2} \exp\left[-\frac{r^2}{2\alpha(t)}\right] \tag{36}$$

where $\alpha(t) = 2Dt$ in the diffusion approximation and $\alpha(t) = \langle u_x^2 \rangle t^2 = \frac{k_B T}{m} t^2$ in the short time limit. From this equation (36) we obtain the <u>gaussian approximation</u> to $F_s(k,t)$:

$$F_s(k,t) = \exp\left(-\frac{1}{2}\alpha(t) k^2\right) \tag{37}$$

It is easy to show by direct identification of the short time expansion of this expression of $F_s(k,t)$ with the equation (25) that:

$$\frac{1}{2}\alpha(t) = \frac{k_B T}{m}\left(\frac{t^2}{2!} - \frac{\Omega_0^2}{4!} t^4 + \cdots\right)$$

More generally it has been shown by Nijboer and Rahman (6) that:

$$\frac{1}{2}\alpha(t) = \frac{k_B T}{m}\left(\frac{t^2}{2!} - \Omega_0^2 \frac{t^4}{4!} + \cdots\right) \tag{38}$$

Inserting this in the expression (37) of $F_s(k,t)$ we obtain for $S_s(k,\omega)$:

$$S_s(k,\omega) = \frac{1}{(2\pi\omega_0^2)^{1/2}} e^{-\frac{\omega^2}{2\omega_0^2}} \left(1 + \frac{1}{4!}\frac{\Omega_0^2}{\omega_0^2} H_4\left(\frac{\omega}{\omega_0}\right) + \cdots\right) \tag{39}$$

where H_4 is the fourth Hermite polynomial. The first term in this expression describes the scattering from an ideal gas whereas the following terms represent corrections due to interactions of the tagged particle with the bath. Let us notice that the gaussian form (37) is an approximation; the next term in the exponent in $F_s(k,t)$ is γk^4 but it has been shown by Schofield (7) that the time expansion of $\gamma(t)$ starts with t^8. Neutron diffraction experiments and molecular dynamics calculations (8) have been frequently interpreted in terms of the long time (eq. 35) and short time (eq. 39) limits. The usual way to do this is to plot the half width at half maximum (HWHM) of $S_{inc}(k,\omega)$ as a function of k or of $k^2 D$.(9) (figure 4).

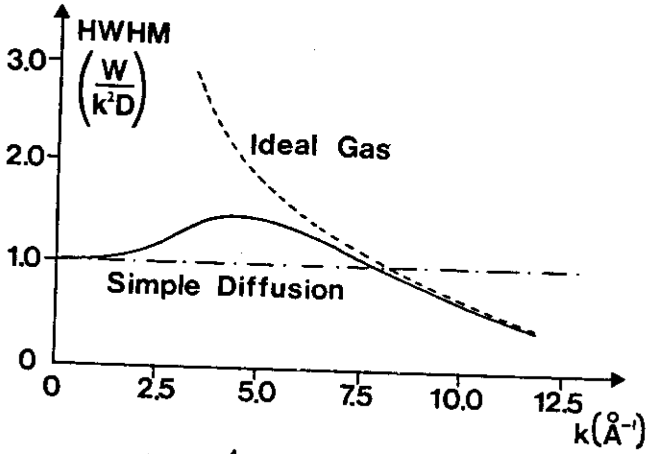

Fig. 4. Half width at half maximum of $S_{inc}(k,\omega)$ (—) and comparison with the simple diffusion result (–.–.–) and the ideal gas (- - -). After Rahman (9).

In the figure 4 it is shown how the exact result interpolates between the large k (ideal gas) and small k (diffusion) limits. Another example is given in the paper of Sköld et al (4), where they compare the full width at half maximum $2\hbar W(k)$ of $\bar{S}_{inc}(k,\omega)$ with the simple diffusion result (35) in liquid Argon at $T = 85.2$ K. (fig 3)

d) Validity of the gaussian approximation.

The validity of the gaussian approximation (37) has been theoretically studied by Nijboer and Rahman (6) who showed that the expansion of $F_s(k,t)$ is actually of the form:

$$(40)\quad F_s(k,t) = e^{-\frac{1}{2}\alpha(t)k^2}\left[1 + \alpha_2(t)\frac{(\alpha k^2/2)^2}{2!} - \left[\alpha_3(t) - 3\alpha_2(t)\right]\frac{(\alpha k^2/2)^3}{3!} + \left[\alpha_4(t) - 4\alpha_3(t) + 6\alpha_2(t)\right]\frac{(\alpha k^2/2)^4}{4!} + \cdots\right]$$

where $\alpha_n(t) = \dfrac{\langle r^{2n}\rangle}{C_n\langle r^2\rangle^n} - 1$ and $C_n = \dfrac{(2n+1)!!}{3^n}$;

$\langle r^{2n}\rangle$ is the $2n^{th}$ moment of the self correlation function $G_s(r,t)$. This theory has been checked experimentally by Sköld et al (4) and numerically by Levesque and Verlet (8) and Rahman (9).

The figure (5) shows that, in the gaussian approximation, the cross-over between the ideal gas and the diffusion regimes is located at about 5×10^{-12} s and that the maximum departure from the gaussian behaviour occurs in the vicinity of 10^{-12} s. More accurately, Levesque and Verlet showed that a good fit to the molecular dynamics data can be obtained with the function:

$$\alpha_2(t) = C\left(\frac{t_c}{t}\right)\exp\left(-\left(\frac{t_c}{t}\right)-1\right)$$

with $C = 0.1186$ and $t_c = 1.835 \times 10^{-12}$ s in liquid Argon at 85.2 K.

e) Another way of describing the intermediate scattering function $F_s(k,t)$ consists in constructing a width function $\alpha(t)$ which fits the small and large time behaviour of $F_s(k,t)$. For instance Egelstaff and Schofield (11) showed that using the width function:

$$(41) \qquad \alpha(t) = 2D\left[\left(t^2+c^2\right)^{1/2} - c\right]$$

with $c = mD/k_B T$, it is possible to represent fairly well the molecular dynamics data of Levesque and Verlet (12). This result is not surprising as $\alpha(t)$ given by the equation (41) varies as $2Dt$ for large t and as $\frac{k_B T}{m} t^2$ at short times. The only concern with the equation (41) is that it does not satisfy the fourth moment requirement (25). An improvement over (41) due to Lovesey (13, 14) is given by the equation

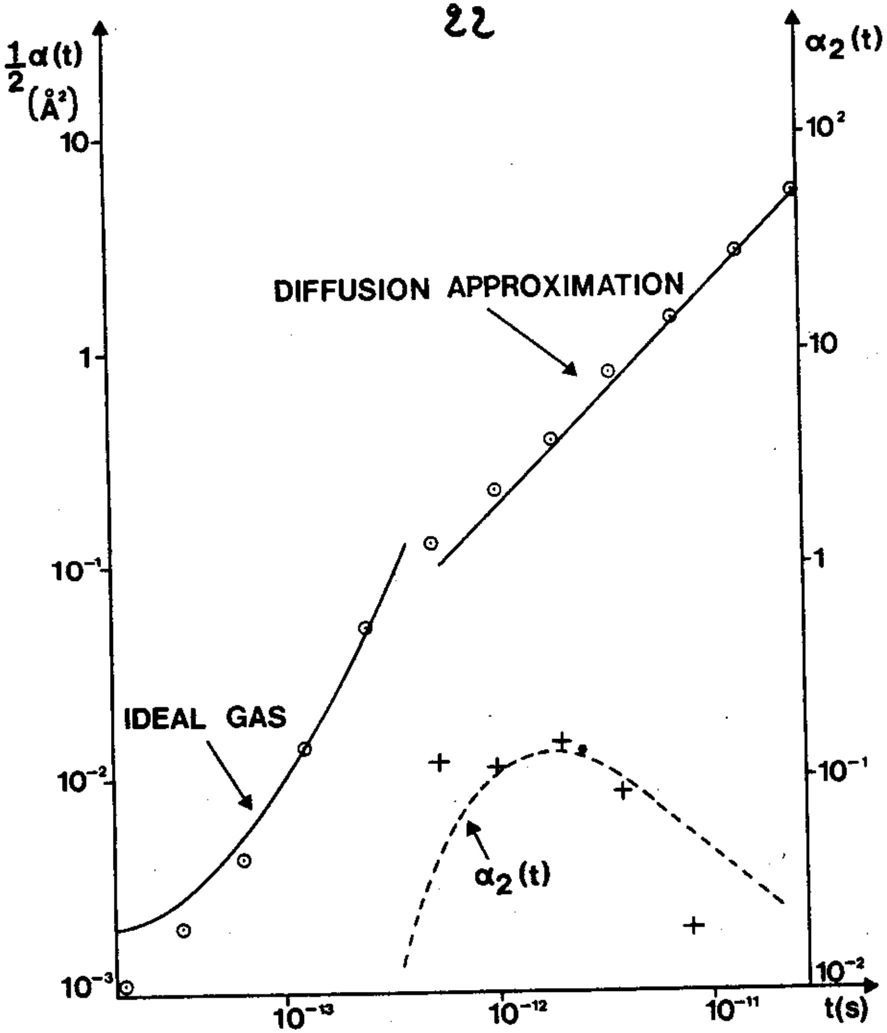

Figure 5. The width function $\frac{1}{2}\alpha(t)$ as defined in the Equation (37). The open circles and crosses are the experimental points obtained by Sköld et al (4). The solid lines represent the limit behaviour of $\frac{1}{2}\alpha(t)$ and the dotted line describes the result of the computer calculation of Levesque and Verlet (8). The full circle shows the result obtained by Rahman (9) for $\alpha_2(t)$ in argon at 94.4 K

(42) which satisfies the fourth moment condition:

$$(42) \qquad \bar{S}_s(k,\omega) = \frac{\pi^{-1}\tau\omega_0^2(\omega_s^2-\omega_0^2)}{[\omega\tau(\omega^2-\omega_s^2)]^2+(\omega^2-\omega_0^2)^2}$$

where $\omega_s^2 = 3\omega_0^2 + \Omega_0^2$ and $\tau^{-1} = \frac{mD}{k_B T}\Omega_0(\omega_s^2-\omega_0^2)^{1/2}$

The comparison of the result obtained for $F_s(k,t)$ when use is made of the width function (41) with computer data is given in the figure (6). For an exhaustive review of the experimental work done before 1975 the reader is referred to the paper of Copley and Lovesey (5).

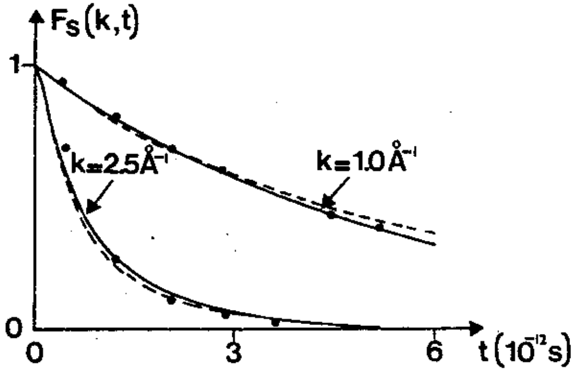

Figure 6. Approximations to $F_s(k,t)$.

— : Fourier transform of the equation (42) with $\Omega_0^2 = 0.58 \times 10^{26}\, s^{-2}$; $\frac{mD}{k_B T}\Omega_0 = 0.81$ (13,14).

• : Eglstaff and Schofield model (Eq. 41) with $c = \frac{mD}{k_B T} = 0.11 \times 10^{-12}\, s.$ (11)

- - - : MD result of Levesque and Verlet. (12)

1,5. Molecular Dynamics calculations.

The study of the motion of a tagged particle in a dense fluid is a difficult many-body problem because of the strong interactions between particles. The tagged particle interacts with the fluid which evolves with its own dynamics (in presence of the tagged particle) and reacts back on it at a later time. With respect to a system where the collisions are independent of each other, this back-flow effect of the fluid leads to a complicated dynamics. As we shall see in the next sections, the theories for describing these correlations are rather involved. It is in such situations that the method of molecular dynamics shows its full value. The method consists in a direct integration, by steps of about 10^{-14} s, of the Newton equations of motion of the particles in the fluid. The general method can be found for instance in the reference (15).

After the pioneering work of Alder et al (16) in hard sphere systems, Rahman (9) and Verlet (8) in Lennard-Jones fluids, we have a good idea of the behaviour of the V.A.F in dense fluids. A typical shape of the VAF is given in the figure (7). According to the density, two regimes can be observed:

a) at intermediate densities ($\frac{V}{V_0} \sim 3$) where V_0 is the close-packing volume, the VAF shows an initial decrease (see Eq. 19), followed by a plateau and a long time $t^{-3/2}$ tail. This long time behaviour can be understood as follows. If the tagged particle is given an initial momentum, it may excite hydrodynamic modes in the fluid and these modes may assist the tagged particle in its forward motion. As hydrodynamic modes decay rather slowly, this explains long lasting positive correlations of the velocity of the tagged particle. The $t^{-3/2}$ law can be also understood with the argument that the excess momentum given to the tagged particle is shared by a volume of fluid which increases as $t^{3/2}$. These features have been shown by Alder and Wainwright by integration of the Navier-Stokes equations.

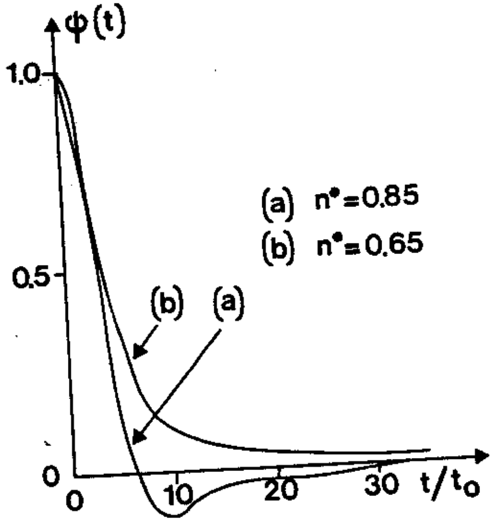

Fig. 7. The VAF $\phi(t)$ in a Lennard-Jones fluid at two different densities. After ref.(2)

b) at larger densities ($\frac{V}{V_0} \sim 1.6$), the VAF has a tendency to oscillate, becomes negative, shows a negative plateau and again decreases slowly in absolute value. This backscattering effect leads to a diffusion coefficient which is much smaller than expected if the collisions are assumed to be independent.

Let us also notice that molecular dynamics studies have also been made on systems with a tagged particle of mass and size different of those of the matrix (16,18), in ionic systems (18), in mixtures (19) and in isotopic mixtures (20,21). We will refer largely to these molecular dynamics calculations in the next sections.

II. THE LANGEVIN EQUATION.

We can learn a lot about the details of the dynamics of a single particle immersed in a fluid by studying the Langevin problem i.e. the dynamics of a large and heavy particle in a bath of small and light particles. Unfortunately we are in general interested by the description of a tagged particle of about the same mass as the bath particles. The results we are going to obtain in this section are not immediately applicable to such problems.

2.1. The simple Langevin equation. (22-25)

a) General method.

