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QUANTUM CORRELATION FUNCTIONS AND NEUTRON SCATTERING FROM SIMPLE LIQUIDS

by

Hadj Slimane Cherif

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ABSTRACT

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by

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The projection operator technique developed by Zwanzig and Mori, and extended by Akcasu and Duderstadt for the study of classical systems is utilized to calculate quantum mechanically the total and incoherent neutron scattering functions for simple liquids. These scattering functions are calculated in two different ways : the hydrodynamic way, where the density operator is taken to be the dynamical variable, and the kinetic way, where the classical phase space density operator, quantized according to Weyl's rule, is taken to be the dynamical variable in configuration space. The projector used is symmetrized in order to preserve the detailed balance property of the scattering functions.

The solution of the equation of motion of the time correlation functions, separated now into a "frequency term" and a "memory term", is obtained by modeling the "damping term".The thermal averages contained in these equations are expanded in a power series in h, valid for non-degenerate

systems at high temperatures. The final form of these equations reduces exactly to the classical analog derived by Akcasu and Duderstadt. The neutron scattering function for a non-degenerate ideal gas is also obtained exactly from our kinetic equations.

A closed form is given for both the total and incoherent scattering functions, where quantum corrections appear everywhere. These corrections are estimated to amount to no more than 10%.

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CHAPTER I
INTRODUCTION

It has long been recognized that thermal neutrons, with a mass of 1.0086 a.m.u., may have energies comparable to those characteristic of the various modes of molecular motions (1 - 100 meV) as well as De Broglie wavelengths of the order of interatomic spacing (1 - 10 Å). Scattering experiments of initially thermal monoenergetic neutrons could provide then considerable information about the dynamical structure of the scatterer and may shed some light on atomic and molecular forces present in the system.

A general theory of neutron scattering from arbitrary systems of scatterers in any form - liquid, gas or solid - was formulated by Van Hove,[1] making use of the Fermi pseudopotential[2] and the Born approximation.[3] This theory expresses the differential scattering cross section as a four dimensional Fourier transform $S(\underline{k},\omega)$ of a space-time correlation function $G(\underline{r},t)$ and is in essence a generalization of the Zernike-Prins static approximation.[4] In this approximation, the differential scattering cross section is given in terms of the static pair distribution function $g(\underline{r})$.

However the calculation of $G(\underline{r},t)$, or equivalently its space Fourier transform $\phi(\underline{k},t)$ is not always possible and is indeed tractable only for scattering systems where

the many-particle Hamiltonian can be replaced by a sum of single particle Hamiltonians as in systems of non-interacting particles -ideal gases- or systems of harmonic oscillators. The calculation of the Van Hove correlation function $G(\underline{r},t)$ for dilute gases (the interactions being weak) and for crystals (assumed to be systems of harmonic oscillators) has indeed yielded good agreement with experiments.

On the other hand, for dense fluids, and more specifically for liquids, the interatomic interactions are rather important, thus complicating the atomic dynamics and the calculation of $G(\underline{r},t)$. The many-body problem cannot any longer be reduced, except for highly simplistic assumptions, to a soluble one-body problem. We are then forced to tackle the complexities of the many-body problems in order to obtain a theory for the differential scattering cross section that could be compared with experiments.

It has been noted that the Van Hove correlation function has a physical interpretation in the classical limit. It is the conditional probability that given an atom at the point $\underline{r}$ at time t=0, there will be an atom, the same or another one, at the point $\underline{r}$ at time t. Also with a classical calculation of $G(\underline{r},t)$, it is possible to avoid most of the complexities of quantum mechanics, and use can be made of models and methods of approach devised earlier for

the study of macroscopic and microscopic properties of classical fluids. But im order to make use of this observation, a way to retain the quantum characteristic of the thermal average in the correlation function $G(\underline{r},t)$ has to be found and a link between the classical and the quantum calculations of $G(\underline{r},t)$ has to be established. Various semi-empirical prescriptions have been proposed in an attempt to establish such a relationship.

The first prescription is due to Vineyard,[5] and consists in replacing $G(\underline{r},t)$ simply by its classical limit. This amounts to a development in which the neutron is treated quantum mechanically and the scatterer classically. This approach does not treat adequately the recoil effects and gives a zero average energy loss, beside violating the principle of detailed balance, a property that can be derived from the quantum mechanical nature of the thermal average.

Schofield[6] suggested setting $G(\underline{r},t+i\beta\hbar)$, where $\beta=\frac{1}{k_B T}$, equal to the classical $G_c(\underline{r},t)$ and thus improving somewhat Vineyard's prescription. This recipe is valid to order $\hbar$ and indeed satisfies the principle of detailed balance.

Later Singwi and Sjolander[7] noted that the replacement of $\left[G(\underline{r},t)\right]_+ = G(\underline{r},t)+G^*(\underline{r},t)$ by its classical equivalent, gives the same effects as the Schofield suggestion. Both of these suggestions were given on intuitive ground. Both of

them fail to yield the correct result for the ideal monoatomic gas, and both of them do not satisfy the zeroth Placzek moment.[8] Any attempt to use this prescription is therefore bound not to give the correct ideal gas limit in the calculation of the cross section. To improve this prescription, Egelstaff[9] and Schofield[10] suggested replacing t^2 by $t^2 - i\hbar\beta t$ in $G_c(\underline{r},t)$, and in so doing, giving the correct expression for the $\hbar^2$ term, but still not yielding the correct ideal gas limit. Finally, Nelkin[11] proposed substituting for $S(\Delta\underline{p},\epsilon)$ the classical expression $S_c(\Delta\underline{p},\epsilon - \frac{\Delta p^2}{2m})$, where $\Delta\underline{p}$ is the momentum transfer and ϵ the energy transfer.

Rather than approaching this problem on intuitive ground, like the above prescriptions, Rosenbaum[12] tried to approach it in a deductive fashion in which he replaced the quantum average in $G(\underline{r},t)$ by a phase-space average, over a Wigner distribution of the Weyl equivalent of the operator present in the thermal average. This procedure was successful in giving the incoherent scattering function as a power series in $\hbar$ with a multiplicative factor representing the detailed balance and the recoil effects. However due to an essential singularity in $G(\underline{r},t)$, the coherent scattering function could not be obtained. Rosenbaum also found that the first term in his expression for the incoherent scattering function was the same as the one proposed empirically by Singwi and Sjolander $\left(\text{i.e. letting } S(\underline{k},\omega) = e^{\frac{\beta\epsilon}{2}} e^{-\beta\frac{\Delta p^2}{8m}} S(k,\omega)\right)$

At any rate, the problem of determining $G(\underline{r},t)$ - or $S(\underline{k},\omega)$ - hinges totally on the ability of developing a technique to evaluate time correlation functions, be it classically or quantum mechanically. To this end, a variety of techniques have been already developed, specially in connection with non-equilibrium statistical mechanics.[13-16] Most procedures used for the calculation of time correlation functions belong to either one of the following two categories : the hydrodynamic-like description of the many-body system, or the kinetic description of the system.

The hydrodynamic description has been used quite extensively as a phenomenological theory in the study of correlation functions in continuous media. In its most elementary form, it makes use of the conventional hydrodynamic equations to describe the linear response of the system, which in turn is related to the correlation functions of interest by means of the fluctuation dissipation theorem.[17-18] Following the formalism described by Landau and Lifschitz,[19] Rytov[20] applied this technique to calculate correlation functions, and subsequently Mountain[21] used it to study light scattering from liquids. More recently Kadanoff and Martin[22] have developed an exact generalization of the hydrodynamic approach which has been applied by Yip[23] et al. for the interpretation of molecular dynamics calculations as well as neutron scattering data for liquid.

The generalized hydrodynamic approach consists in developing equations for the dynamical variables (density, current, etc...) with frequency and wave-vector dependent transport coefficients. Mori[24-25-26] derived such equations to study transport properties of fluids, and very recently Akcasu and Daniels[27] used this approach to compare successfully their results with the results of molecular dynamics calculations of Rahman[28] for classical liquids.

The kinetic description, on the other hand, strives to derive an approximate kinetic equation for the microscopic phase-space density $f(\underline{k},p,t)$, which when multiplied by $f(\underline{k},p',o)$ thermal averaged, Fourier transformed in time and integrated over momenta would give the scattering function $S(\underline{k},\omega)$. Such a description, developed by Nelkin,[29] has been given theoretical justification for dilute gases[30] and has been used to interpret Brillouin scattering from gases.[31-32] However, because the equation used in these studies is a Vlasov-like equation, all attemps to extend this description to dense fluids[33] and liquids has had limited success, except for a new approach used very recently by Akcasu and Duderstadt[34] which compared successfully with Rahman's computer experiment.

To derive either the hydrodynamic or the kinetic equations, the starting point is the Liouville equation for the classical dynamical variables, and the Heisenberg

equation of motion for quantum mechanical operators. One method that has drawn considerable attention lately and which has had fairly good success in deriving such equations is the projection operator technique first introduced by Zwanzig,[35] generalized by Mori,[36] and extended recently by Akcasu and Duderstadt.[34] Mori's approach consists essentially in utilizing projection operators similar to those of Zwanzig to derive a "Generalized Langevin equation" for the time evolution of an arbitrary vector $\underline{A}(\underline{r},t)$ whose components are dynamical variables depending on the coordinates of the particles in the system. - This is in essence the hydrodynamic approach. - Akcasu and Duderstadt then extended the use of projection operators to derive "Generalized Langevin equations" for the time evolution of dynamical variables $B(\underline{r},\underline{p},t)$ that depend on the coordinates of the particles in the system as well as their momenta, thus yielding the so called kinetic equations. The equations so derived are then utilized to calculate time correlations that are in turn related to the scattering function through the different recipes outlined previously if a classical approach to the problem is adopted.

It is the purpose of this study to derive both hydrodynamic and kinetic equations for time correlation functions quantum mechanically starting from the Heisenberg equation of motion and using the projection operator tech-

niques. These equations will contain operators which will be functionals of certain static correlation functions. These static correlation functions will then be calculated within certain approximations. This method of attack will shed light on the quantum effects and their importance in neutron scattering from liquids.

In a first chapter, the general theory of neutron scattering from a system of particles will be derived. The neutron scattering cross section for simple liquids will be written explicitly in terms of the Van Hove incoherent and total scattering functions, taking into account the spin states of the system. The scattering function will be given in terms of operators amenable to calculation through the hydrodynamic or the kinetic approach by introducing operators in phase-space which, when integrated properly over momenta will give desired result. The properties and the equations of motion of these operators will be studied in an appendix. For neutron scattering from systems with internal degrees of freedom (rotational, for instance), the second quantization method will be utilized to obtain the scattering cross section in terms of time correlation functions of Wigner density operators.

A second chapter will be devoted to deriving the quantum hydrodynamic and kinetic equations for arbitrary operators via the projection operator technique. For the

hydrodynamic case, a symmetrized projector will be used so as to cast the final equation in a simpler form by using time-reversibility invariance arguments, while in the kinetic case, a symmetrized projector will be adequate for retaining the detailed balance property of the time correlation function. The final equations so obtained will have a "frequency term" corresponding to the frequency of oscillation of the fluctuations and a "damping term" corresponding to the damping of these oscillations. In certain experiments, just the "frequency term" is needed for the description of the system. However for experiments with thermal neutrons, the "damping term" is necessary for such a complete description.

Since most liquids at normal and high temperatures are non-degenerate, the purpose of a fourth chapter will be to show a way of evaluating quantum thermal averages for non-degenerate systems that will be helpful in calculating static correlation functions of operators of the form $O(\hat{\underline{x}}_1, \ldots, \hat{\underline{x}}_N; \hat{\underline{p}}_1, \ldots, \hat{\underline{p}}_N)$ where $\hat{\underline{x}}$'s are the position operators of the particles and $\hat{\underline{p}}$'s their momentum operators. The quantum thermal average will essentially be expanded in powers of $\frac{\hbar^2 \beta a^2}{m}$, where a is some characteristic, potential dependent wave number. In the limit as $\hbar$ goes to zero, the leading term of this expansion will be just the classical thermal average.

In a fifth and sixth chapters, the incoherent and total scattering functions will be obtained with both the hydrodynamic and the kinetic approaches. The corrections to the classical scattering function due to quantum effects will be displayed and a quantitative comparison will be made for the case of the incoherent scattering function. The different kinds of quantum effects coming from the static and dynamic terms will be contrasted. In the hydrodynamic case, the Markov assumption will be invoked in order to be able to solve the equation obtained for the scattering function, while in the kinetic case modeling of the damping term will be tried by assuming an exponential decay (wave vector dependent) of the fluctuations. We shall also demonstrate how the detailed balance comes about in the final expression.

A final chapter will consist of a summary and conclusion, with suggestions for further extension of this approach to the study of quantum mechanical time correlation functions.

CHAPTER II

NEUTRON SCATTERING CROSS SECTION

Consider the following experiment where neutrons are scattered from an arbitrary macroscopic body (though thin enough so that multiple scattering is negligible) which can be either in the gas, liquid or solid phase. The incident neutrons form a monoenergetic beam with momentum $\hbar\underline{k}$ and spin state $|\tau_i\rangle$ (i.e. they are in the initial state $|\underline{k}_i \tau_i\rangle$) and are scattered into states with momentum $\hbar d\underline{k}$ about $\hbar\underline{k}$ and spin $|\tau_f\rangle$ (i.e. to the final state $|\underline{k}_f \tau_f\rangle$). At the same time, the scatterers undergo a transition from an initial state $|i\rangle$ to a final state $|f\rangle$ (the spin states being included in the kets $|i\rangle$ and $|f\rangle$).

The differential scattering cross section $\frac{d^2\sigma}{d\underline{\Omega}\, d\epsilon_f}$ is defined to be the number of neutrons scattered into an element of solid angle $d\underline{\Omega}$ about $\underline{\Omega} = \frac{\underline{k}_f}{|\underline{k}_f|}$, having a final energy $d\epsilon_f$ about $\epsilon_f = \frac{\hbar^2 k_f^2}{2m}$ per second per atom of the scatterer, divided by the number of incident neutrons of initial energy $\epsilon_i = \frac{\hbar^2 k_i^2}{2m}$ per square centimeter per second. For simplicity consider the case where the incident beam has only one neutron in it. Then the incident current $\underline{J}_{INC}$ is just :

$$\underline{J}_{INC} = \frac{1}{V}\, \underline{v}_{INC} = \frac{\hbar \underline{k}_i}{mV} \qquad (2.1)$$

where $\underline{v}_{INC}$ = incident velocity of the neutron

V = the volume of the box enclosing our total system.

The transition probability per unit time from the initial states to the final states of the neutron and the scatterers as defined above is given by the golden rule :[37]

$$T_{n_f,n_i} = \frac{2\pi}{\hbar} \left| \langle n_f | H^{ns} | n_i \rangle \right|^2 \delta(E_i - E_f - \epsilon_i - \epsilon_f) \quad (2.2)$$

where :

H^{ns} = the interaction Hamiltonian of the neutron with the scaterers.

E_i =the initial energy of the scatterers

E_f = the final energy of the scatterers

$|n_i\rangle = |\underline{k}_i \tau_i\rangle |i\rangle$ = the initial state of the total system

$|n_f\rangle = |\underline{k}_f \tau_f\rangle |f\rangle$ = the final state of the total system.

The transition rate into $d\underline{k}$ will be just T_{n_f,n_i} multiplied by the density of final states in $d\underline{k}_f$:

$$\rho(\underline{k})\, d\underline{k}_f = 2\frac{V p_f^2 dp_f d\Omega}{h^3} = \frac{\text{volume in phase space}}{\text{volume of a unit cell}} \quad (2.3)$$

the factor 2 is for the two possible orientations of the spin of the neutron.

$$\rho(\underline{k})\, d\underline{k}_f = \frac{2V}{(2\pi\hbar)^3} m \hbar k_f\, dE_f\, d\underline{\Omega} \quad (2.4)$$

The transition rate into $d\underline{k}_f$ is :

$$\omega(i \rightarrow f) = \frac{2V}{\hbar} \frac{m k_f\, dE_f\, d\underline{\Omega}}{(2\pi\hbar)^2} \left| \langle n_f | H^{ns} | n_i \rangle \right|^2 (x) \quad (2.5)$$

$$(x)\ \delta(E_i - E_f - \epsilon_i - \epsilon_f)$$

The differential scattering cross section is $\omega(i \to f) d\underline{k}_f$ divided by thr total number of scatterers N and the incident neutron current $\underline{J}_{inc}$, provided we sum over all final states of the system and average over all its initial states since the incident beam is not usually polarized and the scatterers are in thermal equilibrum rather than in an initially prepared state. Let P_{τ_i} and P_i represent respectively the probability of the neutron being in a spin state (note that $P_{\tau_i} = \frac{1}{2}$) and the probability for the scatterers to be in a state $|i\rangle$. Then

$$\frac{d^2\sigma}{d\epsilon_f d\Omega} = \sum_f \sum_i \sum_{\tau_i} \sum_{\tau_f} \frac{1}{2} P_i \frac{2V^2 m^2}{N(2\pi\hbar)^2} \frac{k_f}{k_i} \left| \langle n_f | H^{ns} | n_i \rangle \right|^2 (x) \tag{2.6}$$

$$(x)\, \delta(E_i - E_f - \epsilon_i - \epsilon_f)$$

At this point, the initial and final states of the neutron are taken to be plane waves.

$$|\underline{k}_i\rangle = \frac{1}{V^{1/2}} e^{i \underline{k}_i \cdot \underline{R}} \tag{2.7}$$

$$|\underline{k}_f\rangle = \frac{1}{V^{1/2}} e^{i \underline{k}_f \cdot \underline{R}} \tag{2.8}$$

$\underline{R}$ being the position vector of the neutron and $V^{-1/2}$ is due to the box normalization. The differential scattering cross section reads then :

$$\frac{d^2\sigma}{d\epsilon_f d\Omega} = \sum_f \sum_i \sum_{\tau_i} \sum_{\tau_f} P_i \frac{m^2}{N(2\pi\hbar)^2\hbar^2} \frac{k_f}{k_i} \left| \langle f\tau_f | \int d\underline{R}\, e^{-i(\underline{k}_i - \underline{k}_f)\cdot\underline{R}} H^{ns} | i\tau_i \rangle \right|^2_{(x)} \qquad (2.9)$$

$$(x)\ \delta(E_i - E_f - \epsilon_i - \epsilon_f)$$

This expression is still general, nevertheless the differential scattering cross section will be developed for two cases only : the case of simple liquids (no rotational degrees of freedom allowed) taking into account the spin states of the scattering medium, and the case of molécular liquids where rotational degrees of freedom are allowed via the method of second quantization.

2.1 SIMPLE LIQUIDS :

The interaction Hamiltonian between the neutron and the j^{th} nucleus of the scattering medium shall be characterized by the Fermi pseudo-potential[38-39] which is given by(*)

$$H^{ns} = \frac{2\pi\hbar^2}{m} \sum_{j=1}^{N} a_j\, \delta(\underline{R} - \underline{r}_j) \qquad (2.10)$$

where $\underline{r}_j$ = the position of the j^{th} nucleus

a_j = the scattering length of the j^{th} nucleus.

The Fermi pseudo-potential, in connection with the Born

(*) Osborn and Yip[40] have used a Yukawa potential instead of the Fermi pseudo-potential to calculate the cross section. The agreement is much better with experiment for high energy neutron scattering.

approximation for neutron scattering has been studied extensively in the literature and the range of its validity and rigor have been demontrated.[41-44] The differential scattering cross section becomes, using the integral representation of the delta function :

$$\delta(x) = \frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt\ e^{-it\frac{x}{\hbar}} \tag{2.11}$$

and the closure relation for the set $|\underline{k}_f \tau_f\rangle$, assumed to be complete

$$\sum_{f} \sum_{\tau_f} |f\,\tau_f\rangle\langle f\,\tau_f| = 1 \tag{2.12}$$

$$\frac{d^2\sigma}{d\epsilon_f d\Omega} = \sum_{\tau_i}\sum_{i} P_i \frac{1}{2\pi\hbar N}\frac{k_f}{k_i}\int_{-\infty}^{\infty} dt\ e^{-i t\epsilon/\hbar} \sum_{j=1}^{N}\sum_{l=1}^{N}(x) \tag{2.13}$$

$$(x) \langle i\,\tau_i | a_j^{+} e^{-i\underline{k}\cdot\underline{r}_j} a_l(t)\, e^{i\underline{k}\cdot\underline{r}_l(t)} | i\,\tau_i\rangle$$

where : $\epsilon = \epsilon_i - \epsilon_f$

$\underline{k} = \underline{k}_i - \underline{k}_f$

$\underline{r}_j(t) = e^{i\frac{H^s t}{\hbar}}\ \underline{r}_j\ e^{-i\frac{H^s t}{\hbar}}$

H^s = the Hamiltonian of the scatterers.

In order to sum over all initial spin states of the scattering medium, the dependence of the scattering length a_j on the total angular momentum $\underline{j}$ of the system has to be consi-

dered. If j_ℓ is the spin of the ℓ^{th} particle then :

$$j_\ell = i_\ell \pm \frac{1}{2} \tag{2.14}$$

depending on whether the neutron spin is parallel (+) or antiparallel (-), with corresponding scattering lengths $a^{(+)}$ and $a^{(-)}$. a_ℓ can be expressed as[45]

$$a_\ell = a_\ell^{(+)} \mathcal{P}_\ell^{(+)} + a_\ell^{(-)} \mathcal{P}_\ell^{(-)} \tag{2.15}$$

where $\mathcal{P}_\ell^{(+)}$ and $\mathcal{P}_\ell^{(-)}$ are projection operators defined by

$$\mathcal{P}_\ell^{(\pm)} \left| i_\ell \pm \tfrac{1}{2} \right\rangle = \left| i_\ell \pm \tfrac{1}{2} \right\rangle \tag{2.16}$$

$$\mathcal{P}_\ell^{(\mp)} \left| i_\ell \pm \tfrac{1}{2} \right\rangle = 0 \tag{2.17}$$

These two equations are satisfied by the following two operators :

$$\mathcal{P}^{(+)} = \frac{J^2 - j^2_{i-1/2}}{j^2_{i+1/2} - j^2_{i-1/2}} = \frac{I^2 + 2\underline{I}\cdot\underline{S} + S^2 - i^2 + 1/4}{2i+1} = \frac{i+1+2\underline{I}\cdot\underline{S}}{2i+1} \tag{2.18}$$

$$\mathcal{P}^{(-)} = \frac{J^2 - j^2_{i+1/2}}{j^2_{i-1/2} - j^2_{i+1/2}} = \frac{i - 2\underline{I}\cdot\underline{S}}{2i+1} \tag{2.19}$$

where : I = the scattering particle spin operator

S = the neutron spin operator.

The scattering length becomes :

$$a_\ell = \left[a_\ell^{(+)} \left(\frac{i_\ell + 1}{2i_\ell + 1} \right) + a_\ell^{(-)} \left(\frac{i_\ell}{2i_\ell + 1} \right) \right] + \tag{2.20}$$

$$+ 2 \left\{ \frac{\sqrt{i_\ell (i_\ell + 1)}}{2 i_\ell + 1} \left(a_\ell^{(+)} - a_\ell^{(-)} \right) \right\} \frac{\underline{I}_\ell \cdot \underline{S}}{\sqrt{i_\ell (i_\ell + 1)}}$$

$$= A_\ell + 2 B_\ell \frac{\underline{I}_\ell \cdot \underline{S}}{\sqrt{i_\ell (i_\ell + 1)}}$$

A_ℓ and B_ℓ are respectively the so called coherent and incoherent scattering amplitudes.

Now the trace $\sum_{\tau_i = \pm \frac{1}{2}} \langle \tau_i | a_j^+ a_\ell | \tau_i \rangle$ can be evaluated. By noting that :

$$\sum_{\tau_i = \pm \frac{1}{2}} \langle \tau_i | \underline{I}_\ell \cdot \underline{S} | \tau_i \rangle = \sum_{\alpha=1}^{3} I_\ell \, Tr \, S_\alpha = 0 \qquad (2.21)$$

and

$$\sum_{\tau_i = \pm \frac{1}{2}} \langle \tau_i | (\underline{I}_\ell \cdot \underline{S})(\underline{I}_j \cdot \underline{S}) | \tau_i \rangle = \sum_{\tau_i = \pm \frac{1}{2}} \langle \tau_i | \frac{1}{4} \underline{I}_\ell \cdot \underline{I}_j + \qquad (2.22)$$

$$+ \frac{1}{2} \underline{S} \cdot (\underline{I}_\ell \times \underline{I}_j) | \tau_i \rangle$$

$$= \frac{1}{2} \underline{I}_\ell \cdot \underline{I}_j + \frac{1}{2} \sum_{\alpha=1}^{3} (\underline{I}_\ell \times \underline{I}_j)_\alpha \, Tr \, S_\alpha$$

$$= \frac{1}{2} \underline{I}_\ell \cdot \underline{I}_j$$

the differential scattering cross section reads :

$$\frac{d^2\sigma}{d\epsilon_f d\Omega} = \frac{1}{2\pi\hbar}\frac{k_f}{N k_i}\int_{-\infty}^{\infty} dt\, e^{-i\frac{t\epsilon}{\hbar}} \sum_{j=1}^{N}\sum_{\ell=1}^{N}\sum_{i} P_i \langle i| e^{-i\underline{k}\cdot\underline{r}_j} \quad (*) \quad (2.23)$$

$$(*)\left\{ A_j A_\ell + \frac{B_j B_\ell\, \underline{I}_j \cdot \underline{I}_\ell(t)}{\left[i_\ell i_j (i_j+1)(i_\ell+1)\right]^{1/2}} \right\} e^{i\underline{k}\cdot\underline{r}_\ell(t)} |i\rangle$$

For a scattering system with a spin independent Hamiltonian, the eigenstate $|i\rangle$ may be expressed as a product of spatial and spin eigenstates

$$|i\rangle = |K\rangle|m\rangle \quad (2.24)$$

When exchange interactions are negligeable ($\frac{\hbar^2}{m k_B T d^2} \ll 1$ with d = interatomic distance), P_i can be written as a product :

$$P_i = P_K P_m \quad (2.25)$$

When the directions of the spins of the different nuclei are also uncorrelated :

$$\langle m|\, \underline{I}_j \cdot \underline{I}_\ell |m\rangle = i_\ell(i_\ell+1)\,\delta_{j\ell} \quad (2.26)$$

Noting that for a system in thermal equilibrium P_k is given by

$$P_K = \frac{e^{-\beta E_i^s}}{Z} \quad (2.27)$$

where $\beta = \frac{1}{k_B T}$

Z = the partition function of the scattering system

we obtain :

$$\frac{d^2\sigma}{d\epsilon\, d\underline{\Omega}} = \frac{1}{2\pi\hbar N}\,\frac{k_f}{k_i}\int_{-\infty}^{\infty} dt\, e^{-i\frac{t\epsilon}{\hbar}} \sum_{j=1}^{N}\sum_{\ell=1}^{N}\sum_{i}\frac{e^{-\beta E_i^s}}{Z}(x) \quad (2.28)$$

$$(x)\langle K|\left(A_j A_\ell + B_\ell^2 \delta_{j\ell}\right) e^{-i\underline{k}\cdot\underline{r}_j} e^{i\underline{k}\cdot\underline{r}_\ell(t)}|K\rangle$$

Using the definition of the thermal average of an operator

$$\langle \hat{O}\rangle = Tr\,\frac{e^{-\beta H}}{Z}\hat{O} \quad (2.29)$$

and the fact that

$$h\omega = \epsilon = E_i - E_f = \text{neutron energy change} \quad (2.30)$$

the expression for the cross section becomes :

$$\frac{d^2\sigma}{d\Omega\, d\omega} = \frac{1}{2\pi N}\,\frac{k_f}{k_i}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\left\{\sum_{\ell=1}^{N} B_\ell^2 \langle e^{-i\underline{k}\cdot\underline{r}_\ell} e^{i\underline{k}\cdot\underline{r}_\ell(t)}\rangle\right. \quad (2.31)$$

$$\left. + \sum_{j=1}^{N}\sum_{\ell=1}^{N} A_j A_\ell \langle e^{-i\underline{k}\cdot\underline{r}_j} e^{i\underline{k}\cdot\underline{r}_\ell(t)}\rangle\right\}$$

For the case of a monoatomic, monoisotopic system, the differential scattering cross section is just :

$$\frac{d^2\sigma}{d\underline{\Omega}\, d\omega} = \frac{k_f}{N k_i}\left[B^2 S_s(\underline{k},\omega) + A^2 S(\underline{k},\omega)\right] \quad (2.32)$$

where

$$S_s(\underline{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{j=1}^{N} \langle e^{-i\underline{k}\cdot\underline{r}_j} e^{i\underline{k}\cdot\underline{r}_j(t)} \rangle \qquad (2.33)$$

$$S(\underline{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{j=1}^{N}\sum_{l=1}^{N} \langle e^{-i\underline{k}\cdot\underline{r}_j} e^{i\underline{k}\cdot\underline{r}_l(t)} \rangle \qquad (2.34)$$

$S_s(\underline{k},\omega)$ and $S(\underline{k},\omega)$ are respectively the incoherent and total scattering functions.

In order to determine the problem completely, the thermal averages indicated above have to be evaluated. For simple liquids, where the interparticle potential plays an important role, the evaluation of the thermal averages is exceedingly difficult and one has to resort to models. In any case, there are two ways of attacking the problem.

2.1.a : The hydrodynamic approach :

In this approach, the density operator in configuration space is defined to be :

$$\hat{\rho}(\underline{r},t) = \sum_{j=1}^{N} \delta\left(\underline{r} - \underline{r}_j(t)\right) \qquad (2.35)$$

Its Fourier transform is :

$$\hat{\rho}(\underline{k},t) = \int d\underline{r}\, e^{-i\underline{k}\cdot\underline{r}} \sum_{j=1}^{N} \delta(\underline{r} - \underline{r}_j(t)) \qquad (2.36)$$
$$= \sum_{j=1}^{N} e^{-i\underline{k}\cdot\underline{r}_j(t)}$$

One then proceeds to derive an equation of motion for the above operator and solve it within certain approximations. The equation of motion of $\hat{\rho}(\underline{k},t)$ involves the current density operator $\hat{\underline{J}}(\underline{k},t)$ whose equation of motion in turn involves the pressure density operator $\hat{\Pi}(\underline{k},t)$, etc... In so doing, the hydrodynamic equations are generated, and then truncated somewhere in order to be able to solve for $\hat{\rho}(\underline{k},t)$. Note that when $\hat{\rho}(\underline{k},t)$ is multiplied by $\hat{\rho}(\underline{k},0)$, Fourier transformed in time and the thermal average is performed, the total scattering function is obtained.

2.1.b THE KINETIC APPROACH

Instead of dealing with the density operator in configuration space $\hat{\rho}(\underline{k},t)$, we shall look for an operator depending on new variables (like the momentum $\underline{p}$ for instance) which, when the integration over the newly introduced variables is carried out, we get back $\hat{\rho}(\underline{r},t)$. Classically, a single particle density operator[46] in phase-space $(\underline{r},\underline{p})$ is introduced and defined by

$$f_1^c(\underline{r},\underline{p},t) = \sum_{i=1}^{N} \delta(\underline{r} - \underline{r}_i(t))\,\delta(\underline{p} - \underline{p}_i(t)) \qquad (2.37)$$

where $\underline{p}_i(t)$ is the momentum of the i^{th} particle. Similarly a two-particle density operator is defined by

$$f_2^c(\underline{r},\underline{p},\underline{r}',\underline{p}',t) = \sum_{i=1}^{N}\sum_{j=1}^{N}{}' \delta(\underline{r} - \underline{r}_i(t))\,\delta(\underline{p} - \underline{p}_i(t))\,\delta(\underline{r}' - \underline{r}_j(t))\,\delta(\underline{p}' - \underline{p}_j(t)) \qquad (2.38)$$

where the bar over the summation means i is different than j. These two operators, when averaged over a proper distribution, have a physical meaning. (The average shall be denoted by brackets $\langle \cdot \rangle$). $\langle f_1^c(\underline{r},\underline{p},t)\rangle$ represents the probability of finding a particle at point $\underline{r}$ with momentum $\underline{p}$ at time t, and $\langle f_2^c(\underline{r},\underline{p},\underline{r}',\underline{p}',t)\rangle$ the probability of finding a particle at point $\underline{r}$ with momentum $\underline{p}$ at time t=0 and another particle at point r' with momentum $\underline{p}'$ at time t. It is important to note that when $f_1^c(\underline{r},\underline{p})$ is integrated over the momenta we simply get back $\rho_c(\underline{r},t)$. $f_1^c(\underline{r},\underline{p},t)$ has been utilized quite successfully for the study of plasmas.

To go to the quantum description, $f_1^c(\underline{r},\underline{p})$ has to be quantized. Several recipes have been given by many authors on how to quantize classical operators[47]. We shall follow Weyl's[48-49] procedure of quantization in which the Fourier transform of the operator in question is quantized. Starting from equation (2.37) and the Fourier transform of the delta function

$$\delta(\underline{r} - \underline{r}_i(t)) = \frac{1}{(2\pi)^3}\int d\underline{k}\, e^{i\underline{k}\cdot(\underline{r} - \underline{r}_i(t))} \qquad (2.39)$$

$$\delta(\underline{p} - \underline{p}_i(t)) = \frac{1}{(2\pi)^3}\int d\underline{\ell}\, e^{i\underline{\ell}\cdot(\underline{p} - \underline{p}_i(t))} \qquad (2.40)$$

we obtain

$$f_1^c(\underline{r},\underline{p},t)=\frac{1}{(2\pi)^6}\sum_{i=1}^{N}\int d\underline{k}\,d\underline{\ell}\;e^{i\underline{k}\cdot(\underline{r}-\underline{r}_i(t))+i\underline{\ell}\cdot(\underline{p}-\underline{p}_i(t))} \tag{2.41}$$

The rules for quantizing $\underline{r}$ and $\underline{p}$ are :

$$\underline{r}_i \longrightarrow \hat{\underline{r}}_i \tag{2.42}$$

$$\underline{p}_i \longrightarrow \hat{\underline{p}}_i=-i\hbar\frac{\partial}{\partial \underline{r}_i} \tag{2.43}$$

Then, we define

$$\hat{f}_1(\underline{r},\underline{p},t)=\frac{1}{(2\pi)^6}\sum_{i=1}^{N}\int d\underline{k}\,d\underline{\ell}\;e^{i\underline{k}\cdot(\underline{r}-\hat{\underline{r}}_i(t))+i\underline{\ell}\cdot(\underline{p}-\hat{\underline{p}}_i(t))} \tag{2.44}$$

The operators are denoted by a hat and $\underline{r}$ and $\underline{p}$ are just c-numbers representing the laboratory coordinates of the particles. All of $\hat{f}_1(\underline{r},p,t)$, $\hat{\underline{r}}_i(t)$ and $\underline{p}_i(t)$ obey the Heisenberg equation of motion. For two non-commuting operators $\hat{A}$ and $\hat{B}$, we have the following relation[50]:

$$e^{\hat{A}}e^{\hat{B}}=e^{\hat{A}+\hat{B}+\frac{1}{2}[\hat{A},\hat{B}]+\frac{1}{12}[\hat{A},[\hat{A},\hat{B}]]+\frac{1}{12}[[\hat{A},\hat{B}],\hat{B}]+\cdots} \tag{2.45}$$

where the brackets denote the commutator of the two operators. When

$$[\hat{A},\hat{B}]=\alpha \tag{2.46}$$

and α is a c-number, equation (2.45) reduces to

$$e^{\hat{A}}e^{\hat{B}}=e^{\hat{A}+\hat{B}}e^{\alpha/2} \tag{2.47}$$

The commutator of $\hat{\underline{r}}_i$ and $\hat{\underline{p}}_i$ is just

$$\left[\hat{\underline{r}}_i^{\alpha}, \hat{p}_i^{\beta}\right] = i\hbar\,\delta_{ij}\,\delta_{\alpha\beta} \tag{2.48}$$

where α and β mean the α^{th} and β^{th} components of $\underline{r}_i$ and $\underline{p}_j$ so that

$$e^{-i\underline{K}\cdot\hat{\underline{r}}_i - i\underline{\ell}\cdot\hat{\underline{p}}_i} = e^{-i\underline{K}\cdot\hat{\underline{r}}_i}\, e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}\, e^{i\frac{\hbar}{2}\underline{K}\cdot\underline{\ell}} \tag{2.49}$$

we finally obtain

$$\hat{f}_1(\underline{r},\underline{p},t) = \frac{1}{(2\pi)^6}\sum_{i=1}^{N}\int d\underline{K}\, d\underline{\ell}\; e^{i\underline{K}\cdot(\underline{r}-\hat{\underline{r}}_i(t))}\, e^{i\underline{\ell}\cdot\underline{p}}\, e^{i\frac{\hbar}{2}\underline{K}\cdot\underline{\ell}}\, e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i(t)} \tag{2.50}$$

In a very similar manner, starting from equation (2.38), we define the quantum analog of $f(\underline{r},\underline{p},\underline{r}',\underline{p}',t)$:

$$\hat{f}_2(\underline{r},\underline{p},\underline{r}',\underline{p}',t) = \frac{1}{(2\pi)^{12}}\sum_{i=1}^{N}\sum_{j=1}^{N}\int d\underline{K}\, d\underline{K}'\, d\underline{\ell}\, d\underline{\ell}'\; e^{i\underline{K}\cdot(\underline{r}-\hat{\underline{r}}_i(t))} \tag{2.51}$$

$$\otimes\; e^{i\underline{K}'\cdot(\underline{r}'-\hat{\underline{r}}_j(t))}\, e^{i\underline{\ell}\cdot\underline{p}+i\underline{\ell}'\cdot\underline{p}'}\, e^{i\frac{\hbar}{2}\underline{K}\cdot\underline{\ell}+i\frac{\hbar}{2}\underline{K}'\cdot\underline{\ell}'}$$

$$\otimes\; e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i - i\underline{\ell}'\cdot\hat{\underline{p}}_j}$$

The operators defined above are in configuration space. McCoy's[51] theorem has to be invoked to put these operators in the second quantization formalism. For any operator in the coordinate representation which can be expressed as a sum of single particle operators

(2.52)

changing to the second quantization representation corresponds to the transformation

$$\sum_{i=1}^{N} \hat{F}(\underline{r}_i) \longrightarrow \hat{F}^{SQ} = \int d\underline{x}\, \psi^{+}(\underline{x})\, \hat{F}(\underline{x})\, \psi(\underline{x}) \qquad (2.53)$$

where $\psi^{+}(\underline{r})$ = creation operator of a particle at point $\underline{r}$ (2.54)

$\psi(\underline{r})$ = destruction operator of a particle at point $\underline{r}$ (2.55)

Similarly for any operator in the coordinate representation which has the form

$$\hat{g}(\underline{r}_1, \ldots, \underline{r}_N) = \sum_{i=1}^{N} \sum_{j=1}^{N}{}' \hat{g}(\underline{r}_i, \underline{r}_j) \qquad (2.56)$$

changing to the second quantization formalism corresponds to the transformation

$$\sum_{i=1}^{N} \sum_{j=1}^{N} \hat{g}(\underline{r}_i, \underline{r}_j) \longrightarrow \hat{g}^{SQ} = \int d\underline{x}\, d\underline{x}'\, \psi^{+}(\underline{x})\psi^{+}(\underline{x}')\hat{g}(\underline{x}, \underline{x}')\psi(\underline{x}')\psi(\underline{x}) \qquad (2.57)$$

The application of equations (2.53) and (2.57) to equations (2.50) and (2.51) gives readily :

$$\hat{f}_1^{SQ}(\underline{r},\underline{p},t) = \frac{1}{(2\pi)^3}\int d\underline{\ell}\, e^{i\underline{p}\cdot\underline{\ell}}\, \psi^+\left(\underline{r}+\frac{\underline{\ell}}{2},t\right)\psi\left(\underline{r}-\frac{\underline{\ell}}{2},t\right) \tag{2.58}$$

and

$$\hat{f}_2^{SQ}(\underline{r},\underline{p},\underline{r}',\underline{p}',t) = \frac{1}{(2\pi)^6}\int d\underline{\ell}\, d\underline{\ell}'\, e^{i\underline{p}\cdot\underline{\ell}+i\underline{p}'\cdot\underline{\ell}'}(x) \tag{2.59}$$

$$(x)\,\psi^+\left(\underline{r}+\frac{\underline{\ell}}{2},t\right)\psi^+\left(\underline{r}'+\frac{\underline{\ell}'}{2},t\right)\psi\left(\underline{r}'-\frac{\underline{\ell}'}{2},t\right)\psi\left(\underline{r}-\frac{\underline{\ell}}{2},t\right)$$

where S.Q stands for second quantization.

By defining the following space Fourier transforms :

$$\hat{f}_1(\underline{k},\underline{p}) = \int d\underline{r}\; e^{-i\underline{k}\cdot\underline{r}}\; \hat{f}_1(\underline{r},\underline{p}) \tag{2.60}$$

$$\hat{f}_2(\underline{k},\underline{p},\underline{p}') = \int d\underline{r}\, d\underline{r}'\; e^{-i\underline{k}\cdot(\underline{r}-\underline{r}')}\; \hat{f}_2(\underline{r},\underline{p},\underline{r}',\underline{p}')$$

we obtain in $\underline{k}$ - space :

$$\hat{f}_1(\underline{k},\underline{p}) = \frac{1}{(2\pi)^3}\sum_{i=1}^{N}\int d\underline{\ell}\; e^{i\underline{\ell}\cdot\underline{p}+i\frac{\underline{k}}{2}\underline{k}\cdot\underline{\ell}}\, e^{-i\underline{k}\cdot\hat{\underline{r}}_i}\, e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i} \tag{2.61}$$

$$\hat{f}_2(\underline{k},\underline{p},\underline{p}') = \frac{1}{(2\pi)^6}\sum_{i=1}^{N}\sum_{j=1}^{N'}\int d\underline{\ell}\, d\underline{\ell}'\, e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}(x) \qquad (2.62)$$
$$(x)\, e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'} e^{-i\underline{k}\cdot\underline{r}_i+i\underline{k}\cdot\underline{r}_j} e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i-i\underline{\ell}\cdot\hat{\underline{p}}_j}$$

The properties of $\hat{f}_1(\underline{r},p)$ are studied in appendix A and it is shown that :

i) $\hat{f}_1(\underline{r},p)$ is hermitian

ii) $\hat{f}_1^{+}(\underline{k},p) = f_1(-\underline{k},p)$

iii) The equation of motion of $f(\underline{k},p)$ is :

$$\frac{d}{dt}\hat{f}_1(\underline{k},\underline{p}) = -i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\hat{f}_1(\underline{k},\underline{p}) \qquad (2.63)$$
$$+\frac{i}{\hbar}\frac{1}{(2\pi)^3}\sum_{i=1}^{N}\sum_{\beta=1}^{N_1}\int d\underline{\ell}\, e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}} e^{-i\underline{k}\cdot\underline{r}_i}(x)$$
$$(x)\left[V(\underline{r}_i-\underline{r}_\beta)-V(\underline{r}_i-\hbar\underline{\ell}-\underline{r}_\beta)\right] e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}$$

for a system with a Hamiltonian of the form :

$$H^S = \sum_{i=1}^{N}\frac{\hat{\underline{p}}_i^2}{2m} + U \qquad (2.64)$$

where

$\hat{\underline{p}}_i$ = the momentum operator of the i^{th} particle

$$U = \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N'} V(|\underline{r}_i-\underline{r}_j|) \qquad (2.65)$$

iv) The integral of $\hat{f}_1(\underline{k},p)$ over $\underline{p}$ is just $\hat{\rho}(\underline{k},t)$ which is what we are after.

It would be erroneous to interpret $\langle \hat{f}_1(\underline{r},p,t) \rangle$ the average of $\hat{f}_1(\underline{r},p\underline{t})$over a canonical distribution, as the probability of finding a particle at point $\underline{r}$ with momentum $\underline{p}$ at time t as in the classical case. This clearly violates the basic principle of quantum mechanics, the Heisenberg uncertainty principle which is represented in the definition of $\hat{f}_1(\underline{r},p,t)$ by the factor $e^{i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}$

Finally we shall define the following operator for the i^{th} particle :

$$\hat{f}_i(\underline{k},\underline{p}) = \frac{1}{(2\pi)^3}\int d\underline{\ell}\; e^{-i\underline{k}\cdot\hat{\underline{r}}_i} e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}} e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i} \qquad (2.66)$$

and the following time correlation functions ;

$$\mathcal{F}(\underline{k},\underline{p},\underline{p}',t) = \langle \hat{f}_1(\underline{k},\underline{p},t)\, \hat{f}_1^{\dagger}(\underline{k},\underline{p}') \rangle \qquad (2.67)$$

$$\mathcal{F}_s(\underline{k},\underline{p},\underline{p}',t) = \langle \hat{f}_i(\underline{k},\underline{p},t)\, \hat{f}_i^{\dagger}(\underline{k},\underline{p}') \rangle \qquad (2.68)$$

where the brackets denote the usual thermal average. Note that $\hat{f}_i(\underline{k},p)$ is just the i^{th} term of $\hat{f}_1(\underline{k},p)$ since the summation over all particles has been deleted. It is also easy to see that

$$S(\underline{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\int d\underline{p}\, d\underline{p}'\, \phi(\underline{k},\underline{p},\underline{p}',t) \qquad (2.69)$$

and

$$S_s(\underline{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\int d\underline{p}\, d\underline{p}'\, \phi_s(\underline{k},\underline{p},\underline{p}',t) \qquad (2.70)$$

Our purpose will be to derive equations for these two correlation functions and thus obtain the scattering functions for simple liquids.

2.2 Molecular liquids.

In this section, we shall develop a new approach to the problem of neutron scattering from molecular liquids [52] that will be more amenable to solution using the new powerful methods of quantum field theory. To arrive at this end, we shall consider an aggregate of interacting particles with internal degrees of freedom (and for simplicity we shall assume that the atoms of each molecule in the system are spinless). The interaction potential between the neutron and the molecules will be assumed of the form :

$$H^{ns} = \frac{2\pi\hbar^2 a}{m}\sum_{j=1}^{N} V\left(\underline{r} - \underline{X}_j, \underline{\Theta}_j\right) \qquad (2.71)$$

where

a = the scattering length of the atoms.

$\underline{X}_j$ = the position vector of the center of mass of the j^{th} molecule

$\underline{\theta}_j$ = the orientation in space of the j^{th} molecule.

The sum is over all molecules in the system.

The new approach consists in treating these molecules in the second quantization. In this formalism, the Hamiltonian of the system becomes

$$H = H^n + H^s + \frac{2\pi\hbar^2 a}{m}\int d\underline{X}\, d\underline{\theta}\, V(\underline{r}-\underline{X},\underline{\theta})\,\psi^+(\underline{X},\underline{\theta})\,\psi(\underline{X},\underline{\theta}) \tag{2.72}$$

where

H^N = the kinetic energy of the neutron

H^s = the Hamiltonian of the scattering system.