If a large particle is immersed in a fluid of small particles, it does not respond to impacts of individual atoms (or molecules) but to <u>fluctuations</u> of the total rate of impacts over its surface. The motion of the particle will therefore show an <u>average</u> behaviour, on which is superimposed an erratic motion due to the fluctuations in the force experienced by the particle. The equation of motion of the particle can be written:

$$m\dot{\vec{u}} = \vec{F}\left(t, \vec{u}[t']\right) \tag{43}$$

where the total force $\vec{F}$ on the particle at time t depends on the velocity $\vec{u}(t')$ at earlier times t'. In order to be able to solve the equation (43) the following approximations are made:

-a- the collision time τ_c (the characteristic time of the fluctuations) is assumed to be very small with respect to τ_R, the characteristic decay time of the velocity of the heavy particle. Under this assumption we are now allowed to assume that $\vec{F}$ depends only on the velocity $\vec{u}(t)$ at time t;

-b- $\vec{F}$ can be split into its <u>average value</u> $\langle \vec{F} \rangle_{\vec{u}}$ (given that the velocity of the particle is $\vec{u}$) and a <u>stochastic part</u> $\vec{R}(t)$:

$$\vec{F} = \langle \vec{F} \rangle_{\vec{u}} + \vec{R}(t)$$

-c- the systematic force $\langle \vec{F} \rangle_{\vec{u}}$, also called the friction force, is assumed to be proportional to the velocity of the particle (linear approximation):

$$\langle \vec{F} \rangle_{\vec{u}} = -\zeta \vec{u}$$

where ζ is the friction coefficient ($\zeta = 6\pi\eta a$ for a large sphere of radius a in a fluid of shear viscosity η, as given by Stokes' law). This approximation is clearly valid if the velocity of the Brownian particle is much smaller than the thermal velocity of bath particles.

-d- $\vec{R}(t)$, the random force, fluctuates very rapidly (characteristic time τ_c) with respect to the decay time $\tau_R = m/\zeta$ of u, and is independent of $\vec{u}$.

-e- on the time scale of the motion of the tagged particle, $\vec{R}(t)$ and $\vec{R}(t+\tau)$ are correlated over a very short time:

$$\langle X(t+\tau)\, X(t) \rangle = G\varphi(\tau) \sim G\delta(\tau) \tag{44}$$

for each component X of $\vec{R}$, and $\varphi(\tau)$ is sharply peaked at $\tau = 0$. According to these assumptions the equation (43) becomes:

$$(45) \qquad \frac{d\vec{u}}{dt} = -\frac{\zeta}{m}\vec{u} + \frac{1}{m}\vec{R}(t)$$

This is not an ordinary differential equation because $\vec{R}(t)$ has only statistically defined properties. The problem amounts to solving the Eq. (45) and finding the probability distribution $W(\vec{u}, t; \vec{u}_0)$ of the velocity at time t, given that it was $\delta(\vec{u}-\vec{u}_0)$ at $t = 0$. Moreover for $\tau \gg \tau_R$ the system recovers equilibrium. Therefore we know that W must become a Maxwellian distribution at large times and this requires certain statistical conditions for $\vec{R}(t)$. Solving (45) directly we obtain:

$$(46) \qquad \vec{u}(t) - \vec{u}_0\, e^{-\frac{\zeta}{m}t} = \int_0^t e^{\frac{\zeta}{m}(s-t)} \frac{\vec{R}(s)}{m}\, ds$$

After a large number of collisions, i.e. for $\tau \gg \tau_c$, the probability distribution $W(\vec{A})$ of the r.h.s. of (46) must be Maxwellian, because it is the sum of a large number of random contributions. If we write:

$$\vec{A} = \int_0^t \psi(s)\, \vec{R}(s)\, ds$$

where $\psi(s) = \frac{1}{m}\exp\left(\frac{\zeta}{m}(s-t)\right)$, it is possible to show that:

$$(47) \qquad W(\vec{A}) = \frac{1}{\left(4\pi q \int_0^t \psi^2(s)\, ds\right)^{3/2}} \exp\left[-\frac{|\vec{A}|^2}{4q\int_0^t \psi^2(s)\, ds}\right]$$

where $q = (k_B T)\,\zeta$

Hence it is possible to determine the probability distributions of the velocity $\vec{u}$ and of the position $\vec{r}$ of the Brownian particle. In practise we are more interested in the average $\langle \cdots \rangle_1$ of a physical quantity, given that at $t = 0$ the Brownian particle was at point $\vec{r}_0$ with the velocity $\vec{u}_0$. It is easy to obtain the following results:

$$(48) \qquad (i) \quad \langle \vec{u}(t) \rangle_1 = \vec{u}_0\, e^{-\beta t} \qquad \left(\beta = \frac{\zeta}{m}\right)$$

from which it follows that the velocity autocorrelation function $Z(t) = \langle u_x(t)\, u_x(0) \rangle$ is given by:

$$(49) \qquad Z(t) = \langle u_{0x}^2 \rangle\, e^{-\beta t} = \frac{k_B T}{m} e^{-\beta t}$$

This form is clearly incorrect at small t as $Z(t)$ should be an <u>even</u> function of t and its short time expansion should not contain terms proportional to t (see the eq. 15).

$$(50) \qquad (ii) \quad \langle \vec{r} - \vec{r}_0 \rangle_1 = \frac{\vec{u}_0}{\beta}\left(1 - e^{-\beta t}\right)$$

This shows that the center of gravity of the positions of the Brownian particle at time t is displaced by the so called "diffusive step" $\frac{\vec{u}_0}{\beta}$ from $\vec{r}_0$. Note that $\vec{u}_0/2\beta$ is the distance the particle would travel to rest if it were subjected to the constant friction force $-\beta m \vec{u}_0$.

$$(51) \qquad (iii) \quad \langle u^2(t) \rangle_1 = u_0^2\, e^{-2\beta t} + 3\frac{k_B T}{m}\left(1 - e^{-2\beta t}\right)$$

$$(52) \qquad (iv) \quad \langle (\vec{r} - \vec{r}_0)^2 \rangle_1 = \frac{u_0^2}{\beta^2}\left(1 - e^{-\beta t}\right)^2 + 3\frac{k_B T}{m\beta^2}\left(2\beta t - 3 + 4e^{-\beta t} - e^{-2\beta t}\right)$$

This equation is especially interesting when we consider the case when the initial velocity $\vec{u}_0$ is not fixed, but has a Maxwellian distribution. Averaging (52) over $\vec{u}_0$ we obtain:

$$(53) \qquad \langle\langle(\vec{r}-\vec{r}_0)^2\rangle_1\rangle = \frac{6k_BT}{m\beta^2}\left(\beta t-1+e^{-\beta t}\right)$$

This last equation shows that the mean-square displacement of the Brownian particle varies linearly with time:

$$\langle(\Delta\vec{r})^2\rangle = 6Dt$$

with $\qquad D = \dfrac{k_BT}{\zeta}$

(Einstein law)

b) Calculation of the friction coefficient $\zeta=m\beta$

The friction coefficient ζ is actually related to the autocorrelation function of the total force acting on the Brownian particle. From the equation (46) we have:

$$(54) \qquad \langle(\Delta\vec{u})^2\rangle_1 = \frac{3G}{2\beta m^2}\left(1-e^{-2\beta t}\right)$$

$$(55) \qquad \langle\vec{R}(0).\vec{u}(t)\rangle_1 = \frac{3G}{m}\,\theta(t)\,e^{-\beta t}$$

$$(56) \qquad \langle\vec{u}(0).\vec{u}(t)\rangle_1 = \frac{3k_BT}{m}\,e^{-\beta|t|}$$

where $\theta(t)$ is the step function.

Comparing (51) and (54) we see that $G=(2\beta m)k_BT$ which shows that the fluctuations of the random force $\vec{R}(t)$ are not independent of the friction coefficient β. This point will be made more explicit in what follows. Using the preceding equations it is easy to calculate the autocorrelation function of the total force $\vec{F}(t)$:

$$\mathcal{G}(t) = \langle\vec{F}(0).\vec{F}(t)\rangle = \langle(-m\beta\vec{u}(0)+\vec{R}(0)).(-m\beta\vec{u}(t)+\vec{R}(t))\rangle$$

$$(57) \qquad = 3G\left[\delta(t)-\tfrac{1}{2}\beta e^{-\beta t}\right]$$

The behaviour of $\mathcal{G}(t)$ is shown in the figure (8).

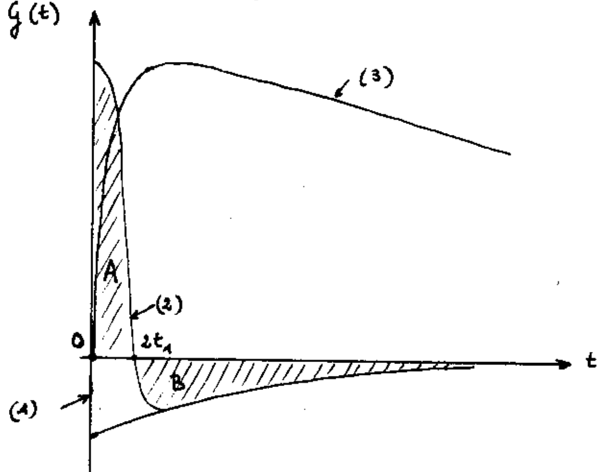

Figure 8. The autocorrelation function of the total force $\vec{F}$ acting on the Brownian particle.

(1) From the formula (57)

(2) Replacing $\delta(t)$ by the more realistic function $\varphi(t)\sim(2t_1)^{-1}$ over the time interval $[0,t_1]$.

(3) Integral of $\langle\vec{F}(0).\vec{F}(t)\rangle$. Notice that the areas A and B are equal.

According to the figure (8), the total force $\vec{F}$ is made of a fluctuating part $\vec{R}$ with a short memory $(\sim t_1)$ superimposed on a systematic force with the correlation time $\beta^{-1} \gg t_1$. The area under the curve (2) of figure (8) vanishes, which emphasizes the connection between the two types of forces. This peculiar behaviour of $G(t)$ provides a simple means for calculating the friction coefficient ζ. The integral $I(t) = \int_0^t G(s)\,ds$ increases rapidly, until the plateau time t_1 is reached. After the time t_1, $I(t)$ decreases very slowly (time scale β^{-1}) and the plateau value of $I(t)$ is:

$$I(t_1) = \int_0^{t_1} \langle \vec{F}(0) . \vec{F}(t) \rangle dt = \frac{3G}{2} = 3 k_B T \zeta$$

as can be seen from the Eq. (57). This shows that the friction coefficient ζ can be expressed as an integral of the autocorrelation function of the total force over an interval of time characteristic of the fluctuating force:

$$(58) \qquad \zeta = \frac{1}{3k_BT} \int_0^{\tau \gtrsim t_1} \langle \vec{F}(0) . \vec{F}(t) \rangle_1 \, dt$$

where the notation $\langle \cdots \rangle_1$ means that the initial momentum of the Brownian particle is $\vec{p}_{10}$. Let us notice that, within the time τ, $\vec{F}(t)$ keeps essentially the value $\vec{F}(0)$ it had at $t=0$. An order of magnitude of ζ is therefore:

$$\zeta = \frac{1}{k_BT} \langle F_x^2 \rangle_1 \tau$$

where $\langle F_x^2 \rangle_1 = k_B T m \Omega_0^2$. Hence we obtain the approximate result:

$$\zeta = m \Omega_0^2 \tau$$

and, according to the Einstein formula:

$$(59) \qquad D = \frac{k_BT/m}{\Omega_0^2 \tau}$$

The expression (58) has been extensively used to calculate diffusion coefficients in liquids and its validity has been demonstrated by Lebowitz$^{(29)}$ and Résibois$^{(30)}$. We notice that ζ can also be put in the form:

$$(60) \quad \zeta = \frac{1}{3k_BT} \left(\langle \vec{F}(0) . \vec{p}_{1\tau} \rangle - \langle \vec{F}(0) . \vec{p}_{10} \rangle \right)$$

where $\vec{p}_{1\tau}$ is the momentum of the Brownian particle at time τ. In an equilibrium system $\vec{F}(0)$ and $\vec{p}_{10}$ are not correlated: $\langle \vec{F}(0) . \vec{p}_{10} \rangle = 0$. Moreover as $\tau \to \infty$, $\langle \vec{F}(0) . \vec{p}_{1\tau} \rangle \to 0$ because the Brownian particle looses the memory of the force it has experienced at $t=0$. According to the equation (58) we can say that the particle is being accelerated in the time 0 to t_1. During this time interval the particle keeps the memory of its initial position and the total force does not vary much. After time t_1 the direct correlation between the fluctuating forces disappears and a new effect sets in, i.e. a friction force which tends to decelerate the particle. This decoupling of the two processes can only be made if $t_1 \ll \beta^{-1}$ that is, if the direct and indirect correlation processes do not overlap. Let us also notice that, for calculating the integral in the Equation (58) there is no need for a friction mechanism! The friction coefficient merely results from an analysis of the autocorrelation function of the total force$^{(26,27)}$.

Many calculations of the friction coefficient ζ using (58) have been made$^{(31-35)}$ along the principles carefully settled by Helfand$^{(27)}$. In particular it is convenient to consider to limiting cases: the limit of <u>small forces</u> acting on the particle and the <u>hard sphere</u> interaction.

b1 - Small forces.

Let us first notice that, if $\varphi(\vec{R}^N, \vec{P}^N)$ is a dynamical variable which depends on the sets $\vec{R}^N = \vec{r}_1, \ldots, \vec{r}_N$ and $\vec{P}^N = \vec{p}_1, \ldots, \vec{p}_N$ of all the particles in the system, the variation in time of φ is governed by the equation:

$$(61) \qquad \frac{\partial \varphi}{\partial t} = \sum_{j=1}^{N} \left[\frac{\vec{p}_j}{m_j} \cdot \vec{\nabla}_{\vec{r}_j} + \vec{F}_j \cdot \vec{\nabla}_{\vec{p}_j} \right] \varphi = iL\varphi$$

where L is the Liouville operator. The time evolution of φ is therefore given by the equation:

$$\varphi(t) = e^{iLt} \varphi(0)$$

Using this, we can formally write the autocorrelation function of the total force $\vec{F} = -\vec{\nabla}_{r_1} U$ experienced by the Brownian particle as follows:

$$(62) \quad \langle \vec{F}(0) \cdot \vec{F}(t) \rangle_1 = \langle \vec{\nabla}_{\vec{r}_1} U(\vec{R}_0^N) \cdot e^{itL} (\vec{\nabla}_{\vec{r}_{10}} U(\vec{R}_0^N)) \rangle_1$$

But according to the equation (16):

$$\langle \vec{\nabla}_{\vec{r}_1} U \cdot \vec{a} \rangle = k_B T \langle \vec{\nabla}_{r_1} \cdot \vec{a} \rangle$$

if the average is taken in an equilibrium system. Hence:

$$(63) \quad \langle \vec{F}(0) \cdot \vec{F}(t) \rangle_1 = k_B T \langle \vec{\nabla}_{\vec{r}_{10}} \cdot e^{itL} \vec{\nabla}_{\vec{r}_{10}} U(\vec{R}_0^N) \rangle_1$$

Now in the case of <u>small forces</u>, either because the interatomic potential is small or because the interatomic forces add vectorially to a small resultant, we can assume that in the time interval $0-\tau$, the trajectories of all particles are <u>linear</u> and that they do not suffer any acceleration along their path. This is the essence of the <u>linear trajectory approximation</u>. Within this approximation:

$$iL \simeq iL_0 = \sum_j \frac{\vec{p}_j}{m_j} \cdot \vec{\nabla}_{\vec{r}_j}$$

and L_0 commutes with $\vec{\nabla}_{\vec{r}_{10}}$ in the Eq. (63) so that we obtain the following expression for the friction coefficient:

$$(64) \qquad \zeta^s = \frac{1}{3} \int_0^\tau \langle \vec{\nabla}^2_{\vec{r}_{10}} U(\vec{R}_0^N + \vec{V}_0^N t) \rangle_1 \, dt$$

where the superscript "s" recalls that this result is only valid in the case of soft forces. This expression is easy to evaluate when the total potential U is taken as a sum of soft pair potentials $V^s(\vec{r}_{12})$. In particular if (64) is applied to the <u>self-diffusion</u> problem (a procedure not allowed in principle because, in all that has been done previously we assumed that the diffusing atom is much larger than bath particles) we obtain$^{(27,32)}$:

$$(65) \qquad \zeta^{S} = -\frac{1}{3}\left(\frac{\pi m}{k_B T}\right)^{1/2} \frac{1}{(2\pi)^2} \int_0^{\infty} k^3 \tilde{V}^S(k)\, \tilde{G}(k)\, dk$$

where n is the number density, $\tilde{V}^S(k)$ and $\tilde{G}(k)$ are respectively the Fourier transforms of $V^S(\vec{r})$ and $[g(r)-1]$.