The differential scattering cross section reads in the Born approximation (c.f. equation (2.9))

$$\frac{d^2\sigma}{d\epsilon\, d\underline{\Omega}} = \sum_f \sum_i P_i \frac{a^2}{2\pi\hbar N}\frac{k_f}{k_i}\int_{-\infty}^{\infty} dt\, e^{-it\epsilon/\hbar}\int d\underline{r}\, e^{-i\underline{k}\cdot\underline{r}}\int d\underline{r}'\, e^{i\underline{k}\cdot\underline{r}'}\,(x) \tag{2.73}$$

$$(x)\int d\underline{X}\, d\underline{\theta}\, d\underline{X}'\, d\underline{\theta}'\; V(\underline{r}-\underline{X},\underline{\theta})\, V^+(\underline{r}'-\underline{X}',\underline{\theta}')\,(x)$$

$$(x)\,\langle i|\psi^+(\underline{X},\underline{\theta})\,\psi(\underline{X},\underline{\theta})|f\rangle\langle f|\psi^+(\underline{X}',\underline{\theta}')\,\psi(\underline{X}',\underline{\theta}')|i\rangle$$

Using the definition of the density operator

$$\rho(\underline{x},\underline{\theta}) = \psi^{+}(\underline{x},\underline{\theta})\psi(\underline{x},\underline{\theta}) \tag{2.74}$$

and its space Fourier transform

$$\rho(\underline{k},\underline{\theta}) = \int d\underline{x}\; e^{-i\underline{k}\cdot\underline{x}}\, \rho(\underline{x},\underline{\theta}) \tag{2.75}$$

as well as the closure relation (equation 2.11), the definition of the thermal average and the Fourier transform of the potential

$$V(\underline{k},\theta) = \int d\underline{R}\; e^{-i\underline{k}\cdot\underline{R}}\, V(\underline{R},\underline{\theta}), \tag{2.76}$$

it is straightforward to obtain the following expression :

$$\frac{d^2\sigma}{d\epsilon\, d\Omega} = \frac{a^2}{(2\pi\hbar)N}\,\frac{k_F}{k_i}\int_{-\infty}^{\infty} dt\, e^{-i\frac{\epsilon t}{\hbar}} \int d\underline{\theta}\, d\underline{\theta}'\, V(\underline{k},\underline{\theta})\, \dot{V}(\underline{k},\theta') \tag{2.77}$$

$$(x) \;<\; \rho(\underline{k},\theta,t)\;\rho^{+}(\underline{k},\theta',0)$$

where

$$\rho(\underline{k},\underline{\theta},t) = e^{i\frac{H^{s}t}{\hbar}}\,\rho(\underline{k},\underline{\theta})\,e^{-i\frac{H^{s}t}{\hbar}} \tag{2.78}$$

If the Hamiltonian of the system can be written as the sum of a translational Hamiltonian and a rotational Hamiltonian,

$$H^{s} = H^{trans} + H^{Rot} \tag{2.79}$$

and if $\{\phi_\alpha(\theta)\}$ * is the complete orthonormal set of eigenfunctions of the rotational Hamiltonian (53)

$$H^{Rot}\,\phi_\alpha(\underline{\theta}) = E_\alpha\,\phi_\alpha(\underline{\theta}), \tag{2.80}$$

then we can expand the operators $\psi(\underline{x},\theta)$ and $\psi^+(\underline{x},\underline{\theta})$ in term of these eigenfunctions (53)

$$\psi(\underline{x},\underline{\theta}) = \sum_\alpha \phi_\alpha(\theta)\,\chi_\alpha(\underline{x}) \tag{2.81}$$

$$\psi^+(\underline{x},\underline{\theta}) = \sum_\alpha \phi^*_\alpha(\underline{\theta})\,\chi^+_\alpha(\underline{x}) \tag{2.82}$$

The density operator becomes then :

$$\rho(\underline{x},\underline{\theta}) = \sum_\alpha \sum_{\alpha'} \phi^*_\alpha(\underline{\theta})\,\phi_{\alpha'}(\theta)\,\chi^+_\alpha(\underline{x})\,\chi_{\alpha'}(\underline{x}) \tag{2.83}$$

At this point, we introduce the Wigner density operator in the second quantization formalism (49)

$$F_{\alpha,\alpha'}(\underline{x},\underline{k},t) = \frac{1}{\pi^3}\int d\underline{\zeta}\; e^{2i\underline{k}\cdot\underline{\zeta}}\,\chi^+_\alpha(\underline{x}-\underline{\zeta},t)\,\chi_{\alpha'}(\underline{x}+\underline{\zeta},t). \tag{2.84}$$

Note immediately that

$$\rho(\underline{x},\underline{\theta},t) = \sum_\alpha \sum_{\alpha'} \phi^*_\alpha(\underline{\theta})\,\phi_{\alpha'}(\theta)\int d\underline{k}\; F_{\alpha,\alpha'}(\underline{x},\underline{k},t), \tag{2.85}$$

* $\{\phi_\alpha(\theta)\}$ are just the Wigner $D^\rho_{m,n}(\underline{\theta})$ functions and α stands for all three indices (l,m,n). (except for a normalization factor.)

and upon taking its Fourier transform :

$$\rho(\underline{k},\underline{\Theta},t)=\sum_{\alpha}\sum_{\alpha'}\phi^{*}_{\alpha}(\Theta)\phi_{\alpha'}(\Theta)\int d\underline{K}\,d\underline{x}\;e^{-i\underline{k}\cdot\underline{x}}\,F_{\alpha,\alpha'}(\underline{x},\underline{K},t). \quad (2.86)$$

After substituting this last expression in equation (2.77), we obtain

$$\frac{d^{2}\sigma}{d\epsilon\, d\underline{\Omega}}=\frac{a^{2}}{2\pi\hbar N}\frac{k_{f}}{k_{i}}\int_{-\infty}^{\infty}dt\;e^{-i\epsilon t/\hbar}\int d\underline{\Theta}\,d\underline{\Theta}'\,V(\underline{k},\underline{\Theta})\,V^{+}(\underline{k},\underline{\Theta}')(x) \quad (2.87)$$

$$(x)\sum_{\alpha}\sum_{\alpha'}\phi^{*}_{\alpha}(\underline{\Theta})\,\phi_{\alpha'}(\Theta)\sum_{\gamma}\sum_{\gamma'}\phi^{*}_{\gamma}(\Theta')\phi_{\gamma'}(\Theta')\;(x)$$

$$(x)\int d\underline{K}\,d\underline{K}'\,d\underline{x}\,d\underline{x}'\;e^{-i\underline{k}\cdot(\underline{x}-\underline{x}')}<F_{\alpha,\alpha'}(\underline{x},\underline{K})\;F^{+}_{\gamma,\gamma'}(\underline{x}',\underline{K}',t)>$$

With

$$F_{\alpha,\alpha'}(\underline{k},\underline{K})=\int d\underline{x}\;e^{-i\underline{k}\cdot\underline{x}}\;F_{\alpha,\alpha'}(\underline{x},\underline{K}) \quad (2.88)$$

the final expression for the cross section is just

$$\frac{d^{2}\sigma}{d\epsilon\, d\underline{\Omega}}=\frac{a^{2}}{2\pi\hbar N}\frac{k_{f}}{k_{i}}\int_{-\infty}^{\infty}dt\;e^{-i\epsilon t/\hbar}\int d\underline{\Theta}\,d\underline{\Theta}'\,V(\underline{k},\underline{\Theta})\,V^{+}(\underline{k},\underline{\Theta}')(x) \quad (2.89)$$

$$(x)\cdot\sum_{\alpha}\sum_{\alpha'}\phi^{*}_{\alpha}(\underline{\Theta})\,\phi_{\alpha'}(\Theta)\sum_{\gamma}\sum_{\gamma'}\phi_{\gamma}(\Theta')\,\phi_{\gamma'}(\Theta')$$

$$(x)\int d\underline{K}\,d\underline{K}'<F_{\alpha,\alpha'}(\underline{k},\underline{K})\;F^{+}_{\gamma,\gamma'}(\underline{k},\underline{K}',t)>$$

The thermal average can be handled now by the methods of field theory and the intermolecular interactions can be included in a straightforward manner in the equation of motion of $F_{\alpha,\alpha'}(\underline{k},\underline{K},t)$.

CHAPTER III

CORRELATION FUNCTIONS AND THE PROJECTION OPERATOR TECHNIQUES

Following the line first developed by Zwanzig, generalized by Mori, and subsequently extended to dynamical variables with continuous parameters in the classical case by Akcasu and Duderstadt, we shall use the projector technique to derive an exact quantum mechanical equation for time correlation functions, first for dynamical variables with continuous parameters and second for dynamical variables with discrete parameters. The final equations so obtained will still be difficult to solve exactly (as difficult as solving the Heisenberg equation of motion for the operator directly), and approximations will be required in order to make any progress. The projector technique is a tool to project the information contained in the time-dependent correlation functions onto static correlation functions, and hence enabling one to separate mathematically the different terms that correspond to the different phenomena (oscillatory motion, damping, etc...) that control the time evolution of the correlation function. All the information contained in the Heisenberg equation of motion is certainly not needed; at least for the experiments performed at this time (and certainly not for neutron scattering). But we hope to extract most of the information detected by experiments

via the projector technique from the Heisenberg equation of motion and leave out whatever is unreachable with laboratory tools.

The starting point, is the following equation for an arbitrary operator $\hat{A}$:

$$\frac{d\hat{A}(t)}{dt} = \frac{i}{\hbar}\left[H, \hat{A}(t)\right] \tag{3.1}$$

The operator $\hat{A}(t)$ is our dynamical variable that depends on the coordinates of all particles in the system and that may depend on other parameters, either discrete or continuous.

3.1 Quantum correlation functions of dynamical variables with continuous parameters.

In this case the operator $\hat{A}(t)$ depends on a continuous parameter $\underline{p}$ (as we shall see later, $\underline{p}$ will represent the laboratory momentum for the study of density correlation functions). Let us define the operator L by :

$$L \cdot = \frac{1}{\hbar}\left[H, \cdot\right] \tag{3.2}$$

The equation of motion for $\hat{A}(\underline{p},t)$ becomes :

$$\frac{d}{dt}\hat{A}(t) = i L \hat{A}(t) \tag{3.3}$$

A projection operator will now be defined by the relation*:

* We shall adopt the convention of dropping the time dependence from the operators whenever they are evaluated at t=0,e.g. $A(p) \equiv A(p,o)$

$$P_{\cdot} = \int dp_1 dp_2 \, \langle \cdot \hat{A}^{+}(p_1) \rangle_{+} \, \phi^{-1}(p_1, p_2) \, A(p_2) \qquad (3.4)$$

where $\langle A(p) B^{+}(q) \rangle_{+} = \frac{1}{2} \langle A(p) B^{+}(q) + B^{+}(q) A(p) \rangle$

$\hat{A}^{+}(p)$ = the hermitian adjoint of $\hat{A}(p)$

and the brackets mean the thermal average with respect to the canonical distribution $D = \frac{e^{-\beta H}}{Z}$.

For P to be a projector, it must satisfy the relation

$$P^2 = P \qquad (3.5)$$

This is insured by including the function $\phi^{-1}(p_1, p_2)$ in the definition of P. Equations (3.4) and (3.5), when combined, will determine for us $\phi^{-1}(p_1, p_2)$ through

$$\int dp_2 \, \phi(p, p_2) \, \phi^{-1}(p_2, p') = \delta(p - p') \qquad (3.6)$$

where

$$\phi(p_1, p_2) = \langle \hat{A}(p_1) \hat{A}^{+}(p_2) \rangle_{+} \qquad (3.7)$$

is the static correlation function.

The projector P is hermitian (as is shown in appendix B) with respect to the thermal average of any two operators $\hat{A}$ and $\hat{B}$, i.e.

$$\langle \{ P \hat{A}(p) \} \hat{B}^{+}(p') \rangle_{+} = \langle \hat{A}(p) \{ P \hat{B}(p') \}^{+} \rangle_{+} \qquad (3.8)$$

and also commutes with $\frac{d}{dt}$.

One more relation will be used in the subsequent derivation, and it is the hermitian property of L :

$$< \{ L \hat{A}(p) \} B^{+}(p') >_{+} = < \hat{A}(p) \{ L \hat{B}(p') \}^{+} >_{+} . \quad (3.9)$$

P operating on $\hat{A}(\underline{p},t)$ will give us the component of $\hat{A}(\underline{p},t)$ along $\hat{A}(p)$. Let us call it $\hat{A}_{\parallel}(\underline{p},t)$:

$$\hat{A}_{\parallel}(p,t) = P\hat{A}(p,t) = \int dp_1 dp_2 < \hat{A}(p,t) \hat{A}^{+}(p_1) > \Phi^{-1}(p_1,p_2) \hat{A}(p_2) \quad (3.10)$$

$$= \int dp_2 \, \Gamma(p, p_2, t) \, \hat{A}(p_2)$$

where

$$\Gamma(p,p_2,t) = \int dp_1 < \hat{A}(p,t) \hat{A}^{+}(p_1) >_{+} \Phi^{-1}(p_1,p_2) \quad (3.11)$$

(1-P) operating on $\hat{A}(\underline{p},t)$ will give us the component of $\hat{A}(\underline{p},t)$ perpendicular to $\hat{A}(p)$ which we shall call $\hat{A}_{\perp}(\underline{p},t)$:

$$\hat{A}_{\perp}(p,t) = (1-P) \hat{A}(p,t) \quad (3.12)$$

With the help of equations (3.10) and (3.12), equation (3.3) can be written as :

$$\frac{d}{dt} \hat{A}(p,t) = iL \hat{A}_{\parallel}(p,t) + iL \hat{A}_{\perp}(p,t) . \quad (3.13)$$

Operating on both sides of this equation by (1-P) we obtain :

$$\frac{d}{dt} \hat{A}_{\perp}(p,t) = (1-P) iL \hat{A}_{\parallel}(p,t) + (1-P) iL \hat{A}_{\perp}(p,t) \quad (3.14)$$

$$= (1-P) iL \hat{A}_{\perp}(p,t) + \int dp_2 \, \Gamma(p, p_2, t) \hat{F}(p_2)$$

where

$$\hat{F}(p_2) = (1-P)\,\dot{\hat{A}}(p_2) \tag{3.15}$$

$$\dot{\hat{A}}(p_2) = iL\,\hat{A}(p_2) \tag{3.16}$$

The solution of equation (3.14) is trivially obtained :

$$\hat{A}_\perp(p,t) = \hat{U}(t)\,\hat{A}_\perp(p) + \int_0^t du\,\hat{U}(t-u)\int dp_2\,\Gamma(p,p_2,u)\,\hat{F}(p_2) \tag{3.17}$$

Note that

$$\hat{A}_\perp(p) = (1-P)\,\hat{A}(p) = 0 \tag{3.18}$$

because

$$P\,\hat{A}(p) = \hat{A}(p) \tag{3.19}$$

so that

$$\hat{A}_\perp(p,t) = \int_0^t du \int dp_2\,\Gamma(p,p_2,u)\,\hat{F}(p_2,t-u) \tag{3.20}$$

where

$$\hat{F}(p,t) = e^{it(1-P)L}\,\hat{F}(p) \tag{3.21}$$

Let us consider the time evolution of $\Gamma(\underline{p},\underline{p}_2,t)$. Differentiating equation (3.10) with respect to time yields

$$\frac{d}{dt}\hat{A}_{11}(p,t) = \int dp_2\,\frac{d}{dt}\Gamma(p,p_2,t)\,\hat{A}(p_2) \tag{3.22}$$

Operating on equation (3.130 with P, we get :

$$\frac{d}{dt}\hat{A}_{\parallel}(p,t) = \int dp_2\, \Gamma(p,p_2,t) P i L \hat{A}(p_2) + P i L \hat{A}_{\perp}(p,t) \quad (3.23)$$

Let us combine now equations (3.22) and (3.23)

$$\int dp_2 \frac{d}{dt}\Gamma(p,p_2,t)\hat{A}(p_2) = \int dp_2\, \Gamma(p,p_2,t) P i L \hat{A}(p_2) \quad (3.24)$$

$$+ P i L \hat{A}_{\perp}(p,t)$$

After multiplying this equation by $\int dp_3 <\cdot \hat{A}^{+}(p_3)>_{+} \phi^{-1}(p_3,p_4)$ (that is multiply (3.24) by $\hat{A}^{+}(\underline{p}_3)\,\phi^{-1}(\underline{p}_3,\underline{p}_4)$ from the right thus obtaining one equation, then multiply it by the same operator from the left yielding an other equation. Add these two equations, divide by 2, take the thermal average and then integrate over $d\underline{p}_3$), we obtain for $\Gamma(\underline{p},\underline{p}_4,t)$:

$$\frac{d}{dt}\Gamma(p,p_4,t) = \int dp_2\, \Gamma(p,p_2,t)\, \Omega(p_2,p_4) \quad (3.25)$$

$$+ \int dp_3 <\left\{P i L \hat{A}_{\perp}(p,t)\right\}\hat{A}^{+}(p_3)>_{+} \phi^{-1}(p_3,p_4)$$

where

$$\Omega(p_2,p_4) = \int dp_3 < \dot{\hat{A}}(p_2)\hat{A}^{+}(p_3)> \phi^{-1}(p_3,p_4) \quad (3.26)$$

With the help of the hermitian properties of P and L,

$$\left\langle \left\{ P_{iL}\, \hat{A}_{\perp}(p,t) \right\} \hat{A}^{+}(p_3) \right\rangle_{+} = - \left\langle \hat{A}_{\perp}(p,t)\, \dot{\hat{A}}^{+}(p_3) \right\rangle_{+}, \tag{3.27}$$

and equation (3.20), the time evolution of $\Gamma(\underline{p},\underline{p}_4,t)$ is just.

$$\frac{d}{dt}\Gamma(p,p_4,t) = \int dp_2\, \Gamma(p,p_2,t)\, \Omega(p_2,p_4) - \int_0^t dt' \int dp_2\, \Gamma(p,p_2,t')\, \mathcal{G}(p_2,p_4,t-t') \tag{3.28}$$

where

$$\mathcal{G}(p_2,p_4,t) = \int dp_3 \left\langle \hat{F}(p_2,t)\, \dot{\hat{A}}^{+}(p_3) \right\rangle_{+} \Phi^{-1}(p_3,p_4) \tag{3.29}$$

Upon taking the Laplace transform of the above equation and noting that

$$\Gamma(p,p_4,0) = \delta(p-p_4) \tag{3.30}$$

we obtain

$$s\,\tilde{\Gamma}(p,p_4,s) - \int dp_2\, \tilde{\Gamma}(p,p_2,s)\, \Omega(p_2,p_4) + \int dp_2\, \tilde{\Gamma}(p,p_2,s)\, \mathcal{G}(p_2,p_4,s) = \delta(p-p_4) \tag{3.31}$$

with $$\tilde{\Gamma}(p,p_4,s) = \int_0^{\infty} e^{-st}\, \Gamma(p,p_4,t)\, dt \tag{3.32}$$

Let us define the inverse function $\tilde{\Pi}^{-1}(\underline{p},\underline{p}_2,s)$ through the relation

$$\int dp\, \tilde{\Gamma}^{-1}(p_1,p,s)\, \tilde{\Gamma}(p,p_2,s) = \delta(p_1-p_2) \tag{3.33}$$

The equation satisfied by this inverse function is obtained by multiplying equation (3.31) by $\tilde{\Gamma}^{-1}(\underline{p}_1,\underline{p},s)$ and integrating over $\underline{p}$:

$$\tilde{\Gamma}^{-1}(p_1,p_4,s) = s\,\delta(p_1-p_4) - \Omega(p_1,p_4) + \Sigma(p_1,p_4,s) \qquad (3.34)$$

Coming back now to the Laplace transform of the equation of motion of $\hat{A}(\underline{p},t)$, from equation (3.13), (3.10) and (3.20) . we have :

$$\tilde{\hat{A}}(p,s) = \int dp_2\, \tilde{\Gamma}(p,p_2,s)\,\hat{A}(p_2) + \int dp_2\, \tilde{\Gamma}(p,p_2,s)\hat{F}(p_2,s) + \hat{A}(p) \qquad (3.35)$$

let us multiply it by $\tilde{\Gamma}^{-1}(\underline{p}_1,\underline{p},s)$ and integrate over $d\underline{p}$:

$$s\,\tilde{\hat{A}}(p_1,s) - \int dp\, \Omega(p_1,p)\tilde{\hat{A}}(p_1,s) + \int dp\, \tilde{\Sigma}(p_1,p,s)\tilde{\hat{A}}(p,s) = \hat{A}(p_1) + \tilde{\hat{F}}(p_1,s) \qquad (3.36)$$

Taking the inverse Laplace transform and changing $\underline{p} \leftrightarrow \underline{p}_1$ we can cast the Heisenberg equation of motion for the operator $\hat{A}$ in the following form :

$$\frac{d}{dt}\hat{A}(p,t) - \int dp_2\, \Omega(p,p_2)\,\hat{A}(p_2,t) + \int_0^t dt' \int dp_2\, \Sigma(p,p_2,t-t')\,\hat{A}(p_2,t') = \hat{F}(p,t) . \qquad (3.37)$$

The equation of motion for the correlation function is obtained very simply from equation (3.37). Multiply the above equation from the right by $\hat{A}^{+}(p')$:

$$\frac{d}{dt}\hat{A}(p,t)\hat{A}^{+}(p') - \int dp_2\, \Omega(p,p_2)\, \hat{A}(p_2,t)\hat{A}^{+}(p') + \int_0^t dt' \int dp_2\, \Psi(p,p_2,t-t')\, \hat{A}(p_2,t)\hat{A}^{+}(p') = \hat{F}(p,t)\hat{A}^{+}(p') \tag{3.38}$$

then from the left :

$$\frac{d}{dt}\hat{A}^{+}(p')\hat{A}(p,t) - \int dp_2\, \Omega(p,p_2)\, \hat{A}^{+}(p')\hat{A}(p_2,t) + \int_0^t dt' \int dp_2\, \Psi(p,p_2,t-t')\, \hat{A}^{+}(p')\hat{A}(p_2,t') = \hat{A}^{+}(p')\hat{F}(p,t) \tag{3.39}$$

Add these two equations, divide by 2, take the thermal average, and remember the definition of the correlation function $\Phi(p,p',t)$:

$$\Phi(p,p',t) = \frac{1}{2}\langle \hat{A}(p,t)\hat{A}^{+}(p') + \hat{A}^{+}(p')\hat{A}(p,t)\rangle \tag{3.40}$$

and also

$$\langle \hat{F}(p_2,t)\hat{A}^{+}(p')\rangle_{+} = \left\langle \left\{ e^{it(1-P)L}(1-P)iL\hat{A}(p) \right\} \hat{A}^{+}(p') \right\rangle_{+} \tag{3.41}$$

$$= \left\langle \left\{ iL\, e^{it(1-P)L}\hat{A}(p) \right\} \left\{ (1-P)\hat{A}(p') \right\}^{\dagger} \right\rangle_{+}$$

$$= 0$$

where use has been made of equation (3.18).

The final equation we are looking for is then :

$$\frac{d}{dt}\Phi(p,p',t) - \int dp_2\, \Omega(p,p_2)\,\Phi(p_2,p',t) + \int_0^t dt' \int dp_2\, \Sigma(p,p_2,t')\,\Phi(p_2,p',t-t') = 0 \tag{3.42}$$

where

$$\Phi(p,p',t) = \langle \hat{A}(p,t)\,\hat{A}^{+}(p') \rangle_{+} \tag{3.43}$$

$$\Omega(p,p_2) = \int dp_3 \langle \dot{\hat{A}}(p)\,\hat{A}^{+}(p_3) \rangle_{+}\,\Phi^{-1}(p_3,p_2) \tag{3.44}$$

$$\Sigma(p,p_3,\tau) = \int dp_3 \langle \hat{F}(p,\tau)\,\dot{\hat{A}}(p_3) \rangle_{+}\,\Phi^{-1}(p_3,p_2) \tag{3.45}$$

$$\hat{F}(p,\tau) = e^{i\tau(1-P)L}(1-P)\,\dot{\hat{A}}(p) \tag{3.46}$$

The term $\int d\underline{p}_2 \Omega(\underline{p},\underline{p}_2)\,\Phi(\underline{p}_2,\underline{p}',t)$ is called the "frequency" term and $\int_0^t dt' \int dp_2\, \Sigma(\underline{p},\underline{p}_2,t')\,\Phi(\underline{p},\underline{p}',t-t)$ is called the "memory" or "damping" term for reasons that will be apparent later.

So far the equation for the time correlation function $\Phi(\underline{p},p',t)$ is exact. Its quantum nature is still preserved and buried in the evaluation of the thermal averages. To proceed further, one should find a way of approximating this function without losing completely its quantum nature, be

able to calculate the static correlation exactly or approximatly and perform all the intermediate integrations involved successfully.

3.2 Quantum time correlation functions of dynamical variables with discrete parameters.

Let us now turn our attention to operators that depend on a discrete parameter i and which can be written as a column with N components :

$$\underline{\hat{A}}(t) = \begin{pmatrix} \hat{A}_1(t) \\ \hat{A}_2(t) \\ \vdots \\ \hat{A}_N(t) \end{pmatrix} \tag{3.47}$$

Each of the components of $\underline{A}(t)$ is a function of the coordinates of all the particles in the system. The method for deriving the equation of motion of time correlation functions involving two operators with discrete parameters is identical with the method of the previous section, where integrations are simply replaced by summations.
Our projector will then be defined to be :

$$P_\cdot = \langle \cdot \underline{\hat{A}}^+ \rangle_+ \cdot \underline{\underline{\Phi}}^{-1} \cdot \underline{A} \tag{3.48}$$

where $\underline{\underline{\Phi}}^{-1}$ is a matrix defined through the relation

$$\underline{\underline{\Phi}} \cdot \underline{\underline{\Phi}}^{-1} = \underline{\underline{I}} \tag{3.49}$$

with

$$\langle \hat{A}_i \hat{B}_j^+ \rangle = \frac{1}{2} \langle \hat{A}_i \hat{B}_j^+ + \hat{B}_j^+ \hat{A}_i \rangle \tag{3.50}$$

$\underline{I}$ = the identity matrix (3.51)

. = matrix multiplication (3.52)

$\underline{\underline{\Phi}} = \langle \hat{\underline{A}}\, \hat{\underline{A}}^{+} \rangle_{+}$ (3.53)

$\hat{\underline{A}} = \hat{\underline{A}}\ (t=0)$ (3.54)

$\hat{\underline{A}}^{+}$ = the adjoint vector operator to $\hat{\underline{A}}$

Upon following all the steps of the calculations of the previous section, we obtain the following equation for the matrix :

$$\underline{\underline{\Phi}}(t) = \langle \hat{\underline{A}}(t)\, \hat{\underline{A}}^{+} \rangle_{+} \ , \tag{3.55}$$

$$\frac{d}{dt}\underline{\underline{\Phi}}(t) - \underline{\underline{\Omega}} \cdot \underline{\underline{\Phi}}(t) + \int_{0}^{t} dt'\, \underline{\underline{\Psi}}(t-t') \cdot \underline{\underline{\Phi}}(t') = 0 \tag{3.56}$$

where

$$\underline{\underline{\Omega}} = \underline{\underline{\Lambda}} \cdot \underline{\underline{\Phi}}^{-1} \tag{3.57}$$

$$\underline{\underline{\Lambda}} = \langle \dot{\hat{\underline{A}}}\, \hat{\underline{A}}^{+} \rangle_{+} \tag{3.58}$$

$$\underline{\underline{\Psi}}(t) = \underline{\underline{\zeta}}(t) \cdot \underline{\underline{\Phi}}^{-1} \tag{3.59}$$

$$\underline{\underline{\zeta}}(t) = \left\langle \left\{ e^{it(1-P)L}\, (1-P)\, \dot{\hat{\underline{A}}} \right\} \dot{\hat{\underline{A}}}^{+} \right\rangle \tag{3.60}$$

Again, this equation is also exact and can be solved

only within certain approximations. If we take the hermitian adjoint of equation (3.56) and then let $t \rightarrow -t$, after a trivial manipulation, we would get

$$\underline{\underline{\Omega}}' = \underline{\underline{\Phi}}^{-1} \cdot \underline{\underline{\Lambda}} \tag{3.61}$$

$$\underline{\underline{\Psi}}'(t) = \underline{\underline{\Phi}}^{-1} \cdot \underline{\underline{\Lambda}} \tag{3.62}$$

and all other definitions are still the same. This is one of the symmetries of equation (3.56). Therefore we may choose to do the computations with equations (3.57) - (3.60) or with equations (3.61) - (3.62).

Depending on wether we want to work with the hydrodynamic approach or the kinetic approach for the calculation of the time correlation function we desire, we can use either equation (3.42) or equation (3.56). At any rate the projector technique gives us a new way of solving the problem. However, because of the final form of the equations, divided into a "frequency term" and a "memory" term, it is expected that this approach would be most suitable for the study of dissipative systems only.

CHAPTER IV

EVALUATION OF THERMAL AVERAGES FOR NON-DEGENERATE SYSTEMS.

The success of the application of the theory developed in the previous chapter for the studies of correlation functions of interacting systems lies partly in the evaluation of the static thermal averages defined in equation (3.43) through (3.46). We shall attempt to present in this chapter a systematic method for determining the thermal averages of operators $\hat{O}(\hat{\underline{x}}_1,\ldots,\hat{x}_N,\hat{\underline{p}}_1,\ldots,\hat{\underline{p}}_N)$ that are functions of the momentum and position operators of all the particles in the system.

$\hat{\underline{x}}_i$= the position operator of the i^{th} particle

$\underline{p}_i=-i\hbar\nabla_{\underline{x}_i}$= the momentum operator of the i^{th} particle.

As we shall see, this method will be valid only for non-degenerate systems at normal and high temperatures. It excludes immediately any study of liquid helium or even helium gas at low temperatures.

The thermal average of an operator $O(\hat{\underline{x}}_i,\hat{\underline{p}}_j)$ is defined to be :

$$\langle \hat{O}(\hat{\underline{x}}_1,\ldots,\hat{x}_N,\hat{p}_1,\ldots,\hat{p}_N)\rangle = \frac{Tr\, e^{-\beta H}\, \hat{O}(\hat{\underline{x}}_1,\ldots,\hat{x}_N;\hat{p}_1,\ldots,\hat{p}_N)}{Tr\, e^{-\beta H}} \qquad (4.1)$$

$$= \frac{\sum_{\underline{k}} \langle \underline{k} | e^{-\beta H} \hat{O}(\hat{\underline{x}}_1, \ldots \hat{\underline{x}}_N; \hat{\underline{p}}_1, \ldots \hat{\underline{p}}_N) | \underline{k} \rangle}{\sum_{\underline{k}} \langle \underline{k} | e^{-\beta H} | \underline{k} \rangle}$$

where H is the Hamiltonian of the system under consideration, namely

$$H = \sum_i \frac{\hat{p}_i^2}{2m} + U \tag{4.2}$$

with

$$U = \frac{1}{2} \sum_i \sum_j{}' V(|\underline{r}_i - \underline{r}_j|) \tag{4.3}$$

and $\{|\underline{k}\rangle\}$ any complete set of properly symmetrized orthonormal functions since the trace can be evaluated in any such set. The symmetrization of these functions is such as to take properly into account the statistics of the system.[54] For a Bose-Einstein system, such functions must be symmetric, and for Fermi-Dirac system, they must be antisymmetric, while for a Boltzmann system no symmetry is required. Let us choose our eigenvectors $\{|\underline{k}\rangle\}$ to be the set of plane waves representing free particles. Then for the three different statistics :

$$|\underline{k}\rangle = \sum_P (+1)^P \prod_{j=1}^N e^{i \underline{k}_j \cdot \underline{x}_j} \quad \text{for Bose-Einstein statistcs} \tag{4.4}$$

$$|k\rangle = \sum_P (-1)^P \prod_{j=1}^N e^{i \underline{k}_j \cdot \underline{x}_j} \quad \text{for Fermi-Dirac statistics} \tag{4.5}$$

$$|k\rangle = \prod_{j=1}^N e^{i \underline{k}_j \cdot \underline{x}_j} \quad \text{for Boltzmann ststistics} \tag{4.6}$$

where

$\sum_P$ means summation over all permutations of the $\underline{K}$ among the particles

$\underline{K}_j$ = the wave vector of the j^{th} particle.

The Bose-Einstein and the Fermi-Dirac statistics both take into account the quantum degeneracies of the system, and in the limit of no degeneracy, both of these statistics reduce to the Boltzmann statistics. Because of the non-degenerate property of the liquids we shall be studying, we shall attempt to calculate thermal averages only for non-degenerate systems.

In the large volume limit, the sum over $\underline{K}$ can be replaced by an integral and equation (4.1) becomes :

$$\langle \hat{O}(\hat{\underline{x}}_1,\dots,\hat{\underline{x}}_N,\hat{\underline{p}}_1,\dots\hat{\underline{p}}_N)\rangle = \frac{\int d[\underline{x}_N]\int d[\underline{k}_N]\left(\prod_{j=1}^{N} e^{-i\underline{k}_j\cdot\underline{x}_j}\right)e^{-\beta H}\,(x)}{\int d[\underline{x}_N]\int d[\underline{k}_N]\left(\prod_{j=1}^{N} e^{-i\underline{k}_j\cdot\underline{x}_j}\right)e^{-\beta H}\left(\prod_{j=1}^{N} e^{i\underline{k}_j\cdot\underline{x}_j}\right)} \tag{4.7}$$

$$(x)\quad \hat{O}(\hat{\underline{x}}_1,\dots,\hat{\underline{x}}_N,\hat{\underline{p}}_1,\dots,\hat{\underline{p}}_N)\left(\prod_{j=1}^{N} e^{i\underline{k}_j\cdot\underline{x}_j}\right)$$

with

$$d[\underline{x}_N] = d\underline{x}_1\, d\underline{x}_2 \dots d\underline{x}_N$$

$$d[\underline{p}_N] = d\underline{p}_1\, d\underline{p}_2 \dots d\underline{p}_N$$

Multiplying numerator and denominator by $\hbar$ and letting

$$\underline{p}_i = \hbar\underline{k}_i \tag{4.8}$$

we obtain :

$$\langle \hat{O}(\hat{x}_1,\dots,\hat{x}_N,\hat{p}_1,\dots,\hat{p}_N)\rangle = \int d[x_N]\,d[p_N]\left(\prod_{j=1}^{N} e^{-i\frac{p_j\cdot x_j}{\hbar}}\right)\frac{e^{-\beta H}}{Z_q(\beta)}\,\hat{O}(x_1,\dots,x_N,\hat{p}_1,\dots,\hat{p}_N) \quad (4.9)$$

$$(x)\left(\prod_{j=1}^{N} e^{i\frac{p_j\cdot x_j}{\hbar}}\right)$$

where

$$Z_q(\beta) = \int d[x_N]\,d[p_N]\left(\prod_{j=1}^{N} e^{-i\frac{p_j\cdot x_j}{\hbar}}\right)e^{-\beta H}\left(\prod_{j=1}^{N} e^{i\frac{p_j\cdot x_j}{\hbar}}\right) \quad (4.10)$$

Both equations (4.9) and (4.10) contain the operator

$$\hat{I}(\beta) = \left(\prod_{j=1}^{N} e^{-i\frac{p_j\cdot x_j}{\hbar}}\right) e^{-\beta H}\left(\prod_{j=1}^{N} e^{i\frac{p_j\cdot x_j}{\hbar}}\right) \quad (4.11)$$

which will be studied in the next section.

4.1 THE OPERATOR $\hat{I} = \left(\prod_{j=1}^{N} e^{-i\frac{p_j\cdot x_j}{\hbar}}\right)e^{-\beta H}\left(\prod_{j=1}^{N} e^{i\frac{p_j\cdot x_j}{\hbar}}\right)$

The method to study this oprator amounts essentially to deriving a Bloch[55] equation for $\hat{I}$ and then trying to solve it by approximations, namely in an expansion in $\hbar$.[56-57]

Differentiating equation (4.11) with respect to β, we get

$$\frac{d\hat{I}(\beta)}{d\beta} = -\left(\prod_{j=1}^{N} e^{-\frac{p_j\cdot x_j}{\hbar}}\right)H\left(\prod_{j=1}^{N} e^{i\frac{p_j\cdot x_j}{\hbar}}\right)\hat{I}(\beta), \quad (4.12)$$

with the initial condition

$$\hat{I}\,(\beta=0) = 1\ . \quad (4.13)$$

With the help of the Hamiltonian given by (4.2)

$$\left(\prod_{j=1}^{N} e^{-i\frac{p_j\cdot x_j}{\hbar}}\right) H \left(\prod_{j=1}^{N} e^{i\frac{p_j\cdot x_j}{\hbar}}\right) = \sum_{i=1}^{N}\frac{p_i^2}{2m} + U + \sum_{i=1}^{N}\left(\frac{\hat{p}_i^2}{2m} + \frac{p_i\cdot\hat{p}_i}{m}\right) \tag{4.14}$$

The $\hat{p}_i$'s are operators ($\hat{p}_i = -ih\nabla_{x_i}$) while the p_i's ($p_i = h K_i$) are c-numbers. With the classical energy defined by

$$E(x_i, p_i) = \sum_{i=1}^{N}\frac{p_i^2}{2m} + U$$

$$\frac{d\hat{I}(\beta)}{d\beta} = -E(x_i, p_i)\hat{I}(\beta) + \sum_{i=1}^{N}\frac{\hbar^2}{2m}\left(\nabla_{x_i}^2 + 2i\frac{p_i}{\hbar}\cdot\nabla_{x_i}\right)\hat{I}(\beta) \tag{4.15}$$

Let

$$\hat{I}(\beta) = e^{-\beta E(x_i, p_i)}\hat{\psi}(\beta) \tag{4.16}$$

Then

$$\frac{\partial\hat{\psi}(\beta)}{\partial\beta} = e^{\beta U}\sum_i\frac{\hbar^2}{2m}\left(\nabla_{x_i}^2 + 2i\frac{p_i}{\hbar}\cdot\nabla_{x_i}\right)e^{-\beta U}\hat{\psi}(\beta) \tag{4.17}$$

The operator $\hat{\psi}$ can now be expanded in a power series in $\hbar$:

$$\hat{\psi}(\beta) = 1 + \hbar\hat{\psi}_1(\beta) + \hbar^2\hat{\psi}_2(\beta) + \cdots \tag{4.18}$$

The terms in this series satisfy the initial conditions :

$$\hat{\psi}_1(\beta=0) = \hat{\psi}_2(\beta=0) = \cdots = \hat{\psi}_N(\beta=0) = 0 \tag{4.19}$$

The first term in equation (4.18) gives us just the classical limit of $\hat{I}$, namely

$$\hat{I}_c = e^{-\beta E(x_i, p_i)} \tag{4.20}$$

Substituting the expansion (4.18) in equation (4.17) and equating terms of the same order in $\hbar$ on both sides of this equation, we obtain :

$$\frac{\partial \hat{\Psi}_1(\beta)}{\partial \beta} = e^{\beta U}\left\{\sum_{i=1}^{N} \frac{\underline{p}_i}{m}\cdot\underline{\nabla}_{\underline{x}_i}\right\}e^{-\beta U} \tag{4.21}$$

$$\frac{\partial \hat{\Psi}_2(\beta)}{\partial \beta} = e^{\beta U}\left\{\sum_{i=1}^{N} \frac{1}{2m}\underline{\nabla}^2_{\underline{x}_i}\right\}e^{-\beta U} \tag{4.22}$$

$$+ e^{\beta U}\left\{i\sum_{i=1}^{N} \frac{\underline{p}_i}{m}\cdot\underline{\nabla}_{\underline{x}_i}\right\}e^{-\beta U}\hat{\Psi}_1(\beta)$$

.
.
.
etc...

Remember that the operator $\hat{I}$ will be operating on functions of the positions of all N-particles in the system $F(\underline{x}_1, \underline{x}_2, \ldots, \underline{x}_N)$. Making use of the properties of differential operators contained in (4.21), we obtain :

$$\frac{\partial \hat{\Psi}_1(\beta)}{\partial \beta} = -i\beta\sum_{i=1}^{N} \frac{\underline{p}_i}{m}\cdot\left(\underline{\nabla}_{\underline{x}_i}U\right) + i\sum_{i=1}^{N} \frac{\underline{p}_i}{m}\cdot\underline{\nabla}_{\underline{x}_i} \tag{4.23}$$

wich can be integrated over β to yield :

$$\hat{\Psi}_1(\beta) = -i\frac{\beta^2}{2}\sum_{i=1}^{N} \frac{\underline{p}_i}{m}\cdot\left(\underline{\nabla}_{\underline{x}_i}U\right) + i\beta\sum_{i=1}^{N} \frac{\underline{p}_i}{m}\cdot\underline{\nabla}_{\underline{x}_i} \tag{4.24}$$

The equation for $\hat{\Psi}_2(\beta)$ can also be rewritten as :

$$\frac{\partial \hat{\Psi}_2}{\partial \beta} = \sum_{i=1}^{N} \frac{1}{2m} \Big\{ \beta^2 \left(\nabla_{\underline{x}_i} U\right)^2 - \beta \left(\nabla^2_{\underline{x}_i} U\right) - 2\beta \left(\nabla_{\underline{x}_i} U\right) \cdot \nabla_{\underline{x}_i} + \nabla^2_{\underline{x}_i} \Big\}$$

$$- \frac{\beta^3}{2} \left(\sum_{i=1}^{N} \frac{\underline{p}_i}{m} \cdot \left(\nabla_{\underline{x}_i} U\right) \right)^2 + \frac{\beta^2}{2} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\underline{p}_i \underline{p}_j}{m^2} : \left(\nabla_{\underline{x}_i} \nabla_{\underline{x}_j} U\right)$$

$$+ \frac{3}{2} \beta^2 \left(\sum_{i=1}^{N} \frac{\underline{p}_i}{m} \cdot \left(\nabla_{\underline{x}_i} U\right) \right) \sum_{j=1}^{N} \frac{\underline{p}_j}{m} \cdot \nabla_{\underline{x}_j}$$

$$- \beta \sum_{i=1}^{N} \left(\frac{\underline{p}_i}{m} \cdot \nabla_{\underline{x}_i} \right) \sum_{j=1}^{N} \left(\frac{\underline{p}_j}{m} \cdot \nabla_{\underline{x}_j} \right) \tag{4.25}$$

where the double dots : mean a tensor product, i.e. :

$$\underline{p}_i \underline{p}_j : \left(\nabla_{\underline{x}_i} \nabla_{\underline{x}_j} U\right) = \left(\left(\underline{p}_i \cdot \nabla_{\underline{x}_i}\right) \left(\underline{p}_j \cdot \nabla_{\underline{x}_j} U\right) \right) \tag{4.26}$$

The integration over β gives :

$$\hat{\Psi}_2(\beta) = - \frac{\beta^4}{8} \left(\sum_{i=1}^{N} \frac{\underline{p}_i}{m} \cdot \left(\nabla_{\underline{x}_i} U\right) \right)^2 + \frac{\beta^3}{6} \sum_{i=1}^{N} \sum_{j=1}^{N} \frac{\underline{p}_i \underline{p}_j}{m^2} : \left(\nabla_{\underline{x}_i} \nabla_{\underline{x}_j} U\right) \tag{4.27}$$

$$+\frac{\beta^3}{6}\sum_{i=1}^{N}\frac{1}{m}\left(\nabla_{\underline{x}_i}U\right)^2 \;-\; \frac{\beta^2}{4}\sum_{i=1}^{N}\frac{1}{m}\left(\nabla^2_{\underline{x}_i}U\right)$$

$$+\frac{\beta^3}{2}\left(\sum_{j=1}^{N}\frac{\underline{p}_j}{m}\cdot\left(\nabla_{\underline{x}_j}U\right)\right)\sum_{i=1}^{N}\frac{\underline{p}_i}{m}\cdot\nabla_{\underline{x}_i}$$

$$-\frac{\beta^2}{2}\left(\sum_{i=1}^{N}\frac{\underline{p}_i}{m}\cdot\nabla_{\underline{x}_i}\right)\left(\sum_{j=1}^{N}\frac{\underline{p}_j}{m}\cdot\nabla_{\underline{x}_j}\right)$$

$$-\frac{\beta^2}{2}\sum_{i=1}^{N}\frac{1}{m}\left(\nabla_{\underline{x}_i}U\right)\cdot\nabla_{\underline{x}_i}$$

$$+\frac{\beta}{2}\sum_{i=1}^{N}\frac{1}{m}\nabla^2_{\underline{x}_i}$$

Equations for $\hat{\Psi}_3(\beta)$, $\hat{\Psi}_4(\beta)$,... can be obtained in a very similar manner.

A first and straightforward application of the above equations is the calculation of the partition function $Z_q(\beta)$ defined by equation (4.10).

4.1 EXPANSION OF THE PARTITION FUNCTION $Z_q(\beta)$.

To obtain $Z_q(\beta)$, let the operator $\hat{I}(\beta)$ operate on unity and then integrate over the positions and momenta of all the particles in the system $d[\underline{x}_N]\,d[\underline{p}_N]$:

$$Z_q(\beta)=\int d[\underline{x}_N]\,d[\underline{p}_N]\;e^{-\beta E(x_i,p_i)}\left\{1+\hbar\hat{\Psi}_1\cdot 1+\hbar^2\hat{\Psi}_2\cdot 1+\cdots\right\} \qquad (4.28)$$

$$= Z_0(\beta) \;+\hbar Z_1(\beta)\; +\hbar^2 Z_2(\beta)+\cdots$$

Note that $Z_0(\beta)$ is just the classical partition function $Z_c(\beta)$

$$Z_0(\beta) = Z_c(\beta) = \int d[\underline{x}_N]\, d[\underline{p}_N]\, e^{-\beta E(\underline{x}_i, \underline{p}_i)} \tag{4.29}$$

so that

$$Z_q(\beta) = Z_c(\beta)\left\{1 + \hbar \langle \hat{\psi}_1 \cdot 1 \rangle_c + \hbar^2 \langle \hat{\psi}_2 \cdot 1 \rangle_c + \cdots \right\} \tag{4.30}$$

where

$$\langle \hat{\psi}_n \cdot 1 \rangle_c = \int d[\underline{x}_N]\, d[\underline{p}_N]\, \frac{e^{-\beta E(\underline{x}_i, \underline{p}_i)}}{Z_c(\beta)}\, \hat{\psi}_n \cdot 1 \tag{4.31}$$

It follows immediately from equation (4.24) and (4.27) that

$$Z_1(\beta) = Z_c \langle \hat{\psi}_1 \cdot 1 \rangle_c = 0 \tag{4.32}$$

because $\hat{\psi}_1$ is an odd function of $\underline{p}_i$; while

$$Z_2(\beta) = Z_c(\beta) \langle \hat{\psi}_2 \cdot 1 \rangle_c = -\frac{\beta^3}{24} \sum_{i=1}^{N} \frac{1}{m} \langle \left(\nabla_{\underline{x}_i} U\right)^2 \rangle_c Z_c \tag{4.33}$$

Having at hand an expansion in powers of $\hbar$ for the partition function $Z_q(\beta)$, we can now turn to the expansion of the normalized operator $\hat{I}\hat{I}(\beta) = \dfrac{\hat{I}(\beta)}{Z_q(\beta)}$

4.3 EXPANSION OF $\hat{I}\hat{I}(\beta) = \dfrac{\hat{I}(\beta)}{Z_q(\beta)}$

Since $$\hat{I}\hat{I}(\beta) = \frac{\hat{I}(\beta)}{Z_q(\beta)} = \left(\prod_{j=1}^{N} e^{-i \underline{k}_j \cdot \underline{x}_j}\right) \frac{e^{-\beta H}}{Z_q(\beta)} \left(\prod_{j=1}^{N} e^{i \underline{k}_j \cdot \underline{x}_j}\right) \tag{4.34}$$

we have

$$Z_q(\beta)\,\hat{\Pi}(\beta) = \hat{I}(\beta) \tag{4.35}$$

An expansion in $\hbar$ of both sides yields

$$\left(Z_0(\beta) + \hbar Z_1(\beta) + \hbar^2 Z_2(\beta) + \cdots\right)\left(\hat{\Pi}_0(\beta) + \hbar\hat{\Pi}_1(\beta) + \cdots\right) = \hat{I}_0(\beta) + \hbar\hat{I}_1(\beta) + \cdots \tag{4.36}$$

Equating terms with the same power in $\hbar$, the series expansion of $\hat{\Pi}(\beta)$ is just :

$$\hat{\Pi}_0(\beta) = \frac{\hat{I}_0(\beta)}{Z_c(\beta)} = \frac{e^{-\beta E(x_i, p_i)}}{Z_c(\beta)} \tag{4.37}$$

$$\hat{\Pi}_1(\beta) = \frac{\hat{I}_1(\beta)}{Z_c(\beta)} = \frac{e^{-\beta E(x_i, p_i)}}{Z_c}\,\hat{\psi}_1(\beta) \tag{4.38}$$

$$\hat{\Pi}_2(\beta) = \frac{\hat{I}_2(\beta)}{Z_c(\beta)} - \frac{Z_2(\beta)}{Z_c(\beta)}\,\hat{\Pi}_0(\beta) \tag{4.39}$$

$$= \frac{e^{-\beta E(x_i, p_i)}}{Z_c(\beta)}\left\{\hat{\psi}_2(\beta) + \frac{\beta^3}{24}\sum_{i=1}^{N}\frac{1}{m}\left\langle\left(\nabla_{x_i} U\right)^2\right\rangle_c\right\}$$

.
.
.

etc...

where use has been made of equations (4.33), (4.32) and (4.16), and where $\hat{\psi}_1$ and $\hat{\psi}_2$ are given respectively by equations (4.24) and (4.27). To arrive at equation (4.39) we have used the following two relations :

$$\langle p_i^{\alpha} p_j^{\gamma} \rangle_c = \frac{m}{\beta} \delta_{ij} \delta_{\alpha\gamma} \tag{4.40}$$

where i and j represent the i^{th} and j^{th} particle and α and β the α^{th} and β^{th} components of the vector $\underline{p}$, and

$$\left\langle \left(\nabla_{\underline{x}_i} U \right)^2 \right\rangle_c = \frac{1}{\beta} \left\langle \nabla^2_{\underline{x}_i} U \right\rangle_c \tag{4.41}$$

The knowledge of the operator $\hat{I}\hat{I}(\beta)$ will help us determine the thermal average of any given operator.