-b2- Hard sphere interactions

Again we could apply the Brownian motion formalism to HS systems if the diffusing particle were much heavier than the others. Nevertheless Kirkwood$^{(26)}$ proposed to use these techniques for the calculation of ζ in the self-diffusion problem. The validity of such a procedure is not proved but we can say that (i) when the calculations are completed along this basis they give results which compare favourably with experimental data ; (ii) in an ordinary fluid, the friction coefficient ζ^H arising from short range strong forces is usually smaller than ζ^S, the friction coefficient due to long range, soft forces.

In a system of hard spheres we evaluate ζ^H using the equation (54). For short times $\beta\tau \ll 1$ and it is easy to obtain :

$$\langle (\Delta \vec{p}_\tau)^2 \rangle = 3 G \tau = 6 k_B T \zeta \tau$$

so that :

$$(66) \quad \zeta = \frac{1}{6 k_B T \tau} \langle (\Delta \vec{p}_\tau)^2 \rangle_1$$

where $\Delta\vec{p}_\tau = \vec{p}_{1\tau} - \vec{p}_{10}$ is the increment of the momentum of the Brownian particle in the time interval τ. We are therefore led to a simple kinetic theory problem : we have to count how many collisions occur in time τ, calculate the

momentum transfer to the tagged particle and average. The result, which can be obtained with other methods, is :

$$(67) \qquad \zeta^H = \frac{8}{3}\, n\, g(\sigma)\, \sigma^2 (\pi m k_B T)^{1/2}$$

where σ is the hard sphere diameter and $g(\sigma)$ is the radial distribution function at contact. This expression has also been obtained using similar arguments by Enskog$^{(36)}$, Longuet-Higgins and Pople$^{(37)}$ and Rice et al.$^{(38)}$. See also the reference (39) for a comprehensive discussion of the application of binary collision techniques for calculating ζ in hard-sphere systems.

-b3- Real systems.

In real systems (liquid argon, normal metals ...) we can split the two-body potential into a hard core repulsion $V^H(r)$ and a soft part $V^S(r)$:

$$V(r) = V^S(r) + V^H(r)$$

The autocorrelation function of the total force can thus be decomposed in three parts :

$$(68) \quad \langle \vec{F}(0) . \vec{F}(t) \rangle = \langle (\vec{F}_0^H + \vec{F}_0^S) . \vec{F}_t^S \rangle + \langle \vec{F}_0^H . \vec{F}_t^H \rangle + \langle \vec{F}_0^S . \vec{F}_t^H \rangle$$

and accordingly :

$$(69) \qquad \zeta = \zeta^S + \zeta^H + \zeta^{SH}$$

ζ^S can be calculated using the linear trajectory approximation (Eq. (65)) ; ζ^H is given by the Equation (67). The cross coefficient ζ^{SH}, initially neglected by Helfand$^{(27)}$ has been studied by Davis and Palyvos$^{(32, 33)}$ and Rice and Gray(24). In a Lennard-Jones fluid they show that

(i) ζ^S predominates at low temperature and large density whereas ζ^H predominates at high temperature and low density;

(ii) at the melting temperature ζ^S account for about 80% of ζ;

(iii) estimations of ζ^{SH} using the linear trajectory approximation show that $\zeta^{SH} \sim \zeta^H$.(34,35) However it is doubtful that the consideration of ζ^{SH} increases noticeably the agreement between theory and experiment (figure 9).

For instance in argon at 84.5 K and 1 atm. (0.0353 mole × cm^{-3}) Helfand(27) obtains $\zeta^S = 3.27 \times 10^{-10}$ g.s^{-1} and $\zeta^H = 0.64 \times 10^{-10}$ g.s^{-1} so that $\zeta = 3.9 \times 10^{-10}$ g.s^{-1} from which it follows that $D_{calc} = 3 \times 10^{-5}$ cm^2.s^{-1} to be compared with the experimental values $D_1 = 1.5 \times 10^{-5}$ cm^2.s^{-1} (40); $D_2 = 2 \times 10^{-5}$ cm^2.s^{-1} (41). The agreement between calculated values and experiments is rather good in view of the crudeness of the approximations that have been made.

2.2. Hydrodynamic calculations of the friction coefficient.

From the Einstein expression of D in terms of the friction coefficient ζ we can hope to obtain reasonable values of D if we can calculate ζ in an approximate way. Using the hydrodynamic theory Stokes(42) calculated ζ for the <u>steady motion</u> at small velocity $\vec{u}$ of a large sphere in a viscous, incompressible fluid. This is done by writing the Navier-Stokes equations for the fluid:

$$\begin{aligned} &\frac{\partial \rho}{\partial t} + \mathrm{div}\,(\rho \vec{v}) = 0 \\ &\rho \frac{\partial \vec{v}}{\partial t} + \rho \vec{v}.\vec{\nabla}\vec{v} = -\vec{\nabla}P + \eta \nabla^2 \vec{v} + \left(\tfrac{1}{3}\eta + \eta_v\right)\vec{\nabla}(\vec{\nabla}.\vec{v}) \end{aligned} \tag{70}$$

where $\vec{v}$ is the velocity of the fluid, ρ its mass density, P the pressure; η and η_v are the usual shear and bulk viscosities.

a) Stokes-Einstein calculation

The equations (70) have been solved by Stokes$^{(42)}$ within the following approximations:

(i) steady motion: the velocity $\vec{u}$ of the sphere is assumed to be constant so that $\partial\rho/\partial t = 0$ and $\operatorname{div}(\rho\vec{v}) = 0$; hence the system behaves as if the fluid were incompressible;

(ii) linearization: the velocity $\vec{v}$ is assumed to be small and terms of second order in $\vec{v}$, like $\vec{v}.\vec{\nabla}\vec{v}$ are omitted,

(iii) boundary conditions: the velocity of the fluid vanishes at large distance and, at the surface of the sphere, Stokes considers two types of boundary conditions:

- "stick" condition: the fluid is assumed to adhere perfectly to the surface of the sphere hence $\vec{v} = u$ along S;
- "slip" condition: S behaves as a perfect mirror for fluid molecules. There is no shear stress in the fluid along the surface S and $v_n = u_n$.

Given the previous assumptions and the boundary conditions, it is possible to calculate the velocity field and the stress tensor at the surface of the sphere from which the force $\vec{F}$ on the sphere can be deduced. Stokes obtained the following results:

$$\text{stick} \quad : \quad \zeta = 3\pi\eta\sigma$$

$$\text{slip} \quad : \quad \zeta = 2\pi\eta\sigma$$

where σ is the diameter of the sphere. These values lead to diffusion coefficients of remarkable approximate validity. For instance in argon we obtain the experimental value of D by using $\sigma_{stick} = 2.35\,\mathring{A}$; $\sigma_{slip} = 3.5\,\mathring{A}$.

b) Zwanzig and Bixon's generalization$^{(43)}$

In the framework of the Langevin theory, the velocity autocorrelation function decreases exponentially with time, contrary to computer data which show that the VAF becomes negative – at least in large density fluids – for $t \sim 4\times10^{-13}$ s. A way to remedy this defect has been shown by Zwanzig and Bixon$^{(43)}$:

(i) in the Langevin spirit, the relaxation time of the velocity of the tagged particle is:

$$\beta^{-1} = \frac{m}{\zeta} = D\,\frac{m}{k_B T} \sim 10^{-13}\ s.$$

On the other hand the time necessary for a sound wave to propagate over an interatomic distance is of the same order of magnitude. In consequence the approximation of fluid incompressibility (or equivalently of an infinite sound velocity) is certainly not safe. We therefore must remove the approximation of stationary motion and make a Fourier analysis in time;

(ii) at high frequencies the fluid behaves elastically whereas, at low frequencies, it can be considered as only viscous. If we wish to cover the whole frequency spectrum we must take account of this viscoelastic behaviour by defining a complex viscosity:

(71) $$\eta(\omega) = \frac{}{1-i\omega\tau}$$

where τ is the relaxation time for viscosity ($\tau \sim 10^{-13}$ s).

(iii) the gradient of the pressure which enters the Navier-Stokes equations can be expressed as a function of two independent variables, for instance the temperature T and the density ρ:

(72) $$\vec{\nabla} P = \left(\frac{\partial P}{\partial \rho}\right)_T \vec{\nabla}\,\delta\rho + \left(\frac{\partial P}{\partial T}\right)_\rho \vec{\nabla} T$$

At high frequencies the fluid is expected to behave isothermally so that:

$$\vec{\nabla} P = c^2\, \vec{\nabla}\,\delta\rho$$

where c is the isothermal sound velocity. This equation, together with the Navier-Stokes equations, allow us to calculate the velocity field and the frequency dependent friction coefficient $\zeta(\omega)$ defined as the ratio of the Fourier component of the force on the sphere by the velocity:

(73) $$\vec{F}_\omega = -\,\zeta(\omega)\,\vec{U}(\omega)$$

where $\vec{u}(\omega)$ is the ω Fourier component of $\vec{u}(t)$.

When ζ is independent of the frequency the normalized VAF is:

(74) $$\psi(t) = e^{-\beta|t|} = \int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t}\, \frac{1}{\pi}\, \frac{1}{-i\omega+\beta}$$

If we replace the constant β by $\beta(\omega) = \zeta(\omega)/m$ obtained through the equation (73), we obtain the VAF given by Zwanzig and Bixon (figure 10).

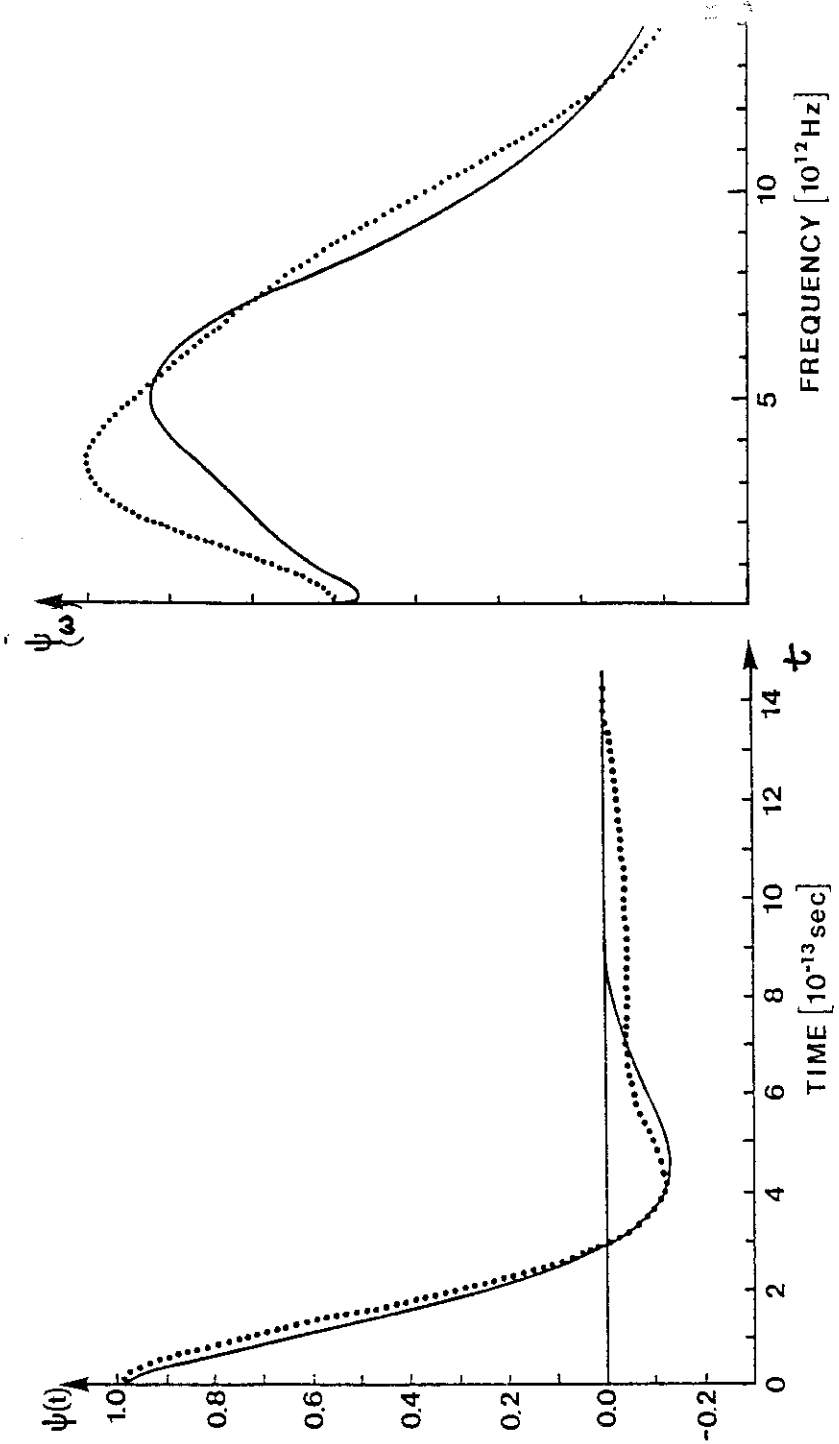

Figure 10. The normalized VAF $\psi(t)$ and its spectrum $\psi(\omega)$ in argon. After Zwanzig and Bixon (43)

It is interesting to look at the limiting behaviour of $\psi(\omega)$ given by the equation (74):

(i) when $\omega \to \infty$, $\psi(\omega) \sim \omega^{-2}$. This has the consequence that, at short time, the VAF has the same time dependence as:

$$(75) \qquad \int_{\alpha}^{\infty} \frac{d\omega}{\omega^2} \cos \omega t$$

where α is a cutoff frequency. From (75) we obtain $\underset{t \to 0}{\psi(t)} \sim a - bt$. Hence $\psi(t)$ exhibits a non physical cusp at $t = 0$ (figure 10) which arises from the fact that the actual interatomic interactions have been described by boundary conditions at the surface of the sphere;

(ii) when $\omega \to 0$, Zwanzig and Bixon show that the generalized hydrodynamics calculation leads to

$$\underset{\omega \to 0}{\psi(\omega)} \sim a' - b' \omega^{1/2}$$

so that

$$\underset{t \to \infty}{\psi(t)} \sim t^{-3/2}$$

A more careful analysis of the Navier - Stokes equations led Dorfman and Cohen (45) to the following asymptotic form of $\psi(t)$:

$$(76) \qquad \underset{t \to \infty}{\psi(t)} \sim \frac{1}{d(d-1)} \frac{1}{n} \frac{1}{\left[4\pi (D+\nu) t\right]^{3/2}}$$

where d is the dimensionality of the system, n the number density and $\nu = \eta / nm$ the kinematic viscosity. This long time behaviour of $\psi(t)$ has been confirmed by Levesque and Ashurst (47) by a molecular dynamics study of a system of 4000 particles interacting through the repulsive part of a Lennard - Jones potential. In hard sphere systems this has been done by Alder and Wainwright. (48)

2,3. The generalized Langevin equation. The memory function formalism.

While the simple Langevin equation is often reliable and enlightening, it suffers from some defects:

(i) it predicts a VAF $\psi(t) \sim \exp(-\beta|t|)$ whereas $\psi(t)$ cannot be exponential at short times. Its first derivative $\frac{m}{k_B T} \frac{d}{dt} \langle u_x(0) u_x(t) \rangle = \frac{1}{k_B T} \langle u_x(0) F_x(t) \rangle$ should vanish at $t = 0$ because $F_x(0)$ and $u_x(0)$ are not correlated, a condition which is not fulfilled by the exponential formula;

(ii) it is assumed that the force at time t depends only of the velocity of the particle at time t. This approximation completly neglects retardation or backflow effects. Actually at times $t' < t$ the tagged particle creates a perturbation in the fluid which propagates in time until time t.

A simple generalization of the Langevin equation is generally used, where these retardation effects are apparent:

$$(77) \qquad \frac{du_x}{dt} + \int_0^t K(t-\tau)\, u_x(\tau)\, d\tau = \frac{R_x(t)}{m} = a_x(t)$$

where $R_x(t)$ and $a_x(t)$ are the fluctuating force and acceleration respectively. Here $K(t)$ is a generalization of the friction coefficient $\beta = \zeta / m$. In particular, if $K(t) = 2\beta\, \delta(t)$ the simple Langevin equation is recovered. Again the fluctuating force $R_x(t)$ vanishes on the average and is not correlated with the initial velocity. Now we shall see that the memory function $K(t)$ is equal to the autocorrelation function of the fluctuating acceleration $a_x(t)$. This can be demonstrated in a number of ways. For instance we can start from the equation (77) and, because $\langle u_x(0)\, R_x(t)\rangle = 0$ we obtain the following equation for $\psi(t)$:

$$(78) \qquad \dot\psi(t) + \int_0^t K(t-\tau)\,\psi(\tau)\,d\tau = 0$$

from which it follows automatically that $\dot\psi(0) = 0$, as it must be. After differentiation, the equation (78) becomes:

$$(79) \qquad \ddot\psi(t) + K(0)\,\psi(t) + \int_0^t \dot K(t-\tau)\,\psi(\tau)\,d\tau = 0$$

so that
$$K(0) = -\frac{\ddot\psi(0)}{\psi(0)} = \frac{\langle \dot u_x(0)\,\dot u_x(0)\rangle}{\langle u_x^2\rangle} = \Omega_0^2$$

We also notice that, by integration by parts, we can also write the equation (79) as follows:

$$(80) \qquad \ddot\psi(t) + K(t)\,\psi(0) + \int_0^t K(t-\tau)\,\dot\psi(\tau)\,d\tau = 0$$

We can now calculate the autocorrelation function of the fluctuating acceleration $a_x(t)$:

$$(81) \quad \langle a_x(t)\,a_x(0)\rangle = \langle \dot u_x(t)\,\dot u_x(0)\rangle + \int_0^t \langle u_x(\tau)\,\dot u_x(0)\rangle\, K(t-\tau)\,d\tau$$

$$= \langle u_x^2\rangle \left(-\ddot\psi(t) - \int_0^t K(t-\tau)\,\dot\psi(\tau)\,d\tau\right)$$

and, from the equation (80):

$$(82) \qquad K(t) = \frac{\langle a_x(t)\,a_x(0)\rangle}{\langle u_x^2\rangle}$$

From the short time expansion of $\psi(t)$:

$$\psi(t) = 1 - \frac{t^2}{2!}\frac{\langle a_x^2\rangle}{\langle u_x^2\rangle} + \frac{t^4}{4!}\frac{\langle \dot a_x^2\rangle}{\langle u_x^2\rangle} - \cdots$$

and the equation (79), it is possible to obtain the short time expansion of $K(t)$:

$$(83) \qquad K(t) = \Omega_0^2 + \frac{t^2}{2!}\left[\left(\frac{\langle a_x^2\rangle}{\langle u_x^2\rangle}\right)^2 - \frac{\langle \dot a_x^2\rangle}{\langle u_x^2\rangle}\right] + \cdots$$

a) Continued fraction expansion.

We may also assume that the fluctuating acceleration $a_x(t)$ obeys a similar generalized Langevin equation. We now have

$$(84) \qquad \dot a_x(t) + \int_0^t M(t-\tau)\,a_x(\tau)\,d\tau = b_x(t)$$

where
$$\langle b_x(t)\,a_x(0)\rangle = 0$$

Now $M(t)$ is related to the autocorrelation function of the new "force" $b_x(t)$:

$$M(t) \sim \langle b_x(t)\,b_x(0)\rangle$$

This process can be continued by writing a generalized Langevin equation for $b_x(t)$ and so on.

The sequence of equations (77), (84), etc are most easily solved when Fourier-Laplace transforms are used. We define

$$\tilde f(s) = \int_0^\infty e^{-st} f(t)\,dt \qquad (s>0)$$

and we get from (78):

$$(84) \qquad \tilde\psi(s) = \frac{\psi(0)}{s + \tilde K(s)}$$

and similarly from (84):

$$(85) \qquad \tilde K(s) = \frac{K(0)}{s + \tilde M(s)}$$

When we insert $\tilde{K}(s)$ in the expression of $\tilde{\psi}(s)$ and continue the same process we get the continued fraction expansion:

$$(86) \qquad \tilde{\psi}(s) = \frac{\psi(0)}{s + \dfrac{K(0)}{s + \tilde{M}(s)}} = \frac{\psi(0)}{s + \dfrac{K(0)}{s + \dfrac{M(0)}{s + \cdots}}}$$

In the sequence of integro-differential equations the memory function of the dynamical variable in the n^{th} equation is the autocorrelation function of the dynamical variable which obeys the $(n+1)^{th}$ equation. Let us notice that $K(0), M(0) \ldots$ can be obtained through the short time expansion of $\psi(t)$.

$$\psi(t) = 1 - \mu_2 \frac{t^2}{2!} + \mu_4 \frac{t^4}{4!} - \cdots$$

from which we obtain:

$$\tilde{\psi}(s) = \frac{1}{s} - \mu_2 \frac{1}{s^3} + \mu_4 \frac{1}{s^5} - \cdots$$

If we now expand the continuous fraction (86) we have:

$$K(0) = \mu_2 = \Omega_0^2$$

$$M(0) = \frac{\mu_4 - \mu_2^2}{\mu_2} \quad \ldots$$

where μ_n are the frequency moments of $\psi(\omega)$.

In order to obtain an approximate VAF we must truncate the continued fraction at some step, which garantees that a number of moments of $\psi(\omega)$ will be correctly reproduced. Let us consider some examples:

- In the simple Langevin theory $K(t) = 2\beta\,\delta(t)$ so that $\tilde{K}(s) = \beta$ and $\tilde{\psi}(s) = (s+\beta)^{-1}$. The Fourier transform $\psi(\omega)$ of ψ is therefore:

$$\psi(\omega) = \frac{1}{\pi} \operatorname{Re} \tilde{\psi}(-i\omega) = \frac{1}{\pi} \operatorname{Re} \frac{1}{-i\omega + \beta}$$

which is the Fourier transform of the Langevin VAF $e^{-\beta|t|}$, with all its defects.

- The next step is the relaxation time approximation. We assume that the memory function is no more a delta function, but decays exponentially with time(50,51):

$$K(t) = \Omega_0^2 \exp\left(-\frac{t}{\tau}\right)$$

so that

$$(87) \qquad \tilde{\psi}(s) = \frac{1}{s + \dfrac{\Omega_0^2}{s + 1/\tau}}$$

This approximation amounts to saying that the correlation time of the fluctuating force is τ, the same τ we used in the equation (58) (see also the figure 8). Then from the equation (87) we obtain for the diffusion coefficient:

$$(88) \qquad D = \frac{k_B T}{m} \tilde{\psi}(0) = \frac{k_B T}{m \Omega_0^2 \tau}$$

An interesting limit is obtained when τ is infinite. From (87) we obtain $\psi(t) = \cos \Omega_0 t$ and the VAF oscillates with the natural frequency Ω_0. Therefore, as τ increases from zero to infinity, $\psi(t)$ evolves from a pure exponential to an oscillatory form. More accurately it is easy to show that the Laplace inverse of (87) is:

$$(89) \qquad \psi(t) = \frac{1}{s_+ - s_-} \left(s_+ e^{-s_- t} - s_- e^{-s_+ t} \right)$$

where s_+ and s_- are the poles of $\tilde{\psi}(s)$:

$$s_{\pm} = -\frac{1}{2\tau}\left[1 \mp \left(1-4\Omega_0^2\tau^2\right)^{1/2}\right]$$

Therefore $\psi(t)$ oscillates, or at least shows a negative region when $s_{\pm}$ are complex numbers i.e. when

$$\tau > \frac{1}{2\Omega_0}$$

This condition, which can also be written:

$$\frac{D m \Omega_0}{k_B T} < 2 \qquad (90)$$

is easily met in classical fluids. For instance for $D = 10^{-5}\ cm^2 \cdot s^{-1}$, $\Omega_0 = 10^{13}\ s^{-1}$, $\mathcal{N} m = 30\ g$, $k_B T = 10^{-2}\ eV$ ($T = 116\ K$) we obtain $D m \Omega_0 / k_B T \sim 0.3$ (0.9 for argon at its triple point).

- A number of postulated memory functions have been used in the literature. Let us mention here the following expressions:

$$K(t) = \Omega_0^2 \exp\left[-\frac{\pi}{4} t^2 \left(\Omega_0^2 \int_0^\infty \psi(t')\,dt'\right)^2\right] \qquad (\text{ref. } 52)$$

$$K(t) = \Omega_0^2 \exp\left[-\frac{t^2}{2}\left(\frac{\langle \dot{a}_x^2\rangle}{\langle u_x^2\rangle} - \frac{\langle a_x^2\rangle}{\langle u_x^2\rangle}\right)\right] \qquad (\text{ref } 50, 53)$$

which evidently satisfies the first two moments of the exact $K(\omega)$.

$$K(t) = \Omega_0^2\, e^{-\alpha t}\left(\frac{\alpha \sin \Omega t + \Omega \cos \Omega t}{\Omega}\right) \qquad (\text{ref. } 54)$$

with
$$\alpha = \frac{3}{2\Omega_0^2}\left(\frac{\langle \dot{a}_x\rangle^2}{\langle u_x^2\rangle} - \frac{\langle a_x^2\rangle}{\langle u_x^2\rangle}\right)\left(\int_0^\infty \psi(t')\,dt'\right)^{-1}$$

and
$$\Omega = \frac{\langle \dot{a}_x^2\rangle}{\langle u_x^2\rangle} - \frac{\langle a_x^2\rangle}{\langle u_x^2\rangle} - \alpha^2$$

These approximate memory functions can be inserted in the integro-differential equation (78) to calculate $\psi(t)$, and to check the result against molecular dynamics calculations.

This has been done in detail by Harp and Berne (51). In the same spirit, once $\psi(t)$ has been obtained, it can be used to generate the approximate mean-square displacement of an atom (55):

$$\langle (\vec{r}(t) - \vec{r}(0))^2 \rangle = 6\,\frac{k_B T}{m}\int_0^t (t-t')\,\psi(t')\,dt'$$

It is interesting to notice that the memory function $K(t)$ can be interpreted as a generalized friction coefficient and that its interpretation may be simpler than that of $\psi(t)$. Using their molecular dynamics results, Levesque and Verlet (8) showed for instance that the three parameter memory function

$$K(t) = \Omega_0^2 \exp\left(-\frac{B_0 t^2}{2}\right) + A_0 t^4 \exp(-\alpha_0 t)$$

fits very well to the computer results. This shows a short time gaussian superimposed on a long time tail, due to collective effects in the surrounding fluid, which may enhance or reduce the self-motion of the tagged particle.

2.4. The Mori-Zwanzig formalism.

In the preceding section we have assumed that the velocity, acceleration, ... obey generalized Langevin equations. It is interesting to show how Mori and Zwanzig have shown that the procedure leading to these equations is valid and that it is equivalent to solving the Liouville equation (56,57,58).

If the force acting on the tagged particle were only the friction force, the velocity of the particle would vary as:

$$u_x(t) = u_x(0)\, e^{-\beta t}$$

and $u_x(t)$ would be entirely determined by $u_x(0)$. The role of the random force in the Langevin equation is to make $u_x(t)$ explore some states which are not necessarily correlated with $u_x(0)$. In the language of vectors, we can say that $u_x(t)$ may explore a space orthogonal, in some sense, to the subspace spanned by $u_x(0)$.

Following Mori and Zwanzig we define the Hilbert space of dynamical variables A, with the inner product:

(91) $$(A|B) = \int A^* B\, f_0\, dp\, dq = \langle A^* B \rangle_0$$

where (for instance) f_0 is the equilibrium distribution function of the system. According to this definition, a dynamical variable B may have a component along A, given by:

(92) $$P\,|B) = |A)\,\frac{(A|B)}{(A|A)}$$

If $P|B)$ is non-zero, B is correlated with A. For instance the random force $R_x(t)$ in the Langevin equation is not correlated with $u_x(0)$ and is therefore orthogonal to the state described by $|u_x(0))$.

In this Hilbert space the time evolution of the dynamical variable A is given by the Liouville equation:

(93) $$\frac{dA(t)}{dt} = iLA(t)$$

where $$iLA = \sum_{p,q} \left(\frac{\partial \mathcal{H}}{\partial p} \frac{\partial A}{\partial q} - \frac{\partial \mathcal{H}}{\partial q} \frac{\partial A}{\partial p} \right) = \{A, \mathcal{H}\}$$

if we call $\mathcal{H}$ the hamiltonian of the system; $(\vec{p}, \vec{q})$ describes the conjugate variables of the system. If L does not depend on time, the formal solution of (93) is:

(94) $$A(t) = e^{iLt} A$$

Our definition of the inner product allows us to write the autocorrelation function:

(95) $$C(t) = \langle A^* A(t) \rangle_0 = (A|A(t))$$

In general the Liouville operator e^{iLt} makes the variable $A(t)$ explore regions of the Hilbert space which are orthogonal to A. We may define the projector P on $|A)$ and its complementary $Q = 1 - P$ so that we can write:

(96) $$A(t) = PA(t) + QA(t)$$

The systematic part $A_S = PA(t)$ remains correlated with A whereas $A_R = QA(t)$ is the random part in the language of the Langevin equation. In order to obtain the autocorrelation function $C(t) = (A|A(t))$ we want to calculate $A_S(t)$:

(97) $$|A_S(t)) = P\,|A(t)) = |A)\,\frac{(A|A(t))}{(A|A)} = |A)\,\frac{C(t)}{C(0)}$$

The time evolution of A_S and A_R is given by operating on the Liouville equation with P and Q respectively. We obtain:

(98) $$\begin{cases} P\,\dfrac{dA(t)}{dt} = \dfrac{dA_S(t)}{dt} = PiLA_S(t) + PiLA_R(t) \\[2ex] \dfrac{dA_R(t)}{dt} = QiLA_S(t) + QiLA_R(t) \end{cases}$$

In the second equation we can calculate $A_R(t)$ once $A_S(t)$ is known (keeping in mind that $A_R(0) = 0$). Replacing the result in (98a) we have:

(99) $$\frac{dA_s(t)}{dt} = PiLA_s(t) + PiL\int_0^t ds\, e^{iQL(t-s)}\, iQLA_s(s)$$

The scalar product with the state $|A)$ gives the following equation for the correlation function $C(t)$:

$$\frac{d}{dt}(A|A_s(t)) = \dot{C}(t) = (A|iLA_s(t)) + (A|iL\int_0^t ds\, e^{iQL(t-s)}\, iQL|A_s(s))$$

Using the equation (97), this result can be cast in the form of a generalized Langevin equation:

(100) $$\dot{C}(t) - i\Omega C(t) + \int_0^t ds\, K(t-s)\, C(s) = 0$$

with the definitions:

(101) $$\begin{cases} i\Omega = \dfrac{(A|iLA)}{(A|A)} \\ K(t) = -\dfrac{(A|iL\,e^{iQLt}\,iQL|A)}{(A|A)} = \dfrac{(LA|e^{iQLt}\,Q|LA)}{(A|A)} \end{cases}$$

Now if the correlation function $C(t)$ obeys the Langevin equation (100), it is clear that the variable $A(t)$ evolves in time according to the equation:

(102) $$\dot{A}(t) - i\Omega A(t) + \int_0^t ds\, K(t-s)\, A(s) = F(t)$$

provided that $F(t)$ be orthogonal to A. This can simply be shown by taking the scalar product of this equation with A. Alternatively, if we project this equation into the subspace orthogonal to $|A)$ we obtain:

$$\dot{A}_R(t) - i\Omega A_R(t) + \int_0^t ds\, K(t-s)\, A_R(t) = F(t)$$

an equation which can be used to determine the random force $F(t)$. To do this, we use again the Laplace transformation

and we obtain:

(103) $$\tilde{A}_R = \frac{1}{s - i\Omega + \tilde{K}}\,\tilde{F}$$

But $A_R(t)$ is given by the solution of (98b):

$$A_R(t) = \int_0^t e^{iQL(t-t')}\, QiL\, A_s(t')\, dt'$$

whose Laplace transform is:

$$\tilde{A}_R(s) = \frac{1}{s - iQL}\, QiL\, \tilde{A}_s(s)$$

with $$\tilde{A}_s(s) = A\,\frac{\tilde{C}(s)}{C(0)} \quad \text{and} \quad \tilde{C}(s) = \frac{C(0)}{s - i\Omega + \tilde{K}(s)}$$

We therefore obtain:

(104) $$\tilde{A}_R(s) = \frac{1}{s - iQL}\, QiLA\, \frac{1}{s - i\Omega + \tilde{K}(s)}$$

On comparing the equations (103) and (104) we immediately identify $\tilde{F}(s)$ as:

$$\tilde{F}(s) = \frac{1}{s - iQL}\, QiLA$$

or

(105) $$\boxed{F(t) = e^{iQLt}\, QiLA},$$

which, of course, remains orthogonal to $|A)$. According to the equation (101), this result shows that the memory function $K(t)$ is the autocorrelation function of the random force:

(106) $$\boxed{K(t) = \frac{(F(0)|F(t))}{(A|A)}}$$

This process can be continued. We can write a Langevin equation for the dynamical variable F (which is already orthogonal to A) in terms of a new random force G now orthogonal to A and F. The memory function of F is the autocorrelation function of G. This gives a justification of the continued fraction expansion we studied in section (2,3).

<u>An example.</u> Let us now study an example, taken from the work of Bosse, Lücke, Götze and Annette Zippelius$^{(59,50,61,62)}$. We are interested in the velocity autocorrelation function $\psi(t) = \langle u_x^2\rangle^{-1}\langle u_x(0)u_x(t)\rangle$. According to the general result (100) we can immediately write the Langevin equation for the variable u_x and for ψ:

$$\dot\psi(t) + \int_0^t ds\ K(t-s)\,\psi(s) = 0 \qquad (107)$$

because $\Omega = \dfrac{(u_x|iLu_x)}{(u_x|u_x)} = 0$, for velocity and acceleration are not correlated. In (107) $K(t)$, the memory function, is the autocorrelation function of the force and:

$$K(t) = \frac{(Lu_x|\,e^{iQLt}\,Q\,|Lu_x)}{(u_x|u_x)}$$

or equivalently by:

$$K(t) = \frac{(Lu_x|\,e^{iQLQt}\,|Lu_x)}{(u_x|u_x)} \qquad (108)$$

because $Q^2 = Q$ and $Q|Lu_x) = |Lu_x)$. On the other hand, we may notice that

$$(Lu_x|Lu_x) = K(0)\,(u_x|u_x) = \frac{k_BT}{m}\,\Omega_0^2$$

The equation (108) shows that $K(t)$ is given by the autocorrelation function of the random force.

$$iLu_x = \dot u_x = F_x(0) = \frac{R_x(0)}{m}$$

is the acceleration of the tagged particle at time $t=0$; $Q \quad Q = L'$ is the restriction of the Liouville operator to the subspace orthogonal to $|u_x)$; $e^{iL't}|iLu_x)$ is hence the <u>random force</u> at time t and the equation (108) is entirely equivalent to (106).

By continuation of this procedure we write a Langevin equation for the autocorrelation of the force and:

$$\dot K(t) + \int_0^t ds\ M(t-s)\,K(s) = 0 \qquad (109)$$

where

$$M(t) = \frac{(L'F_x|\,e^{iQ'L'Q't}\,|L'F_x)}{(F_x|F_x)} = \frac{(QL^2u_x|\,e^{iQ'QLQQ't}\,|QL^2u_x)}{(u_x|L^2|u_x)} \qquad (110)$$

where P' is now the projector on the random force and $Q' = 1-P'$.

We can now Laplace transform the equations (107) and (109) to obtain $\tilde\psi(s)$ and we get the Fourier spectrum of the VAF:

$$\psi''(\omega) = \frac{1}{2}\int_{-\infty}^{+\infty} dt\ e^{i\omega t}\,\psi(t)$$

with the result:

$$\psi''(\omega) = \frac{\Omega_0^2\,M''(\omega)}{\left(\omega^2-\Omega_0^2+\omega M'(\omega)\right)^2 + \left(\omega M''(\omega)\right)^2} \qquad (111)$$

where $M(\omega + i0) = M'(\omega) + i\,M''(\omega)$

As emphasized by Bosse et al.$^{(62)}$, $\varphi''(\omega)$ bears a close resemblance to the response function of a damped harmonic oscillator whose generalized friction coefficient is $M''(\omega)$. The frequency variation of $M''(\omega)$ leads to a frequency shift $\omega M'(\omega)$ of the square of the natural frequency Ω_0.

In the relaxation time approximation we set $\tilde{M}(s) = 1/\tau$ and we get a rough approximation to $\varphi(t)$. In their paper$^{(62)}$, Bosse et al. calculate $M(t)$ using the following method:

1. In order to calculate the matrix element

$$N(t) = (QL^2u_x \,|\, e^{iL''t} \,|\, QL^2u_x) \tag{112}$$

where $L'' = Q'QLQQ'$, we define the Fourier transforms of the tagged particle density and current as:

$$\rho_0(\vec{k}) = e^{-i\vec{k}.\vec{r}_0} \quad ; \quad \vec{j}_0(\vec{k}) = \vec{u}\, e^{-i\vec{k}.\vec{r}_0}$$

where $\vec{r}_0$ denotes the position of the particle. These are related by the continuity equation:

$$\dot{\rho}_0(\vec{k}) = iL\,\rho_0(\vec{k}) = -i\vec{k}.\vec{j}_0(\vec{k})$$

In the same way, the density and current of the bath particles are:

$$\rho(\vec{k}) = \sum_n e^{-i\vec{k}.\vec{r}_n} \quad ; \quad \vec{j}(\vec{k}) = \sum_n \vec{v}_n\, e^{-i\vec{k}.\vec{r}_n}$$

where $\vec{r}_n, \vec{v}_n$ denote the position and velocity of the n^{th} particle.

The equation of motion of the tagged particle is:

$$\begin{aligned} \dot{u}_x = iLu_x &= -\frac{1}{m}\sum_n \frac{\partial}{\partial x_0} V(r_{0n}) \\ &= -\frac{i}{m}\int \frac{d_3k}{(2\pi)^3}\, k_x\, \tilde{V}(k)\, \rho_0(-\vec{k})\, \rho(\vec{k}) \end{aligned} \tag{113}$$

where $V(r_{0n})$ is the interaction potential between the tagged particle and a bath particle located at $\vec{r}_n$. On applying again the derivation operator to (113) we obtain:

$$iL\dot{u}_x = -L^2u_x = \frac{1}{m}\int \frac{d_3k}{(2\pi)^3}\, k_x\, \tilde{V}(k)\, \vec{k}\cdot\Big(\vec{j}_0(-\vec{k})\,\rho(\vec{k}) - \vec{j}(\vec{k})\,\rho_0(-\vec{k})\Big) \tag{114}$$

We see that L^2u_x is given by a sum over two-modes variables $\vec{j}_0(-\vec{k})\,\rho(\vec{k})$ and $\vec{j}(\vec{k})\,\rho_0(-\vec{k})$ where a momentum $\vec{k}$ is exchanged between a particle mode and a bath mode.

2. The next step is to expand the operator $e^{iL''t}$ on the basis (assumed to be complete) of these modes. If we denote by $|q)$ these modes, conveniently normalized, we can write:

$$e^{iL''t} \simeq \sum_q e^{iL''t}\,|q)(q| = \sum_q |q(t))(q| \tag{115}$$

3. Now only the simplest modes $|q) = |\rho_0(\vec{k})\,\vec{j}(-\vec{k}))$ consisting of a tagged particle density mode coupled to a bath particle current mode are considered, and their motion is assumed to be independent. This approximation allows us to write:

$$M(t) \simeq \frac{m}{\Omega_0^2 k_B T}\sum_{\vec{k},\alpha,\beta} \frac{(QL^2u_x\,|\,\rho_0^{\vec{k}} j_{-\vec{k}}^{\alpha})(\rho_0^{\vec{k}}(t)\,|\,\rho_0^{\vec{k}})(j_{-\vec{k}}^{\alpha}(t)\,|\,j_{-\vec{k}}^{\beta})(\rho_0^{\vec{k}} j_{-\vec{k}}^{\beta}\,|\,QL^2u_x)}{(\rho_0^{\vec{k}}\,|\,\rho_0^{\vec{k}})^2\,(j_{-\vec{k}}^{\alpha}\,|\,j_{-\vec{k}}^{\alpha})(j_{-\vec{k}}^{\beta}\,|\,j_{-\vec{k}}^{\beta})} \tag{116}$$

where the factors in the denominator arise from the fact that, when we write (115), the states $|q)$ have to be normalized.

The correlation functions entering the Eq. (116) are now evaluated :

$$* \quad (\rho_0^{\vec{k}}(t) \mid \rho_0^{\vec{k}}) = \left\langle e^{i\vec{k}.(\vec{r}_0(t)-\vec{r}_0)} \right\rangle = F_s(\vec{k},t)$$

$$* \qquad \phi_{\alpha\beta}(\vec{k},t) = \frac{(j^\alpha(\vec{k},t) \mid j^\beta(\vec{k}))}{(j^\alpha(\vec{k}) \mid j^\alpha(\vec{k}))}$$

the current propagator, can be expressed in terms of the coherent longitudinal and transverse excitations spectra $\phi''_L(k,\omega)$ and $\phi''_T(k,\omega)$:

$$(117) \quad \phi_{\alpha\beta}(\vec{k},t) = \int_{-\infty}^{+\infty} \frac{d\omega}{\pi} e^{-i\omega t} \left[\frac{k_\alpha k_\beta}{k^2} \phi''_L(k,\omega) + \left(\delta_{\alpha\beta} - \frac{k_\alpha k_\beta}{k^2} \right) \phi''_T(k,\omega) \right]$$

where ϕ''_L and ϕ''_T have been studied in detail by Bosse, Götze and Lücke.

* The only factors which remain to evaluate in (116) are :

$$(QL^2 u_x \mid \rho_0^{\vec{k}} j^\alpha_{-\vec{k}}) = - \frac{k_B T}{m} \Omega_0^2 V_{x\alpha}(\vec{k})$$

where

$$V_{x\alpha}(\vec{k}) = \frac{N/V}{m\Omega_0^2} \int d\vec{r}\, e^{-i\vec{k}.\vec{r}} g(r) \nabla_x \nabla_\alpha V(r)$$

can be called the average dynamical matrix of the system.

All the ingredients entering the equation (116) are now known and we can separate $M(t)$ into its transverse and longitudinal parts :

$$M(t) = 2M_T(t) + M_L(t)$$

where (118) $M_{T,L}(t) = \frac{\Omega_0^2}{n} \frac{1}{6\pi^2} \int_0^\infty k^2 dk\, V^2_{T,L}(k)\, F_s(k,t)\, \phi_{T,L}(k,t)$

In this expression, $V_T(k)$ describes the coupling of the tagged particle to transverse modes i.e to shear excitations ; $V_T(k)$ is shown to decrease rapidly with k. Conversely $V_L(k)$ describes the coupling to longitudinal modes, oscillates with k and is largely predominant over V_T at large k.

Using the expression (118) Bosse et al.(62) have studied the relaxation spectrum $M''(\omega)$ and the VAF spectrum $\psi''(\omega)$ in argon and rubidium. $M''(\omega)$ shows a peak at the frequency Ω_0 and the figure (11) gives the comparison of their results with the relaxation time approximation and with molecular dynamics data. The most important features in the theory are : (i) the coupling of the tagged particle to coherent bath modes insures that the hydrodynamic modes (long time behaviour of $\psi(t)$ in $t^{-3/2}$) are correctly included ; (ii) the coupling to longitudinal modes predominates ; (iii) the shift of the peak in $\psi''(\omega)$ from Ω_0 is due to a level repulsion between the oscillator with frequency Ω_0 and the pair mode excitations whose resonance is represented by the maximum of $M''(\omega)$.

An analysis of the VAF in fluids, using the generalized Langevin equation has also been made by Dubey et al.(64), McCoy(65) and Munakata and Igarashi(66).