4.4 THERMAL AVERAGE OF OPERATORS OF THE FORM $O(\hat{\underline{x}}_1, \ldots, \hat{\underline{x}}_N; \hat{\underline{p}}_1, \ldots, \hat{\underline{p}}_N) = F(\hat{\underline{x}}_1, \hat{\underline{x}}_2, \ldots, \hat{\underline{x}}_N)\, g(\hat{\underline{p}}_1, \ldots, \hat{\underline{p}}_N)$

The thermal average of such an operator is just

$$\langle F(\hat{\underline{x}}_1, \ldots, \hat{\underline{x}}_N) \hat{g}(\hat{\underline{p}}_1, \ldots, \hat{\underline{p}}_N) \rangle = \int d[\underline{x}_N]\, d[\underline{p}_N] \left(\prod_{j=1}^{N} e^{-i \frac{\underline{p}_j \cdot \underline{x}_j}{\hbar}} \right) (x) \tag{4.42}$$

$$(x) \frac{e^{-\beta H}}{Z_g(\beta)} F(\hat{\underline{x}}_1, \ldots, \hat{\underline{x}}_N) \hat{g}(\hat{\underline{p}}_1, \ldots, \hat{\underline{p}}_N) \left(\prod_{j=1}^{N} e^{i \frac{\underline{p}_j \cdot \underline{x}_j}{\hbar}} \right)$$

The operation of $\hat{g}(\underline{p}_1, \ldots, \underline{p}_N)$ on the plane waves $e^{i \frac{\underline{p}_j \cdot \underline{x}_j}{\hbar}}$ will give us just a function of the momenta $(\underline{p}_1, \ldots, \underline{p}_N)$

$$\hat{g}(\hat{p}_1, \ldots, \hat{p}_N)\, e^{i \frac{\underline{p}_j \cdot \underline{x}_j}{\hbar}} = e^{i \frac{\underline{p}_j \cdot \underline{x}_j}{\hbar}} g(p_1, \ldots, p_N) \tag{4.43}$$

so that

$$\left(\prod_{j=1}^{N} e^{-i\frac{p_j\cdot x_j}{\hbar}}\right)\frac{e^{-\beta H}}{Z_q(\beta)}F(\hat{x}_1,\ldots,\hat{x}_N)\,\hat{g}(\hat{p}_1,\ldots,\hat{p}_N)\left(\prod_{j=1}^{N} e^{i\frac{p_j\cdot x_j}{\hbar}}\right) \quad (4.44)$$

$$= g(p_1,\ldots,p_N)\left(\prod_{j=1}^{N} e^{-i\frac{p_j\cdot x_j}{\hbar}}\right)\frac{e^{-\beta H}}{Z_q(\beta)}\,(*)$$

$$(*)\left(\prod_{j=1}^{N} e^{i\frac{p_j\cdot x_j}{\hbar}}\right)F(\hat{x}_1,\ldots,\hat{x}_N)$$

$$= g(p_1,\ldots,p_N)\,\hat{II}(\beta)\,F(\hat{x}_1,\ldots,\hat{x}_N)$$

$\hat{II}(\beta)$ is given by equation (4.34), (4.37) - (4.39) and operates on the function $F(\underline{x}_1,\ldots,\underline{x}_N)$.

$$\langle F(\hat{x}_1,\ldots,\hat{x}_N)\,\hat{g}(\hat{p}_1,\ldots,\hat{p}_N)\rangle = \int d[x_N]\,d[p_N]\,g(p_1,\ldots,p_N)(*) \quad (4.45)$$

$$(*)\,\frac{e^{-\beta E(x_i,p_i)}}{Z_c(\beta)}\left\{1 + \hbar\hat{\psi}_1 + \hbar^2\hat{\psi}_2 + \cdots\right\}(*)$$

$$(*)\quad F(x_1,\ldots,x_N)$$

The first term of this expression correspond to the classical thermal average of the function $F(\underline{x}_1,\ldots,\underline{x}_N)$ $(*)$ $g(\underline{p}_1,\ldots,\underline{p}_N)$. Note that from the expressions for $\hat{\psi}_1(\beta)$ and $\hat{\psi}_2(\beta)$, the above expression would converge more rapidly as the temperature increases ($\beta = \frac{1}{k_B T}$). Equation (4.45) is not really an expansion in $\hbar$ only, rather it is an expansion in $\frac{\hbar^2\beta a^2}{m}$, where a is some parameter that depends on the thermal average of the potential and with dimensions of inverse length.

A similar expansion is not possible for degenerate systems because of the exchange effects introduced by the symmetrized wave functions in the thermal average. The thermal average would contain factors of the form* $e^{i\frac{p_j\cdot x_\ell}{\hbar}} e^{-i\frac{p_m\cdot x_j}{\hbar}}$ $e^{i\frac{p_\ell\cdot x_s}{\hbar}} e^{-i\frac{p_i\cdot x_s}{\hbar}}$ which would not cancel each other, and any attempt to expand such factors would be meaningless because of the singularity at $\hbar=0$. That is why the above analysis applies to non-degenerate systems only.

There is a certain class of operators where the position dependence is of the form

$$F(x_1,\cdots,x_N) = e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)} \tag{4.46}$$

which deserves more attention. If such operators were treated by the method of this section, it is easy to see that a power series in $\frac{\hbar^2k^2\beta}{m}$ would be generated; and if $\hbar\underline{k}$ is to be interpreted as $\underline{p}$, the momentum transfer, we would be leaving out certain quantum effects. To sum such series, we shall develop another approach for treating these operators.

4.5 THERMAL AVERAGE OF OPERATORS OF THE FORM $O(\underline{x}_1,\ldots,\underline{x}_N) = e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\hat{g}(\hat{\underline{p}}_1,\ldots,\hat{\underline{p}}_N)$.

* These factors come from the symmetrized plane wave eigenvectors $|K\rangle$ and $\langle K|$ when all the different momenta are permutted among all the particles.

By definition

$$\langle e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\hat{g}(\hat{P}_1,\cdots,\hat{P}_N)\rangle = \int d[x_N]\,d[P_N]\left(\prod_{\rho=1}^{N} e^{-i\frac{P_\rho\cdot x_\rho}{\hbar}}\right)(*) \tag{4.47}$$

$$(*)\ \frac{e^{-\beta H}}{Z_g(\beta)}\ e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\hat{g}(\hat{P}_1,\cdots,\hat{P}_N)\left(\prod_{\rho=1}^{m} e^{-i\frac{P_\rho\cdot x_\rho}{\hbar}}\right)$$

$$=\int d[x_N]\,d[P_N]\,g(P_1,\cdots,P_N)\left(\prod_{\rho=1}^{N} e^{-i\frac{P_\rho\cdot x_\rho}{\hbar}}\right)\frac{e^{-\beta H}}{Z_g(\beta)}\,e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\left(\prod_{m=1}^{N} e^{-i\frac{P_m\cdot x_m}{\hbar}}\right)$$

with the help of equation (4.43); or

$$\langle e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\hat{g}(\hat{P}_1,\cdots,\hat{P}_N)\rangle = \int d[x_N]\,d[P_N]\ g(P_1,\cdots,P_N)(*) \tag{4.48}$$

$$(*)\left(\prod_{\rho=1}^{N} e^{-i\frac{P_\rho\cdot x_\rho}{\hbar}}\right)e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\,e^{i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\,\frac{e^{-\beta H}}{Z_g(\beta)}(*)$$

$$(*)\ e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\left(\prod_{m=1}^{N} e^{-i\frac{P_m\cdot x_N}{\hbar}}\right.$$

Since the transformation $e^{i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\,e^{-\beta H}\,e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}$, just shifts the momentum operator of the i^{th} particle by $-\hbar\underline{k}$ and the momentum operator of the j^{th} particle by $+\hbar\underline{k}$ in H, we have :

$$e^{i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)}\,e^{-\beta H}\,e^{-i\underline{k}\cdot(\underline{r}_i-\underline{r}_j)} \tag{4.43}$$

$$= e^{-\beta H(\hat{P}_1,\cdots,\hat{P}_i-\hbar\underline{k},\hat{P}_j+\hbar\underline{k},\cdots,\hat{P}_N)}$$

So

$$\langle e^{-i\underline{k}\cdot(\underline{\lambda}_i-\underline{\lambda}_j)}\hat{g}(\hat{P}_1,\cdots,\hat{P}_N)\rangle = \int d[\underline{x}_N]\,d[P_N]\; g(P_1,\cdots,P_N)\,(*) \tag{4.50}$$

$$(*)\; e^{-i\underline{k}\cdot(\underline{\lambda}_i-\underline{\lambda}_j)}\left(\prod_{\ell=1}^{N} e^{-i\frac{P_\ell\cdot x_\ell}{\hbar}}\right) e^{-\beta H(\hat{P}_1,\cdots,\hat{P}_i-\hbar\underline{k},\hat{P}_j+\hbar\underline{k},\cdots,\hat{P}_N)}\,(*)$$

$$(*)\left(\prod_{n=1}^{N} e^{-i\frac{P_n\cdot x_n}{\hbar}}\right)$$

$$= \int d[\underline{x}_N]\,d[P_N]\; g(P_1,\cdots,P_N)\; e^{-i\underline{k}\cdot(\underline{\lambda}_i-\underline{\lambda}_j)}\,(*)$$

$$(*)\;\frac{e^{-\beta H(\hat{P}_1+P_1,\cdots,\hat{P}_i-\hbar\underline{k}+P_i,\hat{P}_j+\hbar\underline{k}+P_j,\cdots,\hat{P}_N+P_N)}}{Z_\beta(\beta)}$$

by a similar argument as the one given in equation (4.49). Note

$$H(\hat{P}_1+P_1,\cdots,\hat{P}_i-\hbar\underline{k}+P_i,\hat{P}_j+\hbar\underline{k}-P_j,\cdots,\hat{P}_N+P_N) \tag{4.51}$$

$$= \sum_{\ell\neq i,j}\frac{(\hat{P}_\ell+P_\ell)^2}{2m} + \frac{(\hat{P}_i-\hbar\underline{k}+P_i)^2}{2m}$$

$$+ \frac{(\hat{P}_j+\hbar\underline{k}+P_j)^2}{2m} + U$$

$$= E(x_i,P_i) + \frac{\hbar^2k^2}{m} - \frac{\hbar\underline{k}\cdot(P_i-P_j)}{m}$$

$$-\sum_{\ell=1}^{N}\frac{\hbar^2}{2m}\left(\nabla^2_{\underline{x}_\ell} + 2i\,\frac{P_\ell}{\hbar}\cdot\nabla_{\underline{x}_\ell}\right)$$

$$+ i\,\frac{\hbar^2}{m}\,\underline{k}\cdot\left(\nabla_{\underline{x}_i}-\nabla_{\underline{x}_j}\right)$$

where $E(\underline{x}_i, \underline{p}_i)$ is the classical expression for the Hamiltonian.

$$< e^{-i \underline{k} \cdot (\underline{r}_i - \underline{r}_j)} \hat{g}(\hat{P}_1, \cdots, \hat{P}_N) > = \tag{4.52}$$

$$= \int d[\underline{x}_N] d[\underline{p}_N] \; g(\underline{p}_1, \cdots, \underline{p}_N) \; e^{-i \underline{k} \cdot (\underline{r}_i - \underline{r}_j)} \quad (*)$$

$$(*) \quad e^{-\beta \frac{\hbar^2 k^2}{m} + \beta \frac{\hbar \underline{k}}{m} \cdot (\underline{p}_i - \underline{p}_j)}$$

$$(*) \; \frac{e^{-\beta \left\{ E(\underline{x}_i, \underline{p}_i) - \sum_{\ell=1}^{N} \frac{\hbar^2}{2m} \left(\nabla_{\underline{x}_\ell}^2 + 2i \frac{\underline{p}_\ell}{\hbar} \cdot \nabla_{\underline{x}_\ell} - 2i \underline{k} \cdot (\nabla_{\underline{x}_i} - \nabla_{\underline{x}_j}) \right) \right\}}}{Z_0(\beta)}$$

The Bloch equation for the operator

$$\hat{\mathcal{X}}(\beta) = e^{-\beta \left\{ E(\underline{x}_i, \underline{p}_i) - \frac{\hbar^2}{2m} \sum_{\ell=1}^{N} \left(\nabla_{\underline{x}_\ell}^2 + 2i \frac{\underline{p}_\ell}{\hbar} \cdot \nabla_{\underline{x}_\ell} - 2i \underline{k} \cdot (\nabla_{\underline{x}_i} - \nabla_{\underline{x}_j}) \right) \right\}} \tag{4.53}$$

which incidentally operates on unity, and with the initial condition

$$\hat{\mathcal{X}}(\beta = 0) = 1 \tag{4.54}$$

will now be obtained.

It is :

$$\frac{\partial \hat{\mathcal{X}}(\beta)}{\partial \beta} = - \left\{ E(\underline{x}_i, \underline{p}_i) - \frac{\hbar^2}{2m} \sum_{\ell=1}^{N} \left(\nabla_{\underline{x}_\ell}^2 + 2i \frac{\underline{p}_\ell}{\hbar} \cdot \nabla_{\underline{x}_\ell} - 2i \underline{k} \cdot (\nabla_{\underline{x}_i} - \nabla_{\underline{x}_j}) \right) \right\} \tag{4.55}$$

Let

$$\hat{\chi}(\beta) = e^{-\beta E(x_i, p_i)} \hat{\Lambda}(\beta) = e^{-\beta E(x_i, p_i)} \left(1 + \hbar \hat{\Lambda}_1(\beta) + \hbar^2 \Lambda_2(\beta) + \cdots\right) \quad (4.56)$$

and then repeat the same procedure of section 4.2 to obtain the Bloch equation satisfied by $\hat{\Lambda}_1(\beta)$, $\hat{\Lambda}_2(\beta)$, etc... After making use of the expansion for $Z_q(\beta)$, and letting $\hat{\chi}(\beta)$ operate on unity, the final result is :

$$\frac{\hat{\chi}(\beta)\cdot 1}{Z_q(\beta)} = \frac{e^{-\beta E(x_i, p_i)}}{Z_c(\beta)} \left\{ 1 + \hbar \lambda_1(\beta) + \hbar^2 \lambda_2(\beta) + \cdots \right\} \quad (4.57)$$

where

$$\lambda_1(\beta) = \hat{\Lambda}_1(\beta)\cdot 1 = -i \frac{\beta^2}{2} \sum_{\ell=1}^{N} \frac{\underline{p}_\ell}{m} \cdot \left(\nabla_{\underline{x}_\ell} U\right) + i \frac{\hbar \beta^2}{2m} \underline{k} \cdot \left(\nabla_{\underline{x}_i} U - \nabla_{\underline{x}_j} U\right) \quad (4.58)$$

$$\lambda_2(\beta) = \hat{\Lambda}_2(\beta)\cdot 1 + \frac{\beta^3}{24} \sum_{\ell=1}^{N} \frac{1}{m} \left\langle \left(\nabla_{\underline{x}_\ell} U\right)^2 \right\rangle \quad (4.59)$$

$$= -\frac{\beta^4}{8} \left(\sum_{\ell=1}^{N} \frac{\underline{p}_\ell}{m} \cdot \nabla_{\underline{x}_\ell} U \right)^2 + \frac{\beta^3}{6} \sum_{s=1}^{N} \sum_{\ell=1}^{N} \frac{\underline{p}_s \underline{p}_\ell}{m^2} : \nabla_{\underline{x}_s} \nabla_{\underline{x}_\ell} + \frac{\beta^3}{6} \sum_{\ell=1}^{N} \frac{1}{m} \left(\nabla_{\underline{x}_\ell} U\right)^2 - \frac{\beta^2}{4} \sum_{\ell=1}^{N} \frac{1}{m} \left(\nabla^2_{\underline{x}_\ell} U\right)$$

$$+\frac{\beta^3}{24}\sum_{\rho=1}^{N}\frac{1}{m}\left\langle\left(\nabla_{\underline{x}_\rho}U\right)^2\right\rangle_c+\frac{\hbar\beta^4}{8}\left(\nabla_{\underline{x}_i}U-\nabla_{\underline{x}_j}U\right)\sum_{\rho=1}^{N}\frac{\underline{p}_\rho}{m}\cdot\left(\nabla_{\underline{x}_\rho}U\right)$$

$$-\frac{\hbar\beta^3}{3}\sum_{\rho=1}^{N}\underline{k}\cdot\left(\nabla_{\underline{x}_i}-\nabla_{\underline{x}_j}\right)\frac{\underline{p}_\rho}{m}\cdot\nabla_{\underline{x}_\rho}U$$

$$+\frac{\hbar\beta^3}{6m}\sum_{\rho=1}^{N}\frac{\underline{p}_\rho}{m}\cdot\nabla_{\underline{x}_\rho}U\;\underline{k}\cdot\left(\nabla_{\underline{x}_i}U-\nabla_{\underline{x}_j}U\right)$$

$$-\frac{\beta^3}{6m}\left\{\hbar\,\underline{k}\cdot\left(\nabla_{\underline{x}_i}U-\nabla_{\underline{x}_j}U\right)\right\}^2$$

$$+\frac{\hbar^2\beta^3}{6m^2}\,\underline{k}\cdot\left(\nabla_{\underline{x}_i}-\nabla_{\underline{x}_j}\right)\underline{k}\cdot\left(\nabla_{\underline{x}_i}U-\nabla_{\underline{x}_j}U\right)$$

$$\vdots$$

etc...

The expansion of the thermal average of the operator $e^{-i\,\underline{k}\cdot(\underline{x}_i-\underline{x}_j)}\,g(\hat{\underline{p}}_1,\ldots,\hat{\underline{p}}_N)$ is now completely determined. Note the appearance of the factor $e^{-\beta\hbar^2k^2/m}\,e^{\beta\hbar\underline{k}\cdot(\underline{p}_i-\underline{p}_j)}$ in equation (4.52).

This method will be used to calculate thermal averages containing the factor $e^{-i\,\underline{k}\cdot(\underline{x}_i-\underline{x}_j)}$. In appendix C the function $\left\langle\sum_{i=1}^{N}\sum_{j=1}^{N}e^{-i\,\underline{k}\cdot(\underline{x}_i-\underline{x}_j)}\right\rangle$, which is the Fourier transform of the radial pair distribution function, is evaluated.

Now that we have developed a formalism for the evaluation of thermal averages for non-degenerate systems at normal and high temperature, all static correlation functions can be calculated and quantum corrections to their equivalent classical expression obtained.

CHAPTER V

THE TOTAL NEUTRON SCATTERING FUNCTION

We have seen that the total neutron scattering function is given by :

$$S(\underline{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t} \sum_{i=1}^{n}\sum_{j=1}^{n} \langle e^{-i\underline{k}\cdot\underline{r}_i} e^{i\underline{k}\cdot\underline{r}_j(t)} \rangle \qquad (5.1)$$

$$= \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t} \sum_{i=1}^{n}\sum_{j=1}^{n} \langle e^{-i\underline{k}\cdot\underline{r}_i(t)} e^{i\underline{k}\cdot\underline{r}_j} \rangle$$

S(-k,-ω) is obtained from the above expression by changing $\underline{k}$ to $-\underline{k}$ and ω to $-\omega$:

$$S(-\underline{k},-\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t} \sum_{i=1}^{n}\sum_{j=1}^{n} \langle e^{i\underline{k}\cdot\underline{r}_j} e^{-i\underline{k}\cdot\underline{r}_i(t)} \rangle \qquad (5.2)$$

(the indices i and j have been interchanged). S(k,ω) and S(-k,-ω) are related to each other by the detailed balance factor :

$$S(-\underline{k},-\omega) = e^{-\beta\hbar\omega} S(\underline{k},\omega) \qquad (5.3)$$

so that

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t} \sum_{i=1}^{n}\sum_{j=1}^{n} \frac{1}{2}\Big\{ \langle e^{-i\underline{k}\cdot\underline{r}_i(t)}\, e^{i\underline{k}\cdot\underline{r}_j} + e^{i\underline{k}\cdot\underline{r}_j}\, e^{-i\underline{k}\cdot\underline{r}_i(t)} \rangle \Big\} \tag{5.4}$$

$$= \frac{1}{2}\Big\{ S(\underline{k},\omega) + S(-\underline{k},-\omega)\Big\}$$

$$= \frac{1}{2}\Big\{ 1 + e^{-\beta\hbar\omega}\Big\} S(\underline{k},\omega)$$

or

$$S(\underline{k},\omega) = \frac{2}{1+e^{-\beta\hbar\omega}}\, S^{sym}(\underline{k},\omega) \tag{5.5}$$

where

$$S^{sym}(\underline{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t} \sum_{i=1}^{n}\sum_{j=1}^{n} \Big\{ \langle e^{-i\underline{k}\cdot\underline{r}_i(t)}\, e^{i\underline{k}\cdot\underline{r}_j} + e^{i\underline{k}\cdot\underline{r}_j}\, e^{-i\underline{k}\cdot\underline{r}_i(t)} \rangle \Big\} \tag{5.6}$$

We choose to calculate $S^{sym}(k,\omega)$ instead of calculating directly $S(k,\omega)$ in order to have the detailed balance built in our starting equation instead of having to unravel it at the end of our calculations. As indicated in chapter II, $S^{sym}(k,\omega)$, like $S(k,\omega)$, can be calculated via the hydrodynamic approach or via the kinetic approach.

From now on, we shall take the large volume limit and

consider only the number of particles n contained in a unit volume of the liquid (neon, argon or any liquid metal) whose Hamiltonian is given by equation (2.64).

5.1 THE KINETIC APPROACH

Let us define a function $\phi(k,p,p',t)$ by :

$$\phi(\underline{k},\underline{p},\underline{p}',t) = \frac{1}{2}\langle \hat{f}_1(\underline{k},\underline{p},t)\,\hat{f}_1^{+}(\underline{k},\underline{p}') + \hat{f}_1^{+}(\underline{k},\underline{p}')\,\hat{f}_1(\underline{k},\underline{p},t)\rangle \tag{5.7}$$

where $\hat{f}_1(\underline{k},p,t)$ is given by equation (2.61). It is obvious that :

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\int d\underline{p}\, d\underline{p}'\, \phi(\underline{k},\underline{p},\underline{p}',t) = S^{sym}(\underline{k},\omega) \tag{5.8}$$

since the integration of $\hat{f}_1(\underline{k},\underline{p})$ over $d\underline{p}$ yields the density operator $\hat{\rho}(\underline{k})$.