<u>Simple models.</u>

Before concluding this section let us notice that the equation (89) can be written :

$$\psi(t) = e^{-\frac{t}{2\tau}} \left(\cos \Omega t + \frac{1}{\Omega\tau} \sin \Omega t \right)$$

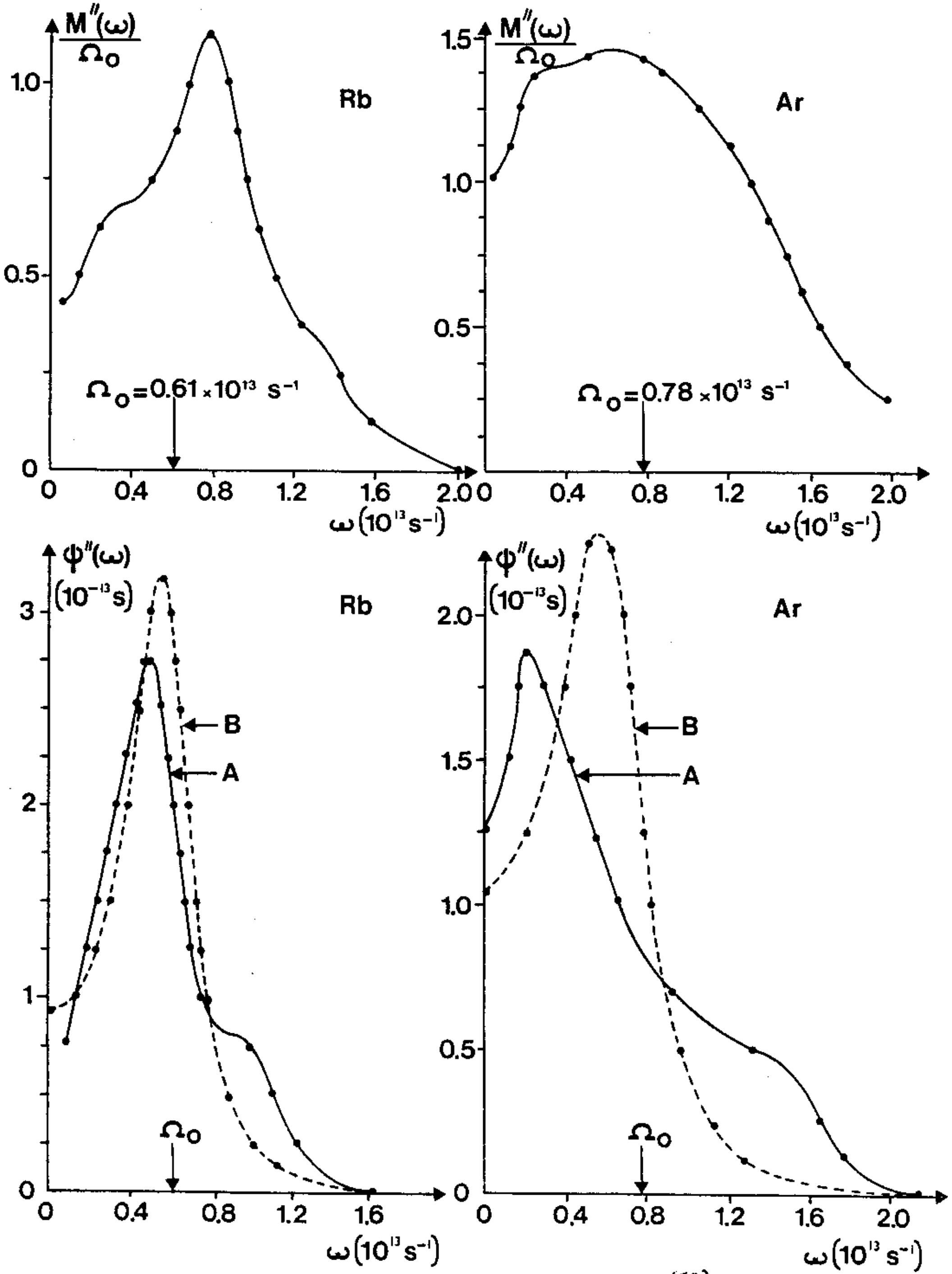

Figure 11. After Bosse et al [62]

with $\Omega^2 = 4\Omega_0^2 - \tau^{-2}$. This expression bears a close resemblance to the time evolution of a damped harmonic oscillator: $\phi(t)$ shows oscillations at short times ($t < 10^{-12}$ s) which decay when diffusive motions actually occur. As a consequence the average position $\vec{R}$ of the tagged particle changes much more slowly than its actual position $\vec{R}_0$. This remark led Sears[67] to the itinerant oscillator model, where the tagged particle vibrates in the cage of its neighbours. The cage itself is subjected to a random force $\vec{B}(t)$ and to a systematic retarding force $-\nu\dot{\vec{R}}(t)$. The equations of motion of the system:

$$(119) \quad \begin{cases} \ddot{\vec{R}}_0(t) + \mu\dot{\vec{R}}_0(t) + \Omega_0^2\left(\vec{R}_0(t) - \vec{R}(t)\right) = \vec{A}(t) \\ \ddot{\vec{R}}(t) + \nu\dot{\vec{R}}(t) = \vec{B}(t) \end{cases}$$

involve seven parameters: the mean square values of the fluctuating forces $\vec{A}$ and $\vec{B}$, their correlation times γ and η, the reduced friction coefficients μ and ν and the natural frequency Ω_0. Sears shows that the diffusion coefficient of the tagged particle is given by:

$$D = \frac{\langle B_\alpha^2 \rangle}{\eta\nu^2}$$

Some of the parameters entering (119) can be evaluated and, using the experimental value of D, the spectrum of $\phi(t)$ can be determined.

A closely related model has been used by Rahman et al[68]; they assume that the displacement of an atom is the superposition of statistically independent "fictitious normal modes", each evolving in time according to the equation:

$$\ddot{\xi}_s + \beta_s \dot{\xi}_s + \omega_s^2 \xi_s = F_s(t)$$

In addition they assume that there is no restoring force for modes whose frequency is smaller than a given value ω', that the friction coefficient β_s is proportional to ω_s. Using this method they are able to fit neutron data.

In the same spirit Hicter et al (69) assume that the diffusing atom vibrates in the cage of its neighbours when its energy E is smaller than a given value ε. Conversely when E is larger than ε the atom is assumed to be free to diffuse along a distance δ. The diffusion coefficient is therefore made of a vibrational and a translational parts and the parameters entering the model can be calculated using the thermodynamic properties of the alloy.

Let us mention also the analyses by Rahman (69), Zwanzig and Bishop (70), and the semi-empirical models of Eyring (71), the free volume model of Turnbull et al. (72) and the continuous fluctuation model given by Swalin (73). All these models rely on adjustable parameters and do not account for the realistic dynamics of the fluid.

III. KINETIC THEORY OF ATOMIC TRANSPORT.

Kinetic theories attempt to calculate the relevant distribution functions of the fluid. For instance if we denote $f_s(1) = f_s(\vec{r}_1, \vec{v}_1, t_1)$ the phase space probability density of the tagged particle at point $\vec{r}_1, \vec{v}_1$ at time t_1, we can write the velocity autocorrelation function as:

$$(120) \qquad \langle u_x(t_1)\, u_x(t_2) \rangle = \int d1\, d2\; v_x(t_1)\, v_x(t_2) \langle f_s(1)\, f_s(2) \rangle$$

and the emphasis will be put, in kinetic theories, on the calculation of $f_s(\vec{r}, \vec{v}, t)$. This is a complicated many-body problem because the tagged particle disturbs at time t_1 the surrounding fluid, the disturbance propagates and reacts back on the tagged particle at time t_2. By a detailed study of the behaviour of f_s, we can hope to identify the mechanisms underlying this backflow effect. Again we shall meet two simple limits: (i) the case where the tagged particle experiences frequent but soft collisions will lead to the Fokker-Planck equation which contains no more physics than the Brownian motion theory; (ii) conversely, when the tagged particle is subjected to rare but violent collisions, we shall meet the Boltzmann and Enskog theories, which are very useful in dilute gases and moderately dense fluids. The actual situation in liquids lies between these two extreme limits and it is very difficult to extract simple physical phenomena from the evolution equations.

3,1. Fokker-Planck equation.

Let us consider for instance a one-dimensional system and study the distribution function $f(v,t)$ of the velocity of the tagged particle. Later we shall reintroduce the space dependence of f. If we assume that a time interval τ can be defined which is (i) long compared to the time scale of molecular fluctuations but (ii) short with respect to the relaxation time of the velocity, we can write:

$$f(v, t+\tau) = \int dv' f(v', t)\, p(v, v'; \tau) \tag{121}$$

where $p(v, v'; \tau)$ is the probability that, if the particle has the velocity v' at time t, it will be found with the velocity v at time $t+\tau$. Clearly the preceding approximations are those of the Brownian motion of a heavy particle. Let us also notice that $f(v,t)$ is not necessarily an equilibrium distribution. It can be the distribution function of the velocity after any given initial configuration of the system.

The transition probability $p(v, v'; \tau)$ is a function of the velocity v and of the velocity increment $w = v - v'$. It can be formally written:

$$p(v, w, \tau) = \left\langle \delta\left(w - \int_0^\tau \frac{F(t')}{m} dt' \right) \right\rangle \tag{122}$$

where $F(t')$ is the total force experienced by the particle and the average is taken on a system where the velocity of the tagged particle is v. As in the Brownian motion theory we can separate $F(t')$ into the systematic retarding force $-\zeta v$ and the random force $R(t')$ so that the moments of $p(v, w, \tau)$ are:

$$(123)\quad \left\{ \begin{aligned} \frac{\overline{w(\tau)}}{\tau} &= \frac{1}{\tau}\int_{-\infty}^{+\infty} p(v, w, \tau)\, w\, dw = \frac{1}{\tau}\int_0^\tau \frac{\langle F(t')\rangle}{m} dt' = -\frac{\zeta}{m} v \\ \frac{\overline{w^2(\tau)}}{2\tau} &= \frac{1}{2\tau}\int_{-\infty}^{+\infty} p(v, w, \tau)\, w^2 dw = \frac{1}{2\tau}\int_0^\tau\!\!\int_0^\tau dt'\,dt'' \frac{\langle R(t')R(t'')\rangle}{m^2} \\ &= \int_0^\tau \frac{\langle R(t')R(0)\rangle}{m^2} = k_B T \frac{\zeta}{m} \end{aligned} \right.$$

according to the equation (58) and because τ is long with respect to the time scale of the fluctuations of the random force. Clearly the transfer w is a random process and its distribution function becomes a gaussian centred on $-(\frac{\zeta}{m} v)\tau$ whose width is given by $\overline{w^2(\tau)}$. We can now write:

$$f(v, t+\tau) = \int_{-\infty}^{+\infty} f(v-w, t)\, p(v, w, \tau)\, dw$$

and we may expand $f(v-w, t)$ in a Taylor series to obtain

$$\frac{\partial f(v,t)}{\partial t} = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} \frac{\partial^n}{\partial v^n} \left[\frac{\overline{w^n}}{\tau} f \right]$$

where $\overline{w^n}$ is the n^{th} moment of $p(v, w, \tau)$. If we restrict this expansion to the first two terms we obtain the Fokker-Planck equation:

$$\frac{\partial f(v,t)}{\partial t} = \frac{\zeta}{m} \frac{\partial}{\partial v} \left(v f + \frac{k_B T}{m} \frac{\partial f}{\partial v} \right) \tag{124}$$

Of course, in an equilibrium system, $\frac{\partial f}{\partial t} = 0$ and this equation has one solution of the form:

$$f(v,t) = A \exp\left(-\frac{mv^2}{2k_B T}\right)$$

which is the (one-dimensional) distribution function of the velocity (Maxwellian distribution).

Now if we denote $f(\vec{r},\vec{v},t)$ the phase-space probability distribution of the tagged particle we obtain, in a straightforward generalization of the equation (124):

$$(125) \qquad \frac{\partial f(\vec{r},\vec{v},t)}{\partial t} + \vec{v}\cdot\frac{\partial f}{\partial \vec{r}} = \frac{\zeta}{m}\frac{\partial}{\partial \vec{v}}\cdot\left(\vec{v} + \frac{k_B T}{m}\frac{\partial}{\partial \vec{v}}\right) f$$

in a three-dimensional system in the absence of an external force. All the ingredients entering this Fokker-Planck equation are the same as in the Brownian theory. There are two principal methods of using this equation:

a) First we can look for the solution of (125) compatible with the initial conditions. In order to make it as simple as possible and to get an insight on the method of resolution, let us assume that we are only interested in the velocity distribution function of the tagged particle immersed in a one-dimensional system. After integration over the space variable, $f(v,t)$ obeys the simple equation (124) which we simplify with the change to the new variables:

$$V = v\, e^{\zeta/m\, t} \ ; \quad F(V,t) = \chi(V,t)\, e^{\zeta t/m} = f(v,t)$$

The Fokker-Planck equation now becomes:

$$(126) \qquad \frac{\partial \chi}{\partial t} = \phi(t)\,\frac{\partial^2 \chi}{\partial V^2}$$

with $$\phi(t) = \frac{k_B T \zeta}{m^2}\exp\left(\frac{2\zeta t}{m}\right)$$

The diffusion equation (126) is easily solved. If $f(v,t=0)=\delta(v)$

its solution is:

$$\chi(V,t) = \frac{1}{\left[4\pi\int_0^t \phi(t')\,dt'\right]^{1/2}}\exp\left(-\frac{V^2}{4\int_0^t \phi(t')\,dt'}\right)$$

This distribution function allows us to calculate the mean-square value of the velocity of the tagged particle (initially at rest) at time t:

$$\langle v^2 \rangle = \frac{k_B T}{m}\left(1 - e^{-\frac{2\zeta}{m}t}\right)$$

This is the one-dimensional equivalent to the result we obtained by a direct integration of the equations of motion in the Brownian theory (eq. (51)). For a solution of the full Fokker-Planck equation (125), we refer the reader to the book of Rice and Gray(24).

b) If we are only interested in the diffusion coefficient of the tagged particle we must study the long time behaviour of $f(\vec{r},\vec{v},t)$, or its space Fourier transform $\tilde{f}(\vec{q},\vec{v},t)$. We know that $f(\vec{r},t)$ obeys the diffusion equation at long times so that:

$$\int \tilde{f}(\vec{q},\vec{v},t)\,d\vec{v} \sim e^{-q^2 D t}$$

By Fourier transformation of the Fokker-Planck equation we obtain:

$$(127) \qquad \frac{\partial \tilde{f}}{\partial t} = \left(\hat{A} - i\vec{q}\cdot\vec{v}\right)\tilde{f}$$

where $$\hat{A} = \frac{\zeta}{m}\frac{\partial}{\partial \vec{v}}\cdot\left(\vec{v} + \frac{k_B T}{m}\frac{\partial}{\partial \vec{v}}\cdot\right)$$

is the Fokker-Planck operator.

In the diffusion regime q can be considered as small and the effect of $-i\vec{q}\cdot\vec{v}$ can be treated as a small perturbation in the equation (127).

The non-perturbed equation:

$$\frac{\partial \tilde{f}}{\partial t} = \hat{A}\,\tilde{f} \tag{128}$$

can be solved if we know the eigenfunctions of the operator $\hat{A}$:

$$\hat{A}\,|\varphi_n^0\rangle = A_n^0\,|\varphi_n^0\rangle$$

where $|\varphi_n^0\rangle$ is a vector in the Hilbert space with the inner product:

$$\langle f|g\rangle = \int d\vec{v}\;\varphi_0(\vec{v})^{-1}\,f^*(v)\,g(v)$$

where $\varphi_0(\vec{v})$ is the equilibrium distribution function of the velocity. Of course $\varphi_0(v)$ itself is a solution of the equation (128) with $A_0^0 = 0$ because it corresponds to a stationary state of the system $\left(\frac{\partial \tilde{f}}{\partial t} = 0\right)$. Once we know the eigenvalues A_n^0, it is easy to show that the general solution of (128) is:

$$\tilde{f} = \sum_n a_n\, e^{A_n^0 t}$$

where the a_n's are determined by the initial conditions. Of course all A_n^0's are negative and the smallest one (in absolute value), which determines the long time behaviour of $\tilde{f}$, is $A_0^0 = 0$. In order to obtain the long time behaviour of the solution to the equation (127), the only thing we have to do is then to study how this eigenvalue is altered when we introduce the perturbation $-i\vec{q}\cdot\vec{v}$. This can be done by standard perturbation theory and we obtain, taking the x-axis along the vector $\vec{q}$:

$$A_0^q = A_0^0 + \langle\varphi_0|-iqv_x|\varphi_0\rangle + \sum_{n\neq 0}\frac{\langle\varphi_0|-iqv_x|\varphi_n^0\rangle\langle\varphi_n^0|-iqv_x|\varphi_0\rangle}{-A_n^0} \tag{129}$$

The first two terms vanishes and we may as well introduce the term $n=0$ in the sum, because $\langle\varphi_0|v_x|\varphi_0\rangle = 0$, under the condition that we add an infinitesimal ϵ to the denominator in order to avoid the divergence due to the fact that $A_0^0 = 0$. We hence obtain:

$$A_0^q = \lim_{\epsilon\to 0} q^2\,\langle\varphi_0|\,v_x\,\frac{1}{\hat{A}-\epsilon}\,v_x\,|\varphi_0\rangle$$

and the diffusion coefficient becomes:

$$D = \lim_{\epsilon\to 0}\,\langle\varphi_0|\,v_x\,\frac{1}{\hat{A}-\epsilon}\,v_x\,|\varphi_0\rangle \tag{130}$$

It is easy to show by direct calculation that $|v_x\varphi_0\rangle$ is an eigenvector of $\hat{A}$ with the eigenvalue $\frac{\zeta}{m}$. Hence,

$$\begin{aligned} D &= \lim_{\epsilon\to 0}\,\langle\varphi_0|\,v_x\,\frac{1}{\frac{\zeta}{m}-\epsilon}\,v_x\,|\varphi_0\rangle = \frac{m}{\zeta}\,\langle\varphi_0|v_x^2|\varphi_0\rangle \\ &= \frac{k_B T}{\zeta} \end{aligned} \tag{131}$$

The process by which we obtained this simple result is pretty more involved than a direct calculation from the Brownian motion theory. The reason why we have done it is that we shall meet an expression similar to (130) when we study the Boltzmann and Enskog equations. More details can be found in the book written by Résibois and De Leener (74).