The equation of motion of $\phi(\underline{k},\underline{p},\underline{p},t)$ shall be taken to be equation (3.42) where the operator $\hat{A}(\underline{p}, t)$ is simply replaced by $\hat{f}_1(\underline{k},\underline{p},t)$. It is again :

$$\frac{d}{dt}\phi(\underline{k},\underline{p},\underline{p}',t) - \int d\underline{p}_2\, \Omega(\underline{k},\underline{p},\underline{p}_2)\,\phi(\underline{k},\underline{p}_2,\underline{p}',t) + \int_0^t dt' \int d\underline{p}_2\, \mathcal{G}(\underline{k},\underline{p},\underline{p}_2,t')\,\phi(\underline{k},\underline{p}_2,t-t') = 0 \tag{5.9}$$

with

$$\Omega(\underline{k},p_3,p_2)=\int dp_3 \langle \dot{\hat{f}}_1(\underline{k},p)\,\hat{f}_1^{+}(\underline{k},p_3)\rangle_{+}\,\phi^{-1}(\underline{k},p_3,p_2) \tag{5.10}$$

$$\mathcal{G}(\underline{k},p_3,p_2,t)=\int dp_3 \langle \hat{F}(\underline{k},p,t)\,\dot{\hat{f}}_1^{+}(\underline{k},p_3)\rangle_{+}\,\phi^{-1}(\underline{k},p_3,p_2) \tag{5.11}$$

$$\hat{F}(\underline{k},p,t)= e^{it(1-P)L}(1-P)\,\dot{\hat{f}}_1(\underline{k},p) \tag{5.12}$$

$$\dot{\hat{f}}_1(\underline{k},p)=\frac{i}{\hbar}\left[H,\hat{f}_1(\underline{k},p)\right] \tag{5.13}$$

and $\phi^{-1}(\underline{k},\underline{p},p')$ is determined through

$$\int dp_2\,\phi(\underline{k},p,p_2)\,\phi^{-1}(\underline{k},p_2,p')=\delta(p-p') \tag{5.14}$$

In order to proceed any further, the functions and integrations contained in (5.9) have to be evaluated. The function $\mathcal{G}(\underline{k},\underline{p},\underline{p}',t)$ has to be approximated since there is no way at the present time of evaluating it exactly. For that purpose, we shall assume the time dependence of the "random force" $F(\underline{k},\underline{p},t)$ to be of the form :

$$F(\underline{k},\underline{p},t) = g(\underline{k},t)\ (1-P)\ \dot{\hat{f}}(\underline{k},\underline{p}) \tag{5.15}$$

where $g(\underline{k},t)$ is a function that depends on time and on the wave vector $\underline{k}$, but not on the momentum $\underline{p}$. This function, in essence, indicates the way the fluctuations in the system

are damped; and the correctness of this assumption can be checked only by comparing our final result with real experiments.

All of our calculations, are based on the evaluation of the static correlation function :$\phi(\underline{k},\underline{p},p')$:

$$\phi(\underline{k},\underline{p},\underline{p}') = \frac{1}{2}\langle \hat{f}_1(\underline{k},\underline{p})\hat{f}_1^{+}(\underline{k},\underline{p}') + \hat{f}_1^{+}(\underline{k},\underline{p}')\hat{f}_1(\underline{k},\underline{p})\rangle \qquad (5.16)$$

$$= \frac{1}{2}\sum_{i=1}^{m}\sum_{j=1}^{m}\int\frac{d\underline{\ell}\,d\underline{\ell}'}{(2\pi)^6}\langle e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}e^{-i\underline{k}\cdot\hat{\underline{x}}_i}e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}(*)$$

$$(*)\ e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}e^{i\underline{k}\cdot\underline{x}_j}e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_j}\rangle$$

$$+\frac{1}{2}\sum_{i=1}^{m}\sum_{j=1}^{m}\int\frac{d\underline{\ell}\,d\underline{\ell}'}{(2\pi)^6}\langle e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}e^{i\underline{k}\cdot\underline{x}_j}e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_j}(*)$$

$$(*)\ e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}e^{-i\underline{k}\cdot\hat{\underline{x}}_i}e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}\rangle$$

With

$$\sum_{i=1}^{m}\sum_{j=1}^{n} = \sum_{i=1}^{n} + \sum_{i=1}^{m}\sum_{j=1}^{m}{}' \qquad (5.17)$$

$$\Phi(\underline{k},\underline{P},\underline{P}') = \frac{1}{2}\sum_{i=1}^{n}\int \frac{d\underline{\ell}\,d\underline{\ell}'}{(2\pi)^6}\, e^{i\underline{\ell}\cdot\underline{P} - i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\, e^{i\underline{\ell}'\cdot\underline{P}' - i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}\,(*) \qquad (5.18)$$

$$(*) \quad < e^{-i\underline{\ell}\cdot\hat{\underline{P}}_i}\, e^{-i\underline{\ell}'\cdot\hat{\underline{P}}_i} >$$

$$+ \frac{1}{2}\sum_{i=1}^{n}\int \frac{d\underline{\ell}\,d\underline{\ell}'}{(2\pi)^6}\, e^{i\underline{\ell}\cdot\underline{P} + i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\, e^{i\underline{\ell}'\cdot\underline{P}' + i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}\,(*)$$

$$(*) \quad < e^{-i\underline{\ell}\cdot\hat{\underline{P}}_i}\, e^{-i\underline{\ell}'\cdot\hat{\underline{P}}_j} >$$

$$+ \sum_{i=1}^{n}\sum_{j=1}^{n'}\int \frac{d\underline{\ell}\,d\underline{\ell}'}{(2\pi)^6}\, e^{i\underline{\ell}'\cdot\underline{P}' - i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}\, e^{i\underline{\ell}\cdot\underline{P} + i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\,(*)$$

$$(*) \quad < e^{-i\underline{k}\cdot(\underline{x}_i - \underline{x}_j)}\, e^{-i\underline{\ell}\cdot\hat{\underline{P}}_i}\, e^{-i\underline{\ell}'\cdot\hat{\underline{P}}_j} >$$

Using the definition of the thermal average

$$\Phi(\underline{k},\underline{P},\underline{P}') = \frac{1}{2}\sum_{i=1}^{n}\int d[\underline{x}_N]\,d[\underline{P}_N]\,\delta(\underline{P}-\underline{P}')\,\delta\left(\underline{P} - \tfrac{\hbar\underline{k}}{2} - \underline{P}_i\right)(*) \qquad (5.19)$$

$$(*)\left(\prod_{j=1}^{n} e^{-i\frac{\underline{P}_j\cdot\underline{x}_j}{\hbar}}\right)\frac{e^{-\beta H}}{Z_8(\beta)}\left(\prod_{\rho=1}^{n} e^{i\frac{\underline{P}_\rho\cdot\underline{x}_\rho}{\hbar}}\right)$$

+

$$+\frac{1}{2}\sum_{i=1}^{n}\int d[x_N]\,d[p_N]\;\delta(p-p')\;\delta\left(p+\frac{\hbar k}{2}-p_i\right)(*)$$

$$(*)\left(\prod_{\ell=1}^{n}e^{-i\frac{p_\ell\cdot x_\ell}{\hbar}}\right)\frac{e^{-\beta H}}{Z_g(\beta)}\left(\prod_{\ell=1}^{n}e^{i\frac{p_\ell\cdot x_\ell}{\hbar}}\right)$$

$$+\sum_{i=1}^{n}\sum_{j=1}^{n}{}'\int d[x_N]\,d[p_N]\;\delta\left(p+\frac{\hbar k}{2}-p_i\right)\delta\left(p'-\frac{\hbar k}{2}-p_j\right)(*)$$

$$(*)\left(\prod_{\ell=1}^{n}e^{-i\frac{p_\ell\cdot x_\ell}{\hbar}}\right)\frac{e^{-\beta H}}{Z_g(\beta)}\,e^{-i\underline{k}\cdot(\underline{x}_i-\underline{x}_j)}\left(\prod_{\ell=1}^{n}e^{i\frac{p_\ell\cdot x_\ell}{\hbar}}\right)$$

The first two terms will be calculated by the method of section (4.2), while the third term will be calculated by the method of section (4.4) because of the factor $e^{-i\underline{k}\cdot(\underline{x}_i-\underline{x}_j)}$.

$$\phi(k,p,p')=\frac{1}{2}\sum_{i=1}^{n}\int d[x_N]d[p_N]\;\delta(p-p')\left\{\delta\left(p-\frac{\hbar k}{2}-p_i\right)+\right. \tag{5.20}$$

$$\left.+\delta\left(p+\frac{\hbar k}{2}-p_i\right)\right\}\frac{e^{-\beta E(x_i,p_i)}}{Z_c(\beta)}\left\{1+\hbar\hat{\psi}_1\cdot 1+\hbar^2\hat{\psi}_2\cdot 1+\cdots\right\}$$

$$+\sum_{i=1}^{n}\sum_{j=1}^{n}\int d[x_N]\,d[p_N]\;\delta\left(p+\frac{\hbar k}{2}-p_i\right)\delta\left(p'-\frac{\hbar k}{2}-p_j\right)e^{-i\underline{k}\cdot(\underline{x}_i-\underline{x}_j)}\tag{*}$$

$$(*)\;\frac{e^{-\beta E(x_i,p_i)}}{Z_c(\beta)}\left\{1+\hbar\lambda_1+\hbar^2\lambda_2+\cdots\right\}e^{-\beta\frac{\hbar^2k^2}{m}}\,e^{\beta\frac{\hbar k}{m}\cdot(p_i-p_j)}$$

with $\hat{\Psi}_1$, $\hat{\Psi}_2$ given by equations (4.24) and (4.27), and λ_1 , λ_2 by (4.58), (4.59). After performing the integrations over $d[\underline{x}_N]$ $d[\underline{p}_N]$,we obtain :

$$\Phi(\underline{k},\underline{p},\underline{p}') = \frac{1}{2} n \delta(\underline{p}-\underline{p}') \left\{ M\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right)\left[1 - \frac{\hbar^2\beta^2 D}{8nm} + \right. \right. \tag{5.21}$$

$$\left. + \frac{\hbar^2\beta^3 D}{24nm^2}\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right)^2\right] + M\left(\underline{p}+\frac{\hbar\underline{k}}{2}\right)\left[1 - \frac{\hbar^2\beta^2 D}{8nm} + \frac{\hbar^2\beta^3 D}{24nm^2}\left(\underline{p}+\frac{\hbar\underline{k}}{2}\right)^2\right] \Bigg\}$$

$$+ n^2 h(\underline{k})\; M\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right) M\left(\underline{p}'+\frac{\hbar\underline{k}}{2}\right) (*)$$

$$(*)\left\{1 + \beta\frac{\hbar^2\underline{k}^2}{m} - \frac{\hbar\beta}{2m}\underline{k}\cdot\left(\underline{p}+\frac{\hbar\underline{k}}{2}\right) + \frac{\hbar\beta}{2m}\underline{k}\cdot\left(\underline{p}'-\frac{\hbar\underline{k}}{2}\right)\right\}$$

where

$M(\underline{p})$ = the Maxwell-Boltzman distribution (5.22)

$$= \left(\frac{\beta}{2\pi m}\right)^{3/2} e^{-\beta\frac{\underline{p}^2}{2m}}$$

$$D = \sum_{i=1}^{n} \left\langle \left(\nabla_{\underline{x}_i}^2 U\right) \right\rangle_c = n^2 \int d\underline{R}\, \frac{\partial^2 V(R)}{\partial R^2}\, g(R) \tag{5.23}$$

$g(R)$ = the classical two particle distribution function (5.24)

$$h(\underline{k}) = \frac{1}{n^2} \sum_{i=1}^{n} \sum_{j=1}^{n}{}' \left\langle e^{-i\underline{k}\cdot(\underline{x}_i - \underline{x}_j)} \right\rangle_c \tag{5.25}$$

Equation (5.21) was obtained from (5.20) by neglecting higher order terms in $\hbar$ because they introduce functionals of the three particle distribution functions, and also because the terms retained in the expansion are already small compared to unity. To estimate their magnitude, let us substitute for p, and p' their average values, and let us consider the case of scattering of neutrons ($k = 2A^{\circ}$) from liquid argon at a temperature $T=85.5^{\circ}K$ and with a density $n=2.1\times10^{22}$ cm . For this liquid $\left\langle \frac{\nabla^2 U}{3m} \right\rangle_c = 45\times10^{24}$ sec^{-2}, so that :

$$\frac{\hbar^2 k^2 \beta}{m} = 0.13 \qquad (5.26)$$

$$\frac{\hbar^2 k^2 \hbar^2 \beta^3 D}{24\times4\times n m^2} = 0.6\times10^{-3} \qquad (5.27)$$

Neglecting (5.26) would amount to about a 13% error while the error introduced by neglecting (5.27) is very small. The next order terms in the expansion come roughly as the squares of (5.26) and (5.29) so that the error introduced by truncating the series at this point is probably less than 3%.

The expression for $\phi(\underline{k},\underline{p},\underline{p}')$ can be rewritten as :

$$\phi(\underline{k},\underline{p},\underline{p}') = \frac{n}{2}\delta(p-p')\,m(p-\tfrac{\hbar k}{2})\left\{1 - \frac{\hbar^2\beta^2 D}{8nm} + \frac{\hbar^2\beta^3 D}{24nm^2}(p-\tfrac{\hbar k}{2})^2\right\} + \qquad (5.28)$$

$$+\frac{n}{2}\,\delta(p-p')\,M(p+\tfrac{\hbar k}{2})\left[1-\frac{\hbar^2\beta^2 D}{8nm}+\frac{\hbar^2\beta^3 D}{24nm^2}(p+\tfrac{\hbar k}{2})^2\right]$$

$$+n^2 R(k)\,M(p-\tfrac{\hbar k}{2})\,M(p'+\tfrac{\hbar k}{2})\left[1-\right.$$

$$\left.-\frac{\hbar\beta}{2m}\,k\cdot(p-\tfrac{\hbar k}{2})+\frac{\hbar\beta}{2m}\,k\cdot(p'+\tfrac{\hbar k}{2})\right]$$

The inverse function $\Phi^{-1}(k,p,p')$ is obtained from equations (5.14) and (5.28)

$$\frac{n}{2}\left\{M(p-\tfrac{\hbar k}{2})\left[1-\frac{\hbar^2\beta^2 D}{8nm}+\frac{\hbar^2\beta^3 D}{24nm^2}(p-\tfrac{\hbar k}{2})^2\right]\right. \tag{5.29}$$

$$\left.+M(p+\tfrac{\hbar k}{2})\left[1-\frac{\hbar^2\beta^2 D}{8nm}+\frac{\hbar^2\beta^3 D}{24nm^2}(p+\tfrac{\hbar k}{2})^2\right]\right\}\Phi^{-1}(k,p,p')$$

$$+n^2 R(k)\,M(p-\tfrac{\hbar k}{2})\int dp_2\,M(p_2+\tfrac{\hbar k}{2})\left\{1-\right.$$

$$\left.-\frac{\hbar\beta}{2m}\,k\cdot(p-\tfrac{\hbar k}{2})+\frac{\hbar\beta}{2m}\,k\cdot(p_2+\tfrac{\hbar k}{2})\right\}\Phi^{-1}(k,p_2,p')$$

$$=\delta(p-p')$$

Like $\Phi(k,p,p')$, $\Phi^{-1}(k,p,p')$ is expanded as :

$$\Phi^{-1}(k,p,p')=\Phi^{-1}_{(0)}(k,p,p')+\hbar^2\Phi^{-1}_{(2)}(k,p,p') \tag{5.30}$$

where each term satisfies the following equations :

$$\frac{n}{2}\left\{M\left(p-\frac{\hbar k}{2}\right)+M\left(p+\frac{\hbar k}{2}\right)\right\}\Phi^{-1}_{(0)}(k,p,p') \tag{5.31}$$

$$+n^2 h(k) M\left(p-\frac{\hbar k}{2}\right)\int dp_2 M\left(p_2+\frac{\hbar k}{2}\right)\Phi^{-1}_{(0)}(k,p_2,p')$$

$$= \delta(p-p')$$

$$\frac{n}{2}\left\{M\left(p-\frac{\hbar k}{2}\right)+M\left(p+\frac{\hbar k}{2}\right)\right\}\Phi^{-1}_{(1)}(k,p,p') \tag{5.32}$$

$$+n^2 h(k) M\left(p-\frac{\hbar k}{2}\right)\int dp_2 M\left(p_2+\frac{\hbar k}{2}\right)\Phi^{-1}_{(1)}(k,p_2,p')$$

$$= -n^2 h(k) M\left(p-\frac{\hbar k}{2}\right)\int dp_2 M\left(p_2+\frac{\hbar k}{2}\right)(*)$$

$$(*)\left[-\frac{\beta}{2m}\hbar k\cdot\left(p-\frac{\hbar k}{2}\right)+\frac{\beta}{2m}\hbar k\cdot\left(p_2+\frac{\hbar k}{2}\right)\right]\Phi^{-1}_{(0)}(k,p_2,p')$$

and

$$\frac{n}{2}\left\{M\left(p-\frac{\hbar k}{2}\right)+M\left(p+\frac{\hbar k}{2}\right)\right\}\Phi^{-1}_{(2)}(k,p,p')+ \tag{5.33}$$

$$+ n^2 \hat{h}(\underline{k})\, M\left(p - \frac{\hbar \underline{k}}{2}\right) \int dp_2\, M\left(p_2 + \frac{\hbar \underline{k}}{2}\right) \Phi^{-1}_{(2)}(\underline{k}, p_2, p')$$

$$= - n^2 \hat{h}(\underline{k})\, M\left(p - \frac{\hbar \underline{k}}{2}\right) \int dp_2\, M\left(p_2 + \frac{\hbar \underline{k}}{2}\right) (*)$$

$$(*)\left[- \frac{\beta}{2m}\, \underline{k} \cdot \left(p - \frac{\hbar \underline{k}}{2}\right) + \frac{\beta}{2m}\, \underline{k} \cdot \left(p_2 + \frac{\hbar \underline{k}}{2}\right)\right] \Phi^{-1}_{(1)}(\underline{k}, p_2, p')$$

$$- \frac{n}{2} \left\{ M\left(p - \frac{\hbar \underline{k}}{2}\right)\left[- \frac{\hbar^2 \beta^2 D}{8 n m} + \frac{\hbar^2 \beta^3 D}{24 n m^2} \left(p - \frac{\hbar \underline{k}}{2}\right)^2\right] \right.$$

$$\left. + M\left(p + \frac{\hbar \underline{k}}{2}\right)\left[- \frac{\hbar^2 \beta^2 D}{8 n m} + \frac{\hbar^2 \beta^3 D}{24 n m^2} \left(p + \frac{\hbar \underline{k}}{2}\right)^2\right] \right\} (*)$$

$$(*)\ \Phi^{-1}_{(0)}(\underline{k}, p, p')$$

Neglecting corrections due to equation (5.33), the solution is :

$$\Phi^{-1}(\underline{k}, p, p') = \frac{\delta(p - p')}{\frac{n}{2}\left[M\left(p - \frac{\hbar \underline{k}}{2}\right) + M\left(p + \frac{\hbar \underline{k}}{2}\right)\right]} \qquad (5.34)$$

$$-\left(\frac{\hbar(\underline{k})}{1+n\hbar(\underline{k})G_1(\underline{k})}\right)\frac{M(\underline{p}-\frac{\hbar\underline{k}}{2})}{\frac{1}{2}\left[M(\underline{p}-\frac{\hbar\underline{k}}{2})+M(\underline{p}+\frac{\hbar\underline{k}}{2})\right]}(*)$$

$$(*)\left\{1-\frac{\hbar\beta}{2m}\underline{k}\cdot(\underline{p}-\frac{\hbar\underline{k}}{2})+\frac{\hbar\beta}{2m}\underline{k}\cdot(\underline{p}'+\frac{\hbar\underline{k}}{2})\right.$$

$$\left.-\frac{\beta\hbar^2k^2}{2m}n\hbar(\underline{k})G_1(\underline{k})\right\}\frac{M(\underline{p}'+\frac{\hbar\underline{k}}{2})}{\frac{1}{2}\left[M(\underline{p}'-\frac{\hbar\underline{k}}{2})+M(\underline{p}'+\frac{\hbar\underline{k}}{2})\right]}$$

where

$$G_1(\underline{k})=\int d\underline{p}\,\frac{M(\underline{p}-\frac{\hbar\underline{k}}{2})\,M(\underline{p}+\frac{\hbar\underline{k}}{2})}{\frac{1}{2}\left[M(\underline{p}-\frac{\hbar\underline{k}}{2})+M(\underline{p}+\frac{\hbar\underline{k}}{2})\right]} \tag{5.35}$$

We can proceed now to calculate the "frequency term" and the "memory term". To evaluate $\Omega(\underline{k},\underline{p},\underline{p}_2)$ we need

$\langle\dot{\hat{f}}_1(\underline{k},\underline{p})\;\hat{f}_1^{+}(\underline{k},\underline{p}')\rangle_{+}$:

$$\langle\dot{\hat{f}}_1(\underline{k},\underline{p})\,\hat{f}_1^{+}(\underline{k},\underline{p}')\rangle_{+}=\frac{1}{2}\frac{i}{\hbar}\left\{\langle[H,\hat{f}_1(\underline{k},\underline{p}]\,\hat{f}_1^{+}(\underline{k},\underline{p}')\right. \tag{5.36}$$

$$\left.+\langle\hat{f}_1^{+}(\underline{k},\underline{p}')\,[H,\hat{f}_1(\underline{k},\underline{p})]\rangle\right\}$$

From the equation of motion of f ($\underline{k}$,$\underline{p}$) :

$$\langle \dot{\hat{f}}_1(\underline{k},\underline{p})\,\hat{f}_1^{+}(\underline{k},\underline{p}')\rangle_{+} = -i\,\frac{\underline{k}\cdot\underline{p}}{m}\,\phi(\underline{k},\underline{p},\underline{p}') \qquad (5.37)$$

$$+\frac{1}{2}\frac{i}{\hbar}\langle\left[U,\hat{f}_1(\underline{k},\underline{p})\right]\hat{f}_1^{+}(\underline{k},\underline{p}') + \hat{f}_1^{+}(\underline{k},\underline{p}')\left[U,\hat{f}_1(\underline{k},\underline{p})\right]\rangle$$

$$= -i\,\frac{\underline{k}\cdot\underline{p}}{m}\,\phi(\underline{k},\underline{p},\underline{p}')$$

$$+\frac{1}{2}\frac{i}{\hbar}\sum_{i=1}^{n}\sum_{\beta\neq i}\int\frac{d\underline{\ell}}{(2\pi)^3}\,e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\langle e^{-i\underline{k}\cdot\hat{\underline{r}}_i}\Big[V(\underline{r}_i-\underline{r}_\beta) -$$

$$-V(\underline{r}_i-\hbar\underline{\ell}-\underline{r}_\beta)\Big]e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}\int\frac{d\underline{\ell}'}{(2\pi)^3}\sum_{j=1}^{m}e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}e^{i\underline{k}\cdot\hat{\underline{r}}_j}e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_j}\rangle$$

$$+\frac{1}{2}\frac{i}{\hbar}\frac{1}{(2\pi)^3}\sum_{j=1}^{m}\int d\underline{\ell}'\,e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}\langle e^{i\underline{k}\cdot\hat{\underline{r}}_j}\,e^{-i\underline{\ell}'\cdot\underline{p}_j}\,(*)$$

$$(*)\sum_{i=1}^{m}\sum_{\beta\neq i}\int d\underline{\ell}\;e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\,e^{-i\underline{k}\cdot\hat{\underline{r}}_i}\,(*)$$

$$(*)\left[V(\underline{r}_i-\underline{r}_\beta) - V(\underline{r}_i-\hbar\underline{\ell}-\underline{r}_\beta)\right]e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}\rangle$$