3,2. The Boltzmann and Enskog equations.

The Fokker-Planck equation was obtained from the equation (121) under the assumption that the average velocity of the tagged particle changes very slowly and that this change results from frequent and slight collisions. Now we consider the opposite case when the tagged particle undergoes rare but large momentum transfers, as it is the case in a dilute gas. If we assume that there exists a time τ long compared with the duration τ_c of a collision, but short with respect to the time τ_R between collisions, we can again write the equation (121) for the velocity distribution function of the tagged particle, where now:

$$(132) \qquad p(v,v',\tau) = \lambda\,\delta(v'-v) + \tau\, W(v',v)$$

The first term corresponds to the absence of collisions during the time interval τ and $W(v',v)$ is the transition probability $v' \to v$ per unit time. If we choose $\tau \ll \tau_R$ and expand $f(v,t+\tau)$ in a Taylor series we obtain the Master Equation for the velocity distribution:

$$(133) \qquad \frac{\partial f(v,t)}{\partial t} = \int dv' \left[W(v',v)\, f(v') - W(v,v')\, f(v) \right]$$

where the first term corresponds to $v' \to v$ transitions (which increase f) and the second term describes $v \to v'$ transitions, which make $f(v,t)$ decrease. In three dimensions and in the absence of an external force, the equation of evolution of the full distribution function $f(\vec{r},\vec{v},t)$ is, by analogy with the equation (133):

$$(134) \qquad \frac{\partial f(\vec{r},\vec{v},t)}{\partial t} + \vec{v}\cdot\frac{\partial f}{\partial \vec{r}} = \int d\vec{v}' \left[W(\vec{v}',\vec{v},\vec{r})\, f(\vec{r},\vec{v}',t) - W(\vec{v},\vec{v}',\vec{r})\, f(\vec{r},\vec{v},t) \right]$$

where we have assumed that the size of the particles is negligible and therefore that the transition probability depends only on $\vec{r}$. $W(\vec{v}',\vec{v},\vec{r})$ depends on the number of bath particles which are located at $\vec{r}$ and that have a velocity $\vec{v}'$ such that, after the collision, the velocity of the tagged particle becomes $\vec{v}$. It depends also on the scattering cross-section for such a collision event, which can be calculated by classical mechanics.

In order to obtain the classical Boltzmann equation we neglect the spatial correlations between the tagged and bath particles. More accurately we assume that the number of bath particles having a velocity in the range $\vec{v}', \vec{v}'+d\vec{v}'$ is $n\varphi_b(\vec{v}')\,d\vec{v}'$ where n is the number density and $\varphi_b(\vec{v}')$ is the equilibrium velocity distribution of bath particles. Under this crude assumption, which can only be valid in a dilute gas, the equation (134) becomes linear:

$$(135) \qquad \frac{\partial f}{\partial t} + \vec{v}\cdot\frac{\partial f}{\partial \vec{r}} = n\, C^{(1)} f$$

where $C^{(1)}$ is the collision operator. This equation bears a close resemblance to the Fokker-Planck equation (125). The formalism we used to obtain the diffusion coefficient can

can again be utilized and we obtain for the diffusion coefficient of the tagged particle:

(136) $$D = -\lim_{\epsilon \to 0} \langle \varphi_0 | v_x \frac{1}{nC^{(1)} - \epsilon} v_x | \varphi_0 \rangle$$

and we have to study the eigenvalues of the operator $C^{(1)}$. This is done in the book of Résibois and De Leener$^{(74)}$. They show that the diffusion coefficient becomes:

(137) $$D = \frac{3k_B T}{8nm\,\Omega^{(1)}(1)}$$

where the collision integral $\Omega^{(1)}(1)$ depends on the detailed dynamics of the collisions. In a hard sphere fluid, it can be shown that (137) reduces to the simple result:

(138) $$D_0 = \frac{3}{8n\sigma^2}\left(\frac{k_B T}{\pi m}\right)^{1/2}$$

where σ is the hard sphere diameter.

A great improvement over this result has been obtained by Enskog$^{(75)}$. The assumption of two-body collisions is conserved but spatial correlations between particles are taken account of. Qualitatively it can be said that the collision rate is not governed by n, the number density of bath particles, but by $n\,g(\sigma)$ where $g(\sigma)$ is the radial distribution function at contact. The argument can be made more rigorous$^{(75)}$ and leads to the Enskog diffusion coefficient in a hard-sphere fluid:

(139) $$D_E = \frac{D_0}{g(\sigma)} = \frac{3}{8n\sigma^2 g(\sigma)}\left(\frac{k_B T}{\pi m}\right)^{1/2}$$

If one uses reasonable values of the hard sphere diameter, this simple result provides values of the self-diffusion coefficient which are of the right order of magnitude. Let us however emphaze that the Enskog result is obtained under the assumption of independent binary collisions. We shall examine the complications which arise when one tries to account for the dynamical polarization of the bath by the tagged particle in a later section.

The equation (139) is extremely useful for evaluating diffusion coefficients in Van der Waals and metallic liquids. Noticing that the equation of state of such fluids is not that different from the equation of state of a hard sphere fluid, we may define an effective hard sphere diameter $\sigma(T)$ which simulates the actual liquid. This has been done by Dymond and Alder$^{(76,77,78)}$ in rare gas liquids, by adjusting $\sigma(T)$ on the equation of state. Because of the softness of the actual interatomic potential the effective diameter shrinks as T increases. This can be qualitatively traced to the fact that, as T increases, the collisions between atoms become more severe and the closest distance of approach decreases. Ascarelli and Paskin$^{(79)}$ applied this theory to metals and obtained rather good results for the self-diffusion constant. Vadovic and Colver$^{(80)}$ improved somewhat the results by using the Carnahan-Starling$^{(81)}$

equation of state to determine $\sigma(T)$, instead of the inferior Percus-Yevick equation. The equation of state of the hard sphere fluid is written in terms of the compressibility factor z:

$$z = \frac{p}{n k_B T} = 1 + 4\eta\, g(\sigma)$$

where $\eta = \pi n \sigma^3/6$ is the packing fraction. Verlet and Weis(82) have shown that the Carnahan-Starling equation:

$$z_{CS} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3}$$

is correct within the accuracy of Monte-Carlo calculations. Therefore in a hard sphere fluid D_E is entirely given by the density n and the diameter $\sigma(T)$.

In order to determine $\sigma(T)$ Protopapas et al.(83) argue that, at the distance of closest approach, the energy $a k_B T$ of the particle is equal to the interatomic potential $V(\sigma(T))$. If $V(r)$ is expanded around its minimum at σ_0 we obtain:

$$A\left(\sigma(T)-\sigma_0\right)^2 = a k_B T$$

hence

$$\sigma(T) = \sigma_0\left(1 - B\left(\frac{T}{T_m}\right)^{1/2}\right) \qquad (140)$$

The coefficient B is nearly the same for all metals. This is an aspect of the Lindemann melting formula. From the equation (140) B is the relative vibration amplitude of the atoms around σ_0 at the melting point and this is known to vary little among metallic systems.

Protopapas et al. found that the values $\eta_m = 0.472$; $B = 0.112$ lead to a good fit to experimental data. Let us notice however that they also corrected the Enskog result (139) by the factor $C_{AW}(\eta) = D/D_E$, the ratio of the actual HS diffusion coefficient (obtained by molecular dynamics calculations) to the Enskog value D_E.

3,3. Density expansion of the diffusion constant.

In the spirit of the Boltzmann-Enskog theory the binary collisions are considered uncorrelated. This is valid at low density but, as the density increases, the tagged particle dynamically polarizes the bath and successive collisions can be highly correlated. The correlation processes are schematized in the figure (12). The figure 12b shows a sequence of two correlated collisions: at the space time point B the tagged particle collides again with the particle (2) with which it had collided before and that may have kept the memory of the previous collision. These collisions are of the general type described in the figure (12c): after the first interaction between (1) and (2) at A, the tagged particle undergoes a series of uncorrelated collisions with bath particles and collides at the point B with a bath particle (n) which (directly or indirectly) has kept the memory of the first encounter at A. The particle (n) may be the same as (2) or can be different. In this "ring collision" mechanism, the collisions at A and B are correlated and it is clear that such correlated sequences must be properly accounted for to properly describe self-diffusion in dense fluids.

A first step to introduce dynamical correlations consists in a generalization of the equation (136):

(141) $$D \sim \frac{1}{n\, C^{(1)}}$$

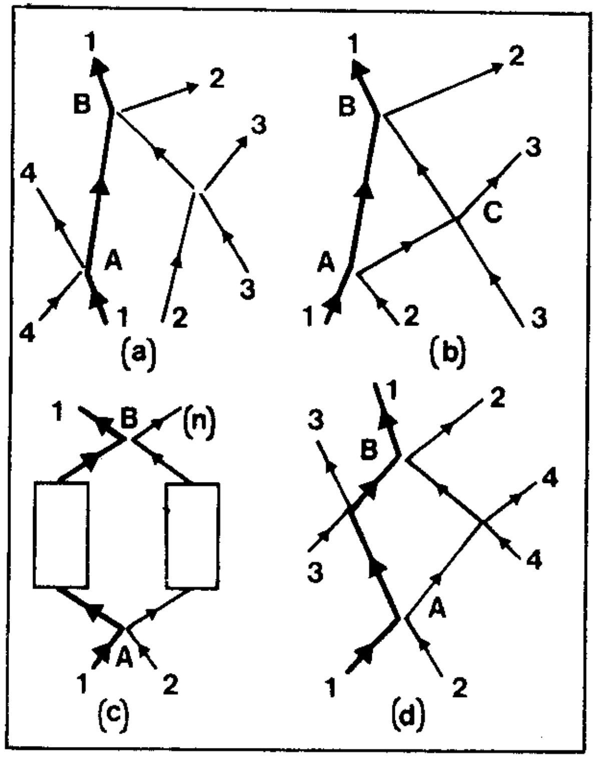

Figure 12. The successive collisions of the tagged particle (1) may be uncorrelated (a) or correlated ((b) and (d)); the figure (c) shows a ring collision.

The equation (141) is obtained with the assumption that the fluid remains in equilibrium, independently of the collisions it may have with the tagged particle. The simplest generalization of this expression consists in an expansion of the collision operator in powers of the density:

(142) $$D \sim \frac{1}{C}$$

where $C = n\, C^{(1)} + n^2 C^{(2)} + \dots$

where $C^{(2)}$ describes a process involving two collisions with bath particles. Consistently with (142) we may try to expand D in powers of n:

(143) $$D = \frac{1}{n}\left(D^{(1)} + n\, D^{(2)} + n^2 D^{(3)} + \dots \right)$$

and, using the perturbation theory, $D^{(2)}$ can be formally written:

$$D^{(2)} \sim \frac{1}{C^{(1)}}\, C^{(2)}\, \frac{1}{C^{(1)}}$$

The important point to notice is that the corrections to D may diverge as n becomes small; therefore the expansion (143) may not be legitimate. It is possible to find simple arguments(74) to show the (unphysical) origin of this divergence. Let us for instance consider the diagram (12b) in the figure (12), and estimate the probability of recollision processes. We denote $\Gamma_1 = \bar{v}/\ell = \bar{v}\, n\, \sigma^2$ the average binary collision frequency, where ℓ is the mean free path and σ^2 is the collision cross-section. The probability that the collision at C occurs in the time interval $\tau, \tau + d\tau$ is $\Gamma_1\, d\tau$. This collision at C leads to a recollision at B only if the particle (2) is focussed toward the tagged particle (1) after the collision at C. The probability of recollision is hence equal to $\Gamma_1 \, d\tau$ times the fraction α of the solid angle from which the tagged particle (1) is seen from the point C. But when the collision at C occurs, the mean distance between particles (1) and (2) is $\sim \bar{v}\tau$ and therefore $\alpha \sim \sigma^2/(\bar{v}\tau)^2$.

According to this argument the fraction of binary collisions that give rise to a recollision at any later time is:

$$\frac{\Gamma_2}{\Gamma_1} \sim \bar{v} n \sigma^4 \int_{\tau_1}^{\infty} \frac{d\tau}{(\bar{v}\tau)^2}$$

where the lowest limit of integration is $\tau_1 \sim \frac{\sigma}{\bar{v}}$. Introducing the dimensionless time $\tilde{\tau} = \tau\bar{v}/\sigma$ we obtain

$$\frac{\Gamma_2}{\Gamma_1} \sim n\sigma^3 \int_{1}^{\infty} \frac{d\tilde{\tau}}{\tilde{\tau}^2} \tag{144}$$

This expression, obtained in a 3-d system, remains finite but in a two-dimensional system, $\alpha \sim \sigma/\bar{v}\tau$ and Γ_2/Γ_1 diverges! In the same way it is easy to show in three dimensions that the higher order diagram shown in the figure (12 d) leads to a similar divergence. Physically these divergences occur because we allow for recollisions that take place a long time after the first encounter. Actually particles (1) and (2) are not free but interact with bath particles which scatter them. Bath particles therefore act as a screen which largely eliminate long time recollision processes. It is hence natural to integrate (144) up to $\tilde{T} \sim \frac{1}{n\sigma^3}$ (3d-system). This argument leads to the following expansions of D in two and three dimensions:

$$\text{(145)} \quad \begin{aligned} &(2d): \quad D \sim \sigma\bar{v}\left(n - K(n\sigma^2)^2 \ln(n\sigma^2) + \cdots\right)^{-1} \\ &(3d): \quad D \sim \sigma\bar{v}\left(n + K_1(n\sigma^3)^2 + K_2(n\sigma^3)^3 \ln(n\sigma^3) + \cdots\right)^{-1} \end{aligned}$$

The proper way to tackle this divergence problem is to consider rings which exhaust the most diverging diagrams. Such ring theories are considered in the next section.

3,4. Full kinetic theories.

REFERENCES

1 - N. H. MARCH. -
in "Theory of Condensed Matter", I. A. E. A., Vienna, p. 93, (1968).

2 - J. P. HANSEN, I. R. Mc DONALD. -
Theory of Simple Liquids. ACADEMIC PRESS (1976).

3 - J. P. HANSEN. -
in "Microscopic Structure and Dynamics of Liquids"
J. DUPUY, A. J. DIANOUX ed., Nato Adv. Study Institutes Series, vol. 33, p. 3.

4 - K. SKÖLD, J. M. ROWE, G. OSTROWSKI, P. D. RANDOLPH. -
Phys. Rev. A, **6**, 1107 (1972).

5 - J. R. D. COPLEY, S. W. LOVESEY. -
Reports Prog. Phys., **38** (4), 461 (1975).

6 - B. R. A. NIJBOER, A. RAHMAN. -
Physica, **32**, 415 (1966).

7 - P. SCHOFIELD. -
Proc. I. A. E. A. Symposium, Vienna, p. 39 (1961).

8 - D. LEVESQUE, L. VERLET. -
Phys. Rev. A, **2**, 2514 (1970).

9 - A. RAHMAN. -
Phys. Rev. **136**,A405 (1964).