Let us separate the term i=j and i≠j :

$$\langle \dot{\hat{f}}_1(\underline{k},\underline{p})\,\hat{f}_1^{+}(\underline{k},\underline{p}')\rangle_{+} = -i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\phi(\underline{k},\underline{p},\underline{p}') \qquad (3.38)$$

$$+\frac{1}{2}\frac{i}{\hbar}\sum_{i=1}^{n}\sum_{\beta\neq i}^{n}\frac{1}{(2\pi)^6}\int d\underline{\ell}\,d\underline{\ell}'\; e^{i\underline{\ell}\cdot\underline{p}-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}} \qquad (*)$$

$$(*)\; e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'} < \left[V(\underline{x}_i-\underline{x}_\beta)-V(\underline{x}_i-\hbar\underline{\ell}-\underline{x}_\beta)\right]e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_i}>$$

$$+\frac{1}{2}\frac{i}{\hbar}\sum_{i=1}^{n}\sum_{\beta\neq i}^{n}\frac{1}{(2\pi)^6}\int d\underline{\ell}\,d\underline{\ell}'\; e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}e^{i\underline{\ell}'\cdot\underline{p}'+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'} \qquad (*)$$

$$(*) < \left[V(\underline{x}_i-\hbar\underline{\ell}'-\underline{x}_\beta)-V(\underline{x}_i-\hbar\underline{\ell}'-\hbar\underline{\ell}-\underline{x}_\beta)\right]e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_i}>$$

$$+\frac{1}{2}\frac{i}{\hbar}\frac{1}{(2\pi)^6}\sum_{i=1}^{n}\sum_{\beta\neq i}^{n}\sum_{j\neq i}^{n}\int d\underline{\ell}\,d\underline{\ell}'\; e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}} \qquad (*)$$

$$(*)\; e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'} < e^{-i\underline{k}\cdot(\underline{x}_i-\underline{x}_j)}\left[V(\underline{x}_i-\underline{x}_\beta)-V(\underline{x}_i-\hbar\underline{\ell}-\underline{x}_\beta)\right](*)$$

$$(*)\; e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_j}>$$

$$+\frac{1}{2}\frac{i}{\hbar}\frac{1}{(2\pi)^6}\sum_{i=1}^{n}\sum_{\beta\neq i}^{n}\sum_{j\neq i}^{n}\int d\underline{\ell}\,d\underline{\ell}'\; e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'} \qquad (*)$$

$$(*) < e^{-i\underline{k}\cdot(\underline{x}_i-\underline{x}_j)}e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_j}\left[V(\underline{x}_i-\underline{x}_\beta)-V(\underline{x}_i-\hbar\underline{\ell}-\underline{x}_\beta)\right]e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}>$$

After evaluating the thermal averages according to the prescription of section (4.3) and keeping only the term that does not intoduce the three particle distribution function, we obtain :

$$\langle \dot{\hat{f}}_1(\underline{k},\underline{p})\, \hat{f}_1^{+}(\underline{k},\underline{p}')\rangle_{+} = -i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\Phi(\underline{k},\underline{p},\underline{p}') \qquad (5.38)$$

$$+ i\frac{\hbar D}{4}\left\{ M\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right)\left[\nabla_{\underline{p}}^{2} - \frac{\beta}{m}\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right]\right.$$

$$\left. - M\left(\underline{p}+\frac{\hbar\underline{k}}{2}\right)\left[\nabla_{\underline{p}}^{2} - \frac{\beta}{m}\left(\underline{p}+\frac{\hbar\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right]\right\}\delta(\underline{p}-\underline{p}')$$

$$+ i\,\frac{\underline{k}\cdot\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right)}{m}\, M\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right) M\left(\underline{p}'+\frac{\hbar\underline{k}}{2}\right) n^{2} P_h(\underline{k})$$

The frequency function, with the help of relation (5.14) is then :

$$\Omega(\underline{k},\underline{p}_1,\underline{p}_2) = -i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\delta(\underline{p}-\underline{p}_2) \qquad (5.38)$$

$$+ i\frac{\hbar D}{4}\left\{ M\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right)\left[\nabla_{\underline{p}}^{2} - \frac{\beta}{m}\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right]\right.$$

$$\left. - M\left(\underline{p}+\frac{\hbar\underline{k}}{2}\right)\left[\nabla_{\underline{p}}^{2} - \frac{\beta}{m}\left(\underline{p}+\frac{\hbar\underline{k}}{2}\right)\right]\right\}\Phi^{1}(\underline{k},\underline{p},\underline{p}_2)$$

$$+ i\,\frac{\underline{k}\cdot\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right)}{m}\, M\left(\underline{p}-\frac{\hbar\underline{k}}{2}\right) n^{2} P_h(\underline{k}) \int d\underline{p}_3\, M\left(\underline{p}_3+\frac{\hbar\underline{k}}{2}\right)\Phi^{1}(\underline{k},\underline{p}_3,\underline{p}_2)$$

which yields :

$$\Omega(\underline{k}, P, P_2) = -i\left(\frac{\underline{k}\cdot\underline{P}}{m}\right)\delta(P - P_2) \tag{5.39}$$

$$+ i\frac{\hbar D}{4}\Big\{M(P - \tfrac{\hbar\underline{k}}{2})\Big[\nabla_P^2 - \frac{\beta}{m}(P - \tfrac{\hbar\underline{k}}{2})\cdot\nabla_P\Big] - M(P - \tfrac{\hbar\underline{k}}{2})\Big[\nabla_P^2 - \frac{\beta}{m}(P + \tfrac{\hbar\underline{k}}{2})\cdot\nabla_P\Big]\Big\}\Phi^{-1}(\underline{k}, P, P_2)$$

$$+ i\,\frac{\underline{k}\cdot(P - \frac{\hbar\underline{k}}{2})}{m}M(P - \tfrac{\hbar\underline{k}}{2})\left(\frac{n\,R(\underline{k})}{1 + n\,R(\underline{k})G_1(\underline{k})}\right)\Bigg\{1 -$$

$$- \left(\frac{n\,R(\underline{k})G_1(\underline{k})}{1 + n\,R(\underline{k})G_1(\underline{k})}\right)\left(\frac{\hbar\beta}{2m}\,\underline{k}\cdot(P_2 + \tfrac{\hbar\underline{k}}{2}) - \frac{\beta\hbar^2k^2}{2m}\,n\,R(\underline{k})G_1(\underline{k})\right.$$

$$\left.- \frac{\hbar\beta}{2m}\,\frac{\underline{k}\cdot\underline{K}_1(\underline{k})}{G_1(\underline{k})}\right)\Bigg\}\,\frac{M(P_2 + \frac{\hbar\underline{k}}{2})}{\frac{1}{2}\left[M(P_2 - \frac{\hbar\underline{k}}{2}) + M(P_2 + \frac{\hbar\underline{k}}{2})\right]}$$

where

$$\underline{K}_1(\underline{k}) = \int dP\,\frac{M(P + \frac{\hbar\underline{k}}{2})\,M(P - \frac{\hbar\underline{k}}{2})\,(P - \frac{\hbar\underline{k}}{2})}{\frac{1}{2}\left[M(P - \frac{\hbar\underline{k}}{2}) + M(P + \frac{\hbar\underline{k}}{2})\right]} \tag{5.40}$$

Under assumption (5.15), we need the function $< \left\{ (1-P)\, \dot{\hat{f}}(\underline{k},\underline{p}) \right\} \dot{\hat{f}}^{+}(\underline{k},\underline{p}_3) >_+$ for the evaluation of the "damping" term.

$$< \left\{ (1-P)\, \dot{\hat{f}}(\underline{k},\underline{p}) \right\} \dot{\hat{f}}^{+}(\underline{k},\underline{p}_3) >_+ \tag{5.41}$$

$$= -\frac{1}{h^2} < \left[u, \hat{f}_1(\underline{k},\underline{p}) \right] \left[u, \hat{f}_1^{+}(\underline{k},\underline{p}') \right] >_+$$

$$+ \frac{1}{h^2} \int d\underline{p}_1\, d\underline{p}_2 < \left[u, \hat{f}_1(\underline{k},\underline{p}) \right] \hat{f}_1^{+}(\underline{k},\underline{p}_1) >_+ \Phi'(\underline{k},\underline{p}_1,\underline{p}_2)(*)$$

$$(*) < \hat{f}_1(\underline{k},\underline{p}_2) \left[u, \hat{f}_1^{+}(\underline{k},\underline{p}') \right] >_+$$

where we have used the fact that

$$(1-P)\, \hat{f}_1(\underline{k},\underline{p}) = 0 \tag{5.42}$$

The calculation proceeds as before. The first term is

$$< \left[u, \hat{f}_1(\underline{k},\underline{p}) \right] \left[u, \hat{f}_1^{+}(\underline{k},\underline{p}') \right] >_+ \tag{5.43}$$

$$= \frac{1}{2} \frac{1}{(2\pi)^6} \sum_{i=1}^{m} \sum_{\beta \neq i}^{m} \int d\underline{\ell}\; e^{i\,\underline{\ell}\cdot\underline{p} + i\,\frac{\underline{k}}{2}\,\underline{k}\cdot\underline{\ell}} < e^{-i\,\underline{k}\cdot\hat{\underline{x}}_i} \left[1 - e^{-\underline{k}\underline{\ell}\cdot\nabla_{\underline{x}_i}} \right] (*)$$

$$(*)\, V(\underline{x}_i - \underline{x}_\beta)\, e^{-i\,\underline{\ell}\cdot\hat{\underline{p}}_i} \sum_{j=1}^{m} \sum_{\alpha \neq j}^{m} \int d\underline{\ell}'\, e^{i\,\underline{\ell}'\cdot\underline{p}' - i\,\frac{\underline{k}}{2}\,\underline{k}\cdot\underline{\ell}'} e^{i\,\underline{k}\cdot\hat{\underline{x}}_j} (*)$$

$$(*) \left[1 - e^{-\underline{k}\underline{\ell}'\cdot\nabla_{\underline{x}_j}} \right] V(\underline{x}_j - \underline{x}_\alpha)\, e^{-i\,\underline{\ell}\cdot\hat{\underline{p}}_j} > \quad +$$

$$+\frac{1}{2}\frac{1}{(2\pi)^6}\sum_{j=1}^{m}\sum_{\alpha\neq j}^{m}\int d\underline{\ell}'\, e^{i\underline{\ell}'\cdot\underline{p}' - i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'} < e^{i\underline{k}\cdot\hat{\underline{x}}_j}\left[1-e^{-\hbar\underline{\ell}'\cdot\nabla_{\underline{x}_j}}\right](*)$$

$$(*)\, e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_j}\sum_{i=1}^{m}\sum_{\beta\neq i}^{m}\int d\underline{\ell}\; e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\, e^{-i\underline{k}\cdot\hat{\underline{x}}_i}\left[1-e^{-\hbar\underline{\ell}\cdot\nabla_{\underline{x}_i}}\right](*)$$

$$(*)\; V(\underline{x}_i-\underline{x}_\beta)\; e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i} >$$

$$= \frac{1}{2}\frac{1}{(2\pi)^6}\sum_{i=1}^{m}\sum_{\beta\neq i}^{m}\sum_{\alpha\neq i}^{m}\int d\underline{\ell}\, d\underline{\ell}'\, e^{i\underline{\ell}\cdot\underline{p}-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\, e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}(*)$$

$$(*) < \left\{\left[1-e^{-\hbar\underline{\ell}\cdot\nabla_{\underline{x}_i}}\right]V(\underline{x}_i-\underline{x}_\beta)\right\}\left\{\left[1-e^{-\hbar\underline{\ell}'\cdot\nabla_{\underline{x}_\delta}}\right]V(\underline{x}_i-\underline{x}_\alpha)\right\}$$

$$(*)\; e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}\, e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_i} >$$

$$+\frac{1}{2}\frac{1}{(2\pi)^6}\sum_{i=1}^{m}\sum_{\beta\neq i}^{m}\sum_{\alpha\neq i}^{m}\int d\underline{\ell}'\, e^{i\underline{\ell}'\cdot\underline{p}'+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}\, e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}} < \left\{\left[1-e^{-\hbar\underline{\ell}'\cdot\nabla_{\underline{x}_\delta}}\right](*)\right.$$

$$\left.(*)\; V(\underline{x}_\delta-\underline{x}_\alpha)\right\}\left\{\left[1-e^{-\hbar\underline{\ell}\cdot\nabla_{\underline{x}_i}}\right]e^{-\hbar\underline{\ell}'\cdot\nabla_{\underline{x}_i}}\, V(\underline{x}_i-\underline{x}_\beta)\right\}e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i - i\underline{\ell}'\cdot\hat{\underline{p}}_i} >$$

$$+\frac{1}{2}\frac{1}{(2\pi)^6}\sum_{i=1}^{m}\sum_{\beta\neq i}^{m}\sum_{\delta\neq i}^{m}\sum_{\alpha\neq\delta}^{m}\int d\underline{\ell}\; d\underline{\ell}'\, e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\, e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}$$

$$(*) < e^{-i\underline{k}\cdot(\underline{x}_i-\underline{x}_\delta)}\left\{\left[1-e^{-\hbar\underline{\ell}\cdot\nabla_{\underline{x}_i}}\right]V(\underline{x}_i-\underline{x}_\beta)\right\}\left[1-e^{-\hbar\underline{\ell}'\cdot\nabla_{\underline{x}_\delta}}\right]e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}\, V(\underline{x}_\delta-\underline{x}_\alpha)\, e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_\delta} >$$

$$+\frac{1}{2}\frac{1}{(2\pi)^6}\sum_{i=1}^{m}\sum_{\beta\neq i}^{m}\sum_{\delta\neq i}^{m}\sum_{\alpha\neq i}^{m}\int d\underline{\ell}\, d\underline{\ell}'\, e^{i\underline{\ell}'\cdot\underline{p}'-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}'}\, e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}(*)$$

$$(*) < e^{-i\underline{k}\cdot(\underline{x}_i-\underline{x}_\delta)}\left\{\left[1-e^{-\hbar\underline{\ell}'\cdot\nabla_{\underline{x}_\delta}}\right]V(\underline{x}_\delta-\underline{x}_\alpha)\right\}\left[1-e^{-\hbar\underline{\ell}\cdot\nabla_{\underline{x}_i}}\right](*)$$

$$(*)\; e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_\delta}\, V(\underline{x}_i-\underline{x}_\beta)\, e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i} >$$

To first order, the result is :

$$< \left[U, \hat{f}_1(\underline{k}, \underline{p}) \right] \left[U, \hat{f}_1(\underline{k}, \underline{p}') \right] >_+ \qquad (5.44)$$

$$= \frac{\hbar^2}{2} < \sum_{i=1}^{n} (\nabla_{1i} U)(\nabla_{1i} U) >_c \left\{ M(\underline{p} - \tfrac{\hbar}{2}\underline{k}) \left[\nabla_{\underline{p}}^2 \right.\right.$$

$$\left.\left. - \frac{\beta}{m} (\underline{p} - \tfrac{\hbar}{2}\underline{k}) \cdot \nabla_{\underline{p}} \right] + M(\underline{p} + \tfrac{\hbar}{2}\underline{k}) \left[\nabla_{\underline{p}}^2 - \frac{\beta}{m} (\underline{p} + \tfrac{\hbar}{2}\underline{k}) \cdot \nabla_{\underline{p}} \right] \right\} \delta(\underline{p} - \underline{p}')$$

$$- \hbar^2 < \sum_{i=1}^{n} \sum_{j=1}^{n}{}' e^{-i\underline{k} \cdot (\underline{x}_i - \underline{x}_j)} (\nabla_{1i} U)(\nabla_{1j} U) >_c : \nabla_{\underline{p}} M(\underline{p} - \tfrac{\hbar}{2}\underline{k}) (*)$$

$$(*) \quad \nabla_{\underline{p}'} M(\underline{p}' + \tfrac{\hbar}{2}\underline{k}) .$$

all the other terms introduce higher order particle distribution functions. This expression can be rewritten by noting the following relations :

$$\sum_{i=1}^{n} < \left(\frac{\partial U}{\partial x_i^\alpha} \right) \left(\frac{\partial U}{\partial x_i^\gamma} \right) >_c = \sum_{i=1}^{n} \int d[x_N] \frac{e^{-\beta U}}{Z_c} \frac{\partial U}{\partial x_i^\alpha} \frac{\partial U}{\partial x_i^\gamma} \qquad (5.45)$$

$$= -\frac{1}{\beta} \sum_{i=1}^{n} \int d[x_N] \frac{1}{Z_c} \frac{\partial U}{\partial x_i^\gamma} \left(\frac{\partial e^{-\beta U}}{\partial x_i^\alpha} \right)$$

$$= \frac{1}{\beta} \sum_{i=1}^{n} \int d[x_N] \frac{e^{-\beta U}}{Z_c} \frac{\partial^2 U}{\partial x_i^\alpha \partial x_i^\gamma}$$

$$= \frac{1}{\beta} D \, \delta_{\alpha\gamma}$$

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where α and γ stands for the components of the vector $\underline{r}_i$ and

$$D_{\alpha\gamma}(\underline{k}) = \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \frac{\partial U}{\partial r_i^\alpha} \frac{\partial U}{\partial r_j^\beta} \right\rangle_c \tag{5.46}$$

$$= -\frac{1}{\beta} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \int d[\underline{r}_N] e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \frac{\partial U}{\partial r_j^\gamma} \frac{1}{Z_c(\beta)} \left(\frac{\partial e^{-\beta U}}{\partial r_i^\alpha} \right)$$

$$= \frac{1}{\beta} \sum_{i=1}^{N} \sum_{j \neq i}^{N} \int d[\underline{r}_N] \frac{e^{-\beta U}}{Z_c(\beta)} \left(e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \frac{\partial^2 U}{\partial r_i^\alpha \partial r_j^\gamma} \right.$$

$$\left. - i\underline{k}_\alpha \frac{\partial U}{\partial r_j^\gamma} e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \right)$$

$$= \frac{1}{\beta} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \frac{\partial^2 U}{\partial r_i^\alpha \partial r_j^\beta} \right\rangle_c$$

$$- i \frac{k_\alpha}{\beta} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \frac{\partial U}{\partial r_j^\gamma} \right\rangle_c$$

$$= C_{\alpha\gamma}(\underline{k}) + \frac{1}{\beta^2} k_\alpha k_\gamma n^2 h(\underline{k})$$

with

$$C_{\alpha\gamma}(\underline{k}) = \frac{1}{\beta} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \frac{\partial^2 U}{\partial r_i^\alpha \partial r_j^\gamma} \right\rangle_c$$

$$= \frac{1}{\beta} \int dR \frac{\partial^2 V(R)}{\partial R^2} g(R) \cos \underline{k}\cdot\underline{R} \; \delta_{\alpha\gamma}$$

(5.44) becomes :

$$< \left[U, \hat{f}_1(\underline{k}, \underline{p}) \right] \left[U, \hat{f}_1^+(\underline{k}, \underline{p}') \right] >_+ \qquad (5.47)$$

$$= \frac{\hbar^2 D}{2\beta} \Bigg\{ M(\underline{p} - \tfrac{\hbar\underline{k}}{2}) \left[\nabla_{\underline{p}}^2 - \frac{\beta}{m} (\underline{p} - \tfrac{\hbar\underline{k}}{2}) \cdot \nabla_{\underline{p}} \right]$$

$$+ M(\underline{p} + \tfrac{\hbar\underline{k}}{2}) \left[\nabla_{\underline{p}}^2 - \frac{\beta}{m} (\underline{p} + \tfrac{\hbar\underline{k}}{2}) \cdot \nabla_{\underline{p}} \right] \Bigg\} \delta(\underline{p} - \underline{p}')$$

$$- \hbar^2 \nabla_{\underline{p}} M(\underline{p} - \tfrac{\hbar\underline{k}}{2}) \cdot \underline{\underline{D}}(\underline{k}) \cdot \nabla_{\underline{p}'} M(\underline{p}' + \tfrac{\hbar\underline{k}}{2})$$

Let us turn our attention to the other term now.

$$\int d\underline{p}_1 d\underline{p}_2 < \left[U, \hat{f}_1(\underline{k}, \underline{p}) \right] f_1^+(\underline{k}, \underline{p}_1) >_+ \Phi^{-1}(\underline{k}, \underline{p}_1, \underline{p}_2) < f_1(\underline{k}, \underline{p}_2) \left[U, f_1^+(\underline{k}, \underline{p}') \right] >_+ \qquad (5.48)$$

$$= \int d\underline{p}_2 \; \frac{\hbar \underline{k} \cdot (\underline{p} - \tfrac{\hbar\underline{k}}{2})}{m} M(\underline{p} - \tfrac{\hbar\underline{k}}{2}) \left(\frac{n \hat{R}(\underline{k})}{1 + n \hat{R}(\underline{k}) G_1(\underline{k})} \right) (*)$$

$$(*) \; \frac{M(\underline{p}_2 + \tfrac{\hbar\underline{k}}{2})}{\tfrac{1}{2} \left[M(\underline{p}_2 - \tfrac{\hbar\underline{k}}{2}) + M(\underline{p}_2 + \tfrac{\hbar\underline{k}}{2}) \right]} \; n^2 \hat{R}(\underline{k}) \; \frac{\underline{k} \cdot (\underline{p}' + \tfrac{\hbar\underline{k}}{2})}{m} M(\underline{p}' + \tfrac{\hbar\underline{k}}{2}) M(\underline{p}_2 - \tfrac{\hbar\underline{k}}{2})$$

$$= - \hbar^2 n^2 \hat{R}(\underline{k}) \; \frac{\underline{k} \cdot (\underline{p} - \hbar \underline{k}_2)}{m} M(\underline{p} - \tfrac{\hbar\underline{k}}{2}) \left(\frac{n \hat{R}(\underline{k}) G_1(\underline{k})}{1 + n \hat{R}(\underline{k}) G_1(\underline{k})} \right) (*)$$

$$(*) \; \frac{\underline{k} \cdot (\underline{p}' + \tfrac{\hbar\underline{k}}{2})}{m} M(\underline{p}' + \tfrac{\hbar\underline{k}}{2})$$

where we have dropped terms of order h . Combining (5.48) and (5.47),we get :

$$
\begin{aligned}
&\left\langle \left\{ (1-P)\,\dot{\hat{F}}(\underline{k},\underline{p}) \right\} \dot{\hat{f}}(\underline{k},\underline{p}') \right\rangle_{+} \qquad (5.49)\\
&= -\frac{D}{2\beta}\left\{ M\left(\underline{p}-\tfrac{t_1\underline{k}}{2}\right)\left[\nabla_{\underline{p}}^{2} - \frac{\beta}{m}\left(\underline{p}-\tfrac{t_1\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right]\right.\\
&\left. + M\left(\underline{p}+\tfrac{t_1\underline{k}}{2}\right)\left[\nabla_{\underline{p}}^{2} - \frac{\beta}{m}\left(\underline{p}+\tfrac{t_1\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right] \right\} \delta(\underline{p}-\underline{p}')\\
&+ M\left(\underline{p}-\tfrac{t_1\underline{k}}{2}\right)\left(\underline{p}-\tfrac{t_1\underline{k}}{2}\right)\cdot\left[\frac{\beta^2}{m^2}\,\underline{\underline{C}}(\underline{k}) + \frac{\underline{k}\,\underline{k}}{m^2}\,\frac{n^2 P(\underline{k})}{1+n P(\underline{k}) G_1(\underline{k})}\right]\cdot\\
&\cdot\left(\underline{p}'+\tfrac{t_1\underline{k}}{2}\right) M\left(\underline{p}'+\tfrac{t_1\underline{k}}{2}\right)
\end{aligned}
$$