10 - J. NAGHIZADEH, S. A. RICE. -
J. Chem. Phys., **36**, 2710 (1962).

11 - P. A. EGELSTAFF, P. SCHOFIELD. -
Nucl. Sci. Eng., **12**, 260 (1962).

12 - D. LEVESQUE, L. VERLET, J. KURKIJÄRVI. -
Phys. Rev. A, **7**, 1690 (1973).

13 - S. W. LOVESEY. -
J. Phys. C, **6**, 1856 (1973).

14 - S. W. LOVESEY. -
in "Dynamics of Solids and Liquids by Neutron Scattering"
(ed. S. W. LOVESEY, T. SPRINGER), SPRINGER-VERLAG (1977)

15 - I. R. Mc DONALD. -
in "Microscopic Structure and Dynamics of Liquids"
ed. J. DUPUY, A. J. DIANOUX, Nato Adv. Study Institutes Series, vol. 33, p. 69

16 - B. J. ALDER, T. E. WAINWRIGHT. -
Phys. Rev. Lett., **18**, 988 (1967).
B. J. ALDER, T. E. WAINWRIGHT. -
J. Phys. Soc. Japan Suppl., **26**, 267 (1968).
B. J. ALDER, T. E. WAINWRIGHT. -
Phys. Rev. A, **1**, 18 (1970).
B. J. ALDER, D. M. GASS, T. E. WAINWRIGHT. -
J. Chem. Phys., **53**, 3813 (1970).
B. J. ALDER, W. E. ALLEY, J. H. DYMOND. -
J. Chem. Phys., **56**, 987 (1972).
J. Chem. Phys., **61**, 1415 (1974).

17 - G. JACUCCI, I. R. Mc DONALD. -
Physica A, **80**, 607 (1975).

18 - J. P. HANSEN, I. R. Mc DONALD. -
Phys. Rev. A, **11**, 2111 (1975).

19 - TOUKUBO, NAKANISHI. -
J. Chem. Phys., **65**, 1937 (1976).

20 - I. EBBSJÖ, P. SCHOFIELD, K. SKÖLD, I. WALLER. -
J. Phys. C, **7**, 3891 (1974).

21 - M. PARRINELLO, M. P. TOSI, N. H. MARCH. -
J. Phys. C, **7**, 2577 (1974).

22 - A. EINSTEIN. -
Ann. d. Physik, **17**, 549 (1905) ; **19**, 371 (1906).
P. LANGEVIN. -
Comptes-Rendus Ac. Sc., **146**, 530 (1908).
S. CHANDRASEKHAR. -
Rev. Mod. Phys., **15**, 1 (1943).

23 - L. S. ORNSTEIN, W. R. VAN WIJK. -
Physica, **1**, 235 (1933).

24 - S. A. RICE, P. GRAY. -
The statistical mechanics of simple liquids
Monographs in statistical physics, vol. 3, Inters. Publishers, (1965).

25 - Ph. NOZIERES. -
Lectures notes
Grenoble University (unpublished)

26 - J. G. KIRKWOOD. -
J. Chem. Phys., **14** (3), 180 (1946).

27 - E. HELFAND. -
Phys. Fluids, **4** (6), 681 (1961).

28 - A. SUDDABY, P. GRAY. -
Proc. Phys. Soc. (London), A **75**, 109 (1960)

29 - J. LEBOWITZ, E. RUBIN. -
Phys. Rev., **131**, 2381 (1963).

30 - P. RÉSIBOIS, H. T. DAVIS. -
Physica, 30, 1077 (1964).

31 - BOATO. -
J. Chem. Phys., **40**, 2419 (1964).

32 - J. A. PALYVOS, H. T. DAVIS. -
J. Phys. Chem., **71**, 439 (1967).

33 - H. T. DAVIS, J. A. PALYVOS. -
J. Chem. Phys., **46** (10), 4043 (1967).

34 - R. V. GOPALA RAO, A. K. MURTHY. -
Z. Naturforsch., **30** a, 619 (1975).

35 - K. ICHIKAWA, M. SHIMOJI. -
Phil. Mag., **20**, 341 (1969).

36 - S. CHAPMAN, T. G. COWLING. -
The mathematical theory of non-uniform gases
Cambridge University Press, New York, (1958).

37 - H. C. LONGUET-HIGGINS, J. A. POPLE. -
J. Chem. Phys., **25**, 884 (1956).

38 - S. A. RICE, J. G. KIRKWOOD, J. ROSS, R. W. ZWANGIG. -
J. Chem. Phys., **31**, 575 (1959).

39 - J. T. O'TOOLE, J. S. DAHLER. -
J. Chem. Phys., **33**, 1496 (1960).

40 - G. CINI-CASTAGNOLI, F. P. RICCI. -
J. Chem. Phys., **32**, 19 (1960).

41 - T. W. CORBETT, J. H. WANG. -
J. Chem. Phys., **25**, 422 (1956).

42 - STOKES. -

43 - R. ZWANGIG, M. BIXON. -
Phys. Rev. A, **2**, 2005 (1970).

44 - A. RAHMAN. -
J. Chem. Phys., **45**, 2585 (1966).

45 - J. R. DORFMAN, E. G. D. COHEN. -
Phys. Rev. Letters, **25**, 1257 (1970).
Phys. Rev. A, **6**, 776 (1972).
Phys. Rev. A, **12**, 292 (1975).

46 - M. H. ERNST, E. H. HAUGE, J. M. J. van LEEUWEN. -
Phys. Rev. Letters, **25**, 1254 (1970).
Phys. Rev. A, **4**, 2055 (1971).

47 - D. LEVESQUE, W. T. ASHURST. -
Phys. Rev. Letters, **33**, 277 (1974).

48 -

49 -

50 - B. J. BERNE, J. P. BOON, S. A. RICE. -
J. Chem. Phys., **45**, 1086 (1966).

51 - G. D. HARP, B. J. BERNE. -
Phys. Rev. A, **2**, 975 (1970).

52 - K. SINGWI, S. TOSI. -
Phys. Rev., **157**, 153 (1967).

53 - P. MARTIN, S. YIP. -
Phys. Rev., **170**, 151 (1968).

54 - H. MORI. -
Prog. Theoret. Phys. (Kyoto), **33**, 423 (1965).
Prog. Theoret. Phys. (Kyoto), **34**, 399 (1965).

55 - R. DESAI, S. YIP. -
Phys. Rev., **166**, 129 (1968).

56 - R. ZWANGIG. -
in *Molecular Fluids*,
Ed. BALIAN, WEILL, GORDON and BREACH, London (1973).

57 - H. MORI. -
Prog. Theoret. Phys., **33**, 423 (1965).

58 - H. MORI. -
Prog. Theoret. Phys., **34**, 399 (1965).

59 - J. BOSSE, W. GÖTZE, M. LÜCKE. -
Phys. Rev. A, **17**, 434 (1978).
Phys. Rev. A, **17**, 447 (1978).

60 - A. ZIPPELIUS, W. GÖTZE. -
Phys. Rev. A, **17**, 414 (1978).

61 - J. BOSSE, W. GÖTZE, M. LÜCKE. -
Phys. Rev. A, **18**, 1176 (1978).

62 - J. BOSSE, W. GÖTZE, A. ZIPPELIUS. -
Phys. Rev. A, **18**, 1214 (1978).

63 - D. FORSTER. -
Hydrodynamic Fluctuations, Broken Symmetry and Correlation Functions.
W. A. BENJAMIN Inc. (1975).

64 - G. S. DUBEY, V. K. JINDAL, K. N. PATHAK. -
Prog. Theoret. Phys., 64, 1893 (1980).

65 - B. F. Mc COY. -
Phys. Rev. A, **12**, 1678 (1975).

66 - T. MUNAKATA, I. IGARASHI. -
Prog. Theoret. Phys., **58**, 1345 (1977).
Prog. Theoret. Phys., **60**, 45 (1978).

67 - V. F. SEARS. -
Proc. Phys. Soc. (London), **86**, 953 (1965).

68 - A. RAHMAN, K. S. SINGWI, A. SJÖLANDER. -
Phys. Rev., **126**, 997 (1962).

69 - A. RAHMAN. -
J. Chem. Phys., **45**, 2585 (1966).

70 - R. ZWANZIG, M. BISHOP. -
J. Chem. Phys., **60**, 295 (1974).

71 - H. EYRING, R. P. MARCH. -
J. Chem. Phys., **40**, 562 (1963).

72 - M. H. COHEN, D. TURNBULL. -
J. Chem. Phys., **31**, 1164 (1959).

73 - R. A. SWALIN. -

74 - P. RÉSIBOIS, M. de LEENER. -
Classical kinetic theory of fluids
John WILEY and Sons (1977).

75 - S. CHAPMAN, T. G. COWLING. -
The Mathematical Theory of Non-Uniform Gases
Cambridge U. P., New York (1970).

76 - J. H. DYMOND, B. J. ALDER. -
J. Chem. Phys., **48**, 343 (1968).

77 - J. H. DYMOND. -
Physica, **75**, 100 (1974).

78 - J. H. DYMOND. -
J. Chem. Phys., **60**, 969 (1972).

79 - P. ASCARELLI, A. PASKIN. -
Phys. Rev. B, 165, 222 (1968).

80 - C. J. VADOVIC, C. P. COLVER. -
Phys. Rev. B, 1, 4850 (1970).

81 - N. F. CARNAHAN, K. E. STARLING. -
J. Chem. Phys., **51**, 635 (1969).

82 - L. VERLET, J. J. WEIS. -
Phys. Rev. A, 5, 939 (1971).

83 - P. PROTOPAPAS, H. C. ANDERSEN, N. A. D. PARLEE. -
J. Chem. Phys., **59**, 15 (1973).
P. PROTOPAPAS, N. A. D. PARLEE. -
J. Chem. Phys., **11**, 201 (1975).
P. PROTOPAPAS, N. A. D. PARLEE. -
High Temp. Sc., **7**, 259 (1975).

84. A. Z. Akcasu, E. Daniels, Phys. Rev. **A2**, 962 (1970)

85. A. Z. Akcasu, J.J. Duderstadt, Phys. Rev. **188**, 479 (1969)

86. P. Résibois, J.L. Lebowitz, J. Stat. Phys. **12**, 483 (1975)
P. Résibois, J. Stat. Phys. **13**, 393 (1975)

87. G.F. Mazenko, Phys. Rev **A7**, 209 (1973); Phys. Rev. **A7**, 222 (1973),
Phys Rev. **A9**, 360 (1974)

88. P.H. Furtado, G.F. Mazenko, S. Yip, Phys Rev **A12**, 1653 (1975)

89. J.L. Lebowitz, J.K. Percus, J. Sykes, Phys. Rev. **188**, 487 (1969)

90. K.S. Singwi, A. Sjölander, Phys. Rev **167**, 152 (1968)

91. K.S. Singwi in "Theory of Condensed Matter"
IAEA Vienna (1968) p. 603.

91. [illegible], Phys. Rep. 15C, 65 ([illegible])

92. C. D. Boley, Ann. Phys. 86, 91 (1974); Phys. Rev. A11, 328 (1975)

93. E. P. Gross, J. Stat. Phys. 11, 503 (1974); 15, 181 (1976)

94. J. R. Mehaffey, R. C. Desai, R. Kapral, J. Chem. Phys. 66, 1665 (1977)
J. R. Mehaffey, R. I. Cukier, Phys. Rev. A17, 1181 (1978)

95. L. Sjögren, A. Sjölander, Ann. Phys. 110, 122 (1978); Ann. Phys. 110, 421 (1978); J. Phys. C 12, 4369 (1979)

96. L. Sjögren, J. Phys. C 13, 705 (1980)

97. A. Sjölander, in "Liquid and Amorphous Metals". (E. Lüscher, H. Coufal ed.) Nato Adv. Inst. Series n° 36, Sijthoff and Noordhoff (1980); p. 63.

Appendix A. Correlation functions (2)

We make frequent use of the time correlation function $C_{BA}(t)$ of two dynamical variables $A(t) = A[\vec{r}^N(t), \vec{p}^N(t)]$ and $B(t) = B[\vec{r}^N(t), \vec{p}^N(t)]$ which are determined by the state of the system at time t. The correlation function can be defined either:

a) as the ensemble average:

$$C_{BA}(t) = \langle B(t+s)\, A(s) \rangle = \int B(t+s)\, f_0^{(N)}(s)\, A(s)\, d\Gamma_N \tag{A1}$$

which means that, $A(s)$ being given by a microscopic state $[\vec{r}^N(s), \vec{p}^N(s)]$ of the system at time s, we let it evolve until the time $(t+s)$ when the dynamical variable B takes the value $B(t+s)$ and we finally average over the equilibrium distribution function $f_0^{(N)}(s)$;

b) or as the time average:

$$\langle B(t+s)\, A(s) \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_0^{\tau} B(t+s+t')\, A(s+t')\, dt' \tag{A2}$$

This shows clearly that, in an equilibrium system, the correlation function is stationary, i.e. independent of the origin of time:

$$C_{BA}(t) = \langle B(t+s)\, A(s) \rangle = \langle B(t)\, A \rangle$$

The stationarity has the important consequence that:

$$\frac{d\, C_{AB}}{ds} = 0 = \langle \dot{B}(t+s)\, A(s) \rangle + \langle B(t+s)\, \dot{A}(s) \rangle$$

hence (A3) $\langle \dot{B}(t)\, A \rangle = - \langle B(t)\, \dot{A} \rangle$

In particular a dynamical variable is not correlated with its first derivative at the same time:

$$\langle \dot{A}(t)\, A \rangle = - \langle A(t)\, \dot{A} \rangle$$

so that $\langle \dot{A}\ A \rangle = \langle \dot{A}(0)\, A(0) \rangle = 0$

On the other hand:

$$\langle \ddot{B}(t)\, A \rangle = - \langle \dot{B}(t)\, \dot{A} \rangle = + \langle B(t)\, \ddot{A} \rangle$$

The autocorrelation function $C_{AA}(t)$ has interesting properties. It is generally an even function of time so that its expansion in powers of t can be written:

$$(A4) \qquad C_{AA}(t) = \langle AA \rangle - \frac{t^2}{2!} \langle \dot{A}\dot{A} \rangle + \frac{t^4}{4!} \langle \ddot{A}\ddot{A} \rangle - \dots$$

It is also useful to define:

- the Fourier transform $C_{AA}(\omega)$:

$$(A5) \qquad C_{AA}(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt\, e^{i\omega t}\, C_{AA}(t)$$

- the Laplace transform $\tilde{C}_{AA}(s)$:

$$\tilde{C}_{AA}(s) = \int_0^{\infty} dt\, e^{-st}\, C_{AA}(t)$$

so that

$$(A6) \qquad C_{AA}(\omega) = \frac{1}{\pi} \operatorname{Re} \tilde{C}_{AA}(-i\omega)$$

The inverse Fourier transform of (A6) is:

$$C_{AA}(t) = \int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t}\, C_{AA}(\omega)$$

and, after differentiation with respect to time

$$\frac{d^n C_{AA}(t)}{dt^n} = \int_{-\infty}^{+\infty} d\omega\, e^{-i\omega t} (-i\omega)^n C_{AA}(\omega)$$

so that

$$\left. \frac{d^n C_{AA}(t)}{dt^n} \right|_{t=0} = (-i)^n \langle \omega^n \rangle$$

where $\langle \omega^n \rangle$ is the n^{th} frequency moment of $C_{AA}(\omega)$:

$$\langle \omega^n \rangle = \int_{-\infty}^{+\infty} d\omega\, \omega^n\, C_{AA}(\omega)$$

The coefficients in the expansion (A4) of $C_{AA}(t)$ are hence the moments of $C_{AA}(\omega)$.