Finally the expression for the damping term is :

$$
\begin{aligned}
&\mathcal{G}(\underline{k},\underline{p}_1,\underline{p}_2,t) \qquad (5.50)\\
&\qquad = g(\underline{k},t)\int d\underline{p}_3 \left\langle \hat{F}(\underline{k},\underline{p}_3,0)\,\dot{\hat{f}}_1^{\dagger}(\underline{k},\underline{p}_3)\right\rangle_{+} \Phi^{-1}(\underline{k},\underline{p}_3,\underline{p}_2)
\end{aligned}
$$

$$= g(\underline{k},t)\int d\underline{p}_3 \left\{ -\frac{D}{2\beta}\left[M\left(\underline{p}-\frac{t_1\underline{k}}{2}\right)\left(\nabla_{\underline{p}}^2 - \frac{\beta}{m}\left(\underline{p}-\frac{t_1\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right)\right.\right.$$

$$\left.\left. + M\left(\underline{p}+\frac{t_1\underline{k}}{2}\right)\left(\nabla_{\underline{p}}^2 - \frac{\beta}{m}\left(\underline{p}+\frac{t_1\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right)\right] \delta(\underline{p}-\underline{p}_3 \right.$$

$$\left. + M\left(\underline{p}-\frac{t_1\underline{k}}{2}\right)\left(\underline{p}-\frac{t_1\underline{k}}{2}\right)\cdot\left[\frac{\beta^2}{m^2}\,\underline{\underline{C}}(\underline{k}) + \frac{\underline{k}\,\underline{k}}{m^2}\,\frac{n^2 P(k)}{1+n P(k) G_1(k)}\right]\right.$$

$$\left.\cdot\left(\underline{p}_3+\frac{t_1\underline{k}}{2}\right) M\left(\underline{p}_3+\frac{t_1\underline{k}}{2}\right)\right\}(*)\left\{\frac{\delta(\underline{p}_3-\underline{p}_2)}{\frac{n}{2}\left[M\left(\underline{p}_3-\frac{t_1\underline{k}}{2}\right)+M\left(\underline{p}+\frac{t_1\underline{k}}{2}\right)\right]}\right.$$

$$\left. - \left(\frac{P(k)}{1+n P(k) G_1(k)}\right)\frac{M\left(\underline{p}_3-\frac{t_1\underline{k}}{2}\right)}{\frac{1}{2}\left[M\left(\underline{p}_3-\frac{t_1\underline{k}}{2}\right)+M\left(\underline{p}_3+\frac{t_1\underline{k}}{2}\right)\right]}(*)\right.$$

$$(*)\left[1 - \frac{t_1\beta}{2m}\,\underline{k}\cdot\left(\underline{p}_3-\frac{t_1\underline{k}}{2}\right) + \frac{t_1\beta}{2m}\,\underline{k}\cdot\left(\underline{p}_2+\frac{t_1\underline{k}}{2}\right)\right.$$

$$\left.\left. - \beta\frac{t_1^2\underline{k}^2}{2m}\, n P(k) G_1(k)\right]\frac{M\left(\underline{p}_2+\frac{t_1\underline{k}}{2}\right)}{\frac{1}{2}\left[M\left(\underline{p}_2-\frac{t_1\underline{k}}{2}\right)+M\left(\underline{p}_2+\frac{t_1\underline{k}}{2}\right)\right]}\right\}$$

After performing the integration, we obtain :

$$\Psi(\underline{k}, \underline{p}, \underline{p}_2, t) = \left(\frac{-D}{2\beta n}\right)\Bigg\{M\left(\underline{p} - \frac{t\underline{k}}{2}\right)\left[\nabla_{\underline{p}}^2 - \frac{\beta}{m}\left(\underline{p} - \frac{t\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right] \tag{5.51}$$

$$+ M\left(\underline{p} + \frac{t\underline{k}}{2}\right)\left[\nabla_{\underline{p}}^2 - \frac{\beta}{m}\left(\underline{p} + \frac{t\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right]\Bigg\}\frac{\delta(\underline{p} - \underline{p}_2)}{\frac{1}{2}\left[M\left(\underline{p}_2 - \frac{t\underline{k}}{2}\right) + M\left(\underline{p}_2 + \frac{t\underline{k}}{2}\right)\right]}$$

$$+ g(\underline{k}, t)\, M\left(\underline{p} - \frac{t\underline{k}}{2}\right)\left(\underline{p} - \frac{t\underline{k}}{2}\right)\cdot\left[\frac{\beta^2}{m^2}\underline{\underline{C}}(\underline{k}) + \frac{\underline{k}\,\underline{k}}{m^2}\frac{n\hat{P}(\underline{k})}{1 + m\hat{P}(\underline{k})G_1(\underline{k})}\right]\cdot$$

$$\cdot\left(\underline{p}_2 + \frac{t\underline{k}}{2}\right)\frac{M\left(\underline{p}_2 + \frac{t\underline{k}}{2}\right)}{\frac{1}{2}\left[M\left(\underline{p}_2 - \frac{t\underline{k}}{2}\right) + M\left(\underline{p}_2 + \frac{t\underline{k}}{2}\right)\right]}$$

$$+ g(\underline{k}, t)\left(\frac{D}{2\beta n}\right)\Bigg\{M\left(\underline{p} - \frac{t\underline{k}}{2}\right)\left[\nabla_{\underline{p}}^2 - \frac{\beta}{m}\left(\underline{p} - \frac{t\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right]$$

$$+ M\left(\underline{p} + \frac{t\underline{k}}{2}\right)\left[\nabla_{\underline{p}}^2 - \frac{\beta}{m}\left(\underline{p} + \frac{t\underline{k}}{2}\right)\cdot\nabla_{\underline{p}}\right]\Bigg\}\left(\frac{n\hat{P}(\underline{k})}{1 + m\hat{P}(\underline{k})G_1(\underline{k})}\right)(*)$$

$$(*)\frac{M\left(\underline{p} - t\underline{k}_1\right)}{\frac{1}{2}\left[M\left(\underline{p} - \frac{t\underline{k}}{2}\right) + M\left(\underline{p} + \frac{t\underline{k}}{2}\right)\right]}\Bigg[1 - \frac{t\beta}{2m}\,\underline{k}\cdot\left(\underline{p} - \frac{t\underline{k}}{2}\right) + \frac{t\beta}{2m}\,\underline{k}\cdot\left(\underline{p}_2 + \frac{t\underline{k}}{2}\right)$$

$$- \frac{\beta t^2 k^2}{2m} n\hat{P}(\underline{k})G_1(\underline{k})\Bigg]\frac{M\left(\underline{p}_2 + \frac{t\underline{k}}{2}\right)}{\frac{1}{2}\left[M\left(\underline{p}_2 - \frac{t\underline{k}}{2}\right) + M\left(\underline{p}_2 + \frac{t\underline{k}}{2}\right)\right]}$$

$$- g(\underline{k},t)\left(\frac{n\tilde{R}(\underline{k})}{1+n\tilde{R}(\underline{k})G_1(\underline{k})}\right) M\left(\underline{p}-\frac{t_1\underline{k}}{2}\right)\left(\underline{p}-\frac{t_1\underline{k}}{2}\right)\cdot\left[\frac{\beta^2}{m^2}\frac{\underline{\underline{C}}(\underline{k})}{n}+\right.$$

$$\left.+\frac{\underline{k}\,\underline{k}}{m^2}\left(\frac{n\tilde{R}(\underline{k})}{1+n\tilde{R}(\underline{k})G_1(\underline{k})}\right)\right]\cdot\left[-\frac{t_1\beta}{2m}\underline{\underline{H}}\cdot\underline{k}\right.$$

$$\left.+\underline{\underline{K}}_2(\underline{k})\left(1+\frac{t_1\beta}{2m}\underline{k}\cdot\left(\underline{p}_2+\frac{t_1\underline{k}}{2}\right)-\frac{\beta t_1^2\underline{k}^2}{2m}n\tilde{R}(\underline{k})G_1(\underline{k})\right)\right](*)$$

$$(*)\quad\frac{M\left(\underline{p}_2+\frac{t_1\underline{k}}{2}\right)}{\frac{1}{2}\left[M\left(\underline{p}_2-\frac{t_1\underline{k}}{2}\right)+M\left(\underline{p}_2+\frac{t_1\underline{k}}{2}\right)\right]}$$

where

$$\underline{\underline{H}}(\underline{k})=\int d\underline{p}\;\frac{M\left(\underline{p}-\frac{t_1\underline{k}}{2}\right)M\left(\underline{p}+\frac{t_1\underline{k}}{2}\right)}{\frac{1}{2}\left[M\left(\underline{p}-\frac{t_1\underline{k}}{2}\right)+M\left(\underline{p}+\frac{t_1\underline{k}}{2}\right)\right]}\left(\underline{p}+\frac{t_1\underline{k}}{2}\right)\left(\underline{p}-\frac{t_1\underline{k}}{2}\right) \qquad (5.52)$$

and

$$\underline{\underline{K}}_2(\underline{k})=\int d\underline{p}\;\frac{M\left(\underline{p}-\frac{t_1\underline{k}}{2}\right)M\left(\underline{p}+\frac{t_1\underline{k}}{2}\right)}{\frac{1}{2}\left[M\left(\underline{p}-\frac{t_1\underline{k}}{2}\right)+M\left(\underline{p}+\frac{t_1\underline{k}}{2}\right)\right]}\left(\underline{p}+\frac{t_1\underline{k}}{2}\right) \qquad (5.53)$$

The last integrations will be carried out to obtain the equation of motion and the time correlation function $\phi(\underline{k},\underline{p},\underline{p}',t)$. It is just a lot of algebra. The final result is :

$$\frac{d}{dt}\phi(\underline{k},\underline{P},\underline{P}',t) + i\left(\frac{\underline{k}\cdot\underline{P}}{m}\right)\phi(\underline{k},\underline{P},\underline{P}',t) \qquad (5.54)$$

$$- i\,\frac{\underline{k}\cdot\left(\underline{P}-\frac{t_1\underline{k}}{2}\right)}{m}\,M\left(\underline{P}-\frac{t_1\underline{k}}{2}\right)\left(\frac{n\,R(\underline{k})}{1+m\,R(\underline{k})G_1(\underline{k})}\right)\int d\underline{P}_2\left\{1 +\right.$$

$$\left. + \left(\frac{n\,R(\underline{k})G_1(\underline{k})}{1+m\,R(\underline{k})G_1(\underline{k})}\right)\left(\frac{\beta t_1^2\underline{k}^2}{2m}\,n\,R(\underline{k})G_1(\underline{k}) + \frac{t_1\beta}{2m}\,\frac{\underline{k}\cdot\underline{K}_1(\underline{k})}{G_1(\underline{k})}\right)\right\}(*)$$

$$(*)\quad \frac{M\left(\underline{P}_2+\frac{t_1\underline{k}}{2}\right)\,\phi(\underline{k},\underline{P}_2,\underline{P}',t)}{\frac{1}{2}\left[M\left(\underline{P}_2-\frac{t_1\underline{k}}{2}\right)+M\left(\underline{P}_2+\frac{t_1\underline{k}}{2}\right)\right]}$$

$$+ i\,\frac{\underline{k}\cdot\left(\underline{P}-\frac{t_1\underline{k}}{2}\right)}{m}\,M\left(\underline{P}-\frac{t_1\underline{k}}{2}\right)\left(\frac{n\,R(\underline{k})}{1+m\,R(\underline{k})G_1(\underline{k})}\right)^2\frac{t_1\beta}{2m}\,G_1(\underline{k})\int d\underline{P}_2\,(*)$$

$$(*)\;\underline{k}\cdot\left(\underline{P}_2+\frac{t_1\underline{k}}{2}\right)\frac{M\left(\underline{P}_2+\frac{t_1\underline{k}}{2}\right)}{\frac{1}{2}\left[M\left(\underline{P}_2-\frac{t_1\underline{k}}{2}\right)+M\left(\underline{P}_2+\frac{t_1\underline{k}}{2}\right)\right]}\,\phi(\underline{k},\underline{P}_2,\underline{P}',t)$$

$$- i\left(\frac{t_1 D}{4n}\right)\left\{M\left(\underline{P}-\frac{t_1\underline{k}}{2}\right)\left[\nabla_P^2 - \frac{\beta}{m}\left(\underline{P}-\frac{t_1\underline{k}}{2}\right)\cdot\nabla_P\right]\right.$$

$$\left. - M\left(\underline{P}+\frac{t_1\underline{k}}{2}\right)\left[\nabla_P^2 + \frac{\beta}{m}\left(\underline{P}+\frac{t_1\underline{k}}{2}\right)\cdot\nabla_P\right]\right\}\frac{\phi(\underline{k},\underline{P},\underline{P}',t)}{\frac{1}{2}\left[M\left(\underline{P}-\frac{t_1\underline{k}}{2}\right)+M\left(\underline{P}+\frac{t_1\underline{k}}{2}\right)\right]}$$

$$+ i\left(\frac{\hbar D}{4n}\right)\left(\frac{n R(\underline{k})}{1 + m R(\underline{k}) G_1(\underline{k})}\right)\left\{ - 2 M\left(p + \frac{\hbar \underline{k}}{2}\right)\frac{\beta^2}{m^2}\hbar \underline{k}\cdot\left[\underline{p} - \right.\right.$$

$$\left.\left. - (\underline{p} + 2\hbar \underline{k})\, e^{-\frac{\beta}{2m}\hbar \underline{k}\cdot \underline{p}}\right]\right\}(*)\int d\underline{p}_2 \frac{M(p_2 + \hbar k_2)\, \phi(\underline{k}, \underline{p}_2, \underline{p}', t)}{\frac{1}{2}\left[M\left(p_2 - \frac{\hbar k}{2}\right) + M\left(p_2 + \frac{\hbar k}{2}\right)\right]}$$

$$+ \int_0^t dt'\, g(\underline{k}, t - t')\left\{\left\{\left(\frac{-D}{2\beta}\right)\left\{M\left(p - \frac{\hbar \underline{k}}{2}\right)\left[\nabla_p^2 - \frac{\beta}{m}\left(p - \frac{\hbar \underline{k}}{2}\right)\cdot \nabla_p\right]\right.\right.\right.$$

$$\left.\left.\left. + M\left(p + \frac{\hbar \underline{k}}{2}\right)\left[\nabla_p^2 - \frac{\beta}{m}\left(p + \frac{\hbar \underline{k}}{2}\right)\cdot \nabla_p\right]\right\}\frac{\phi(\underline{k}, p, p', t)}{\frac{1}{2}\left[M\left(p - \frac{\hbar \underline{k}}{2}\right) + M\left(p + \frac{\hbar \underline{k}}{2}\right)\right]}\right.$$

$$+ M\left(p - \frac{\hbar \underline{k}}{2}\right)\left(p - \frac{\hbar \underline{k}}{2}\right)\cdot\left[\frac{\beta^2}{m^2}\frac{\underline{\underline{C}}(\underline{k})}{n} + \frac{\underline{k}\,\underline{k}}{m^2}\left(\frac{n R(\underline{k})}{1 + m R(\underline{k}) G_1(\underline{k})}\right)\right]\cdot \int d\underline{p}_2 (*)$$

$$(*)\left(p_2 - \hbar k/2\right)\frac{M\left(p_2 + \hbar k/2\right)}{\frac{1}{2}\left[M\left(p_2 - \frac{\hbar k}{2}\right) + M\left(p_2 + \frac{\hbar k}{2}\right)\right]}\phi(\underline{k}, \underline{p}_2, \underline{p}', t)$$

$$+ \left(\frac{D}{2\beta n}\right)\left(\frac{n R(\underline{k})}{1 + n R(\underline{k}) G_1(\underline{k})}\right)(-2)\, M\left(p + \frac{\hbar \underline{k}}{2}\right)\frac{\beta^2}{m^2}\hbar \underline{k}\cdot\left[\underline{p}\right.$$

$$\left. + (\underline{p} + 2\hbar \underline{k})\, e^{-\frac{\beta}{m}\hbar \underline{k}\cdot \underline{p}}\right](*)\int d\underline{p}_2 \frac{M\left(p_2 + \frac{\hbar \underline{k}}{2}\right)}{\frac{1}{2}\left[M\left(p_2 - \frac{\hbar \underline{k}}{2}\right) + M\left(p_2 + \frac{\hbar \underline{k}}{2}\right)\right]}(*)$$

$$(*)\left[1 - \frac{\hbar\beta}{2m}\underline{k}\cdot\left(\underline{p} - \frac{\hbar\underline{k}}{2}\right) + \frac{\hbar\beta}{2m}\underline{k}\cdot\left(\underline{p}_2 - \frac{\hbar\underline{k}}{2}\right) - \beta\frac{\hbar^2k^2}{2m} n R(k) G_1(k)\right](*)$$

$$(*)\ \phi(\underline{k}, \underline{p}_2, \underline{p}', t)$$

$$-\left(\frac{n R(k)}{1 + n R(k) G_1(k)}\right) M\left(\underline{p} - \frac{\hbar\underline{k}}{2}\right)\left(\underline{p} - \frac{\hbar\underline{k}}{2}\right)\cdot\left[\frac{\beta^2}{m^2}\frac{\underline{\underline{\zeta}}(k)}{m} + \right.$$

$$+ \frac{\underline{k}\,\underline{k}}{m^2}\left(\frac{n R(k)}{1 + n R(k) G_1(k)}\right)\cdot\int d\underline{p}_2\left[\frac{\hbar\beta}{2m}\underline{\underline{H}}(k)\cdot\underline{k}\right.$$

$$\left.\left. + \underline{\underline{\zeta}}_2(k)\left(1 + \frac{\hbar\beta}{2m}\underline{k}\cdot\left(\underline{p}_2 + \frac{\hbar\underline{k}}{2}\right) - \frac{\beta\hbar^2k^2}{2m} n R(k) G_1(k)\right)\right](*)\right.$$

$$\left.(*)\ \frac{M\left(\underline{p}_2 + \frac{\hbar\underline{k}}{2}\right)}{\frac{1}{2}\left[M\left(\underline{p}_2 - \frac{\hbar\underline{k}}{2}\right) + M\left(\underline{p}_2 + \frac{\hbar\underline{k}}{2}\right)\right]}\ \phi(\underline{k}, \underline{p}_2, \underline{p}', t)\right\}$$

Neglecting the terms containing $\frac{\hbar D}{4n}\left(\frac{n R(k)}{1 + n R(k)}\right)\frac{\beta^2}{m^2}k^2\hbar^2$ because they are small as compared to other terms (for liquid argon at $k = 2A^\circ$ this term is equal to 7×10^{-3}), as well as the last term because it is of highest order in $\hbar$, and taking the Laplace transform in time, we obtain :

$$s\tilde{\phi}(\underline{k},\underline{p},\underline{p}',s) + i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\tilde{\phi}(\underline{k},\underline{p},\underline{p}',s) \qquad (5.55)$$

$$-i\,\frac{\underline{k}\cdot(\underline{p}-t_1\frac{\underline{k}}{2})}{m}\,M(\underline{p}-t_1\tfrac{\underline{k}}{2})\left(\frac{n\,R(\underline{k})}{1+n\,R(\underline{k})G_1(\underline{k})}\right)G_2(\underline{k})(*)$$

$$(*)\int d\underline{p}_2\,\frac{M(\underline{p}_2+t_1\frac{\underline{k}}{2})}{\frac{1}{2}\left[M(\underline{p}_2-t_1\frac{\underline{k}}{2})+M(\underline{p}_2+t_1\frac{\underline{k}}{2})\right]}\,\phi(\underline{k},\underline{p}_2,\underline{p}',t)$$

$$-i\left(\frac{t_1 D}{4n}\right)\Bigg\{M(\underline{p}-t_1\tfrac{\underline{k}}{2})\left[\nabla_p^2-\frac{\beta}{m}(\underline{p}-t_1\tfrac{\underline{k}}{2})\right.$$

$$\left.-M(\underline{p}+t_1\tfrac{\underline{k}}{2})\left[\nabla_p^2-\frac{\beta}{m}(\underline{p}+t_1\tfrac{\underline{k}}{2})\cdot\nabla_p\right]\right\}\frac{\phi(\underline{k},\underline{p},\underline{p}',t)}{\frac{1}{2}\left[M(\underline{p}-t_1\frac{\underline{k}}{2})+M(\underline{p}+t_1\frac{\underline{k}}{2})\right]}$$

$$-\tilde{g}(\underline{k},s)\left(\frac{D}{2\beta n}\right)\Bigg\{M(\underline{p}-t_1\tfrac{\underline{k}}{2})\left[\nabla_p^2-\frac{\beta}{m}(\underline{p}-t_1\tfrac{\underline{k}}{2})\cdot\nabla_p\right]$$

$$+M(\underline{p}+t_1\tfrac{\underline{k}}{2})\left[\nabla_p^2-\frac{\beta}{m}(\underline{p}+t_1\tfrac{\underline{k}}{2})\cdot\nabla_p\right]\Bigg\}\frac{\phi(\underline{k},\underline{p},\underline{p}',t)}{\frac{1}{2}\left[M(\underline{p}-t_1\frac{\underline{k}}{2})+M(\underline{p}+t_1\frac{\underline{k}}{2})\right]}$$

$$+\tilde{g}(\underline{k},s)\,M(\underline{p}-t_1\tfrac{\underline{k}}{2})(\underline{p}-t_1\tfrac{\underline{k}}{2})\cdot\left[\frac{\beta^2}{m^2}\,\frac{\underline{\underline{C}}(\underline{k})}{n}+\frac{\underline{k}\,\underline{k}}{m^2}\left(\frac{n\,R(\underline{k})}{1+n\,R(\underline{k})G_1(\underline{k})}\right)\right.$$

$$\left.+i\,\frac{\underline{k}\,\underline{k}}{m^2}\,\frac{t\,\beta\,G_1(\underline{k})}{\tilde{g}(\underline{k},s)}\left(\frac{n\,R(\underline{k})}{1+n\,R(\underline{k})G_1(\underline{k})}\right)^2\right]\cdot\int d\underline{p}_2\,(\underline{p}_2-t_1\tfrac{\underline{k}}{2})\,(*)$$

$$(*)\,\frac{M(\underline{p}_2+t_1\underline{k}/2)}{\frac{1}{2}\left[M(\underline{p}_2-t_1\frac{\underline{k}}{2})+M(\underline{p}_2+t_1\frac{\underline{k}}{2})\right]}\,\tilde{\phi}(\underline{k},\underline{p}_2,\underline{p}',s)$$

$$=\phi(\underline{k},\underline{p},\underline{p},0)$$

where

$$G_2(\underline{k}) = 1 + \left(\frac{n\tilde{R}(\underline{k})G_1(\underline{k})}{1+n\tilde{R}(\underline{k})G_1(\underline{k})}\right)\left(\frac{\beta\hbar^2k^2}{2m}n\tilde{R}(\underline{k})G_1(\underline{k}) + \frac{\hbar\beta\,\underline{k}\cdot\underline{K}_1(\underline{k})}{2mG_1(\underline{k})}\right) \quad (5.56)$$

and $\phi(\underline{k},\underline{p},\underline{p}';0)$ is given by equation (5.21).

It is the solution of this equation that will give us the total neutron scattering function. But let us look first at two limiting cases : the ideal gas limit and the classical limit.

5.1 a : THE IDEAL GAS LIMIT

Upon letting the potential go to zero in equation (5.55), we obtain :

$$s\tilde{\phi}(\underline{k},\underline{p},\underline{p}',s) + i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\tilde{\phi}(\underline{k},\underline{p},\underline{p}',s) \quad (5.57)$$

$$= \frac{n}{2}\delta(\underline{p}-\underline{p}')\left[M(\underline{p}-\frac{\hbar\underline{k}}{2}) + M(\underline{p}+\frac{\hbar\underline{k}}{2})\right]$$

Let us solve this equation for the scattering function. The integration over dp' is easily carried out :

$$\tilde{\phi}(\underline{k},\underline{p},s) = \frac{n}{2}\,\frac{\left[M(\underline{p}-\frac{\hbar\underline{k}}{2}) + M(\underline{p}+\frac{\hbar\underline{k}}{2})\right]}{s + i\,\frac{\underline{k}\cdot\underline{p}}{m}} \quad (5.58)$$

Let $S \to -i\omega + \epsilon$ and integrate over $d\underline{p}$:

$$S^{sym}(\underline{k},\omega) = \frac{Re}{(2\pi)} \lim_{\epsilon \to 0} \frac{n}{2} \int d\underline{p} \, \frac{\left[M(p-\underline{k}\frac{h}{2}) + M(p+\underline{k}\frac{h}{2})\right]}{-i\omega + i\frac{\underline{k}\cdot\underline{p}}{m} + \epsilon} \qquad (5.59)$$

If we choose $\underline{k}$ to be along the z-axis we can integrate over dp_x and dp_y :

$$S^{sym}(\underline{k},\omega) = Re \lim_{\epsilon \to 0} \frac{i}{2\pi} \frac{n}{2} \int \frac{dp \left[M(p-\underline{k}\frac{h}{2}) + M(p+\underline{k}\frac{h}{2})\right]\left(\frac{m}{k}\right)}{\frac{m\omega}{k} - p + i\epsilon} \qquad (5.60)$$

Using the relation

$$\lim_{\epsilon \to 0^+} \frac{1}{\omega - \omega' + i\epsilon} = P\frac{1}{\omega - \omega'} - i\pi\delta(\omega - \omega')$$

and taking the real part.

$$S^{sym}(\underline{k},\omega) = \frac{n}{2}\left(\frac{m\beta}{2\pi}\right)^{1/2}\frac{1}{k}\left[M\left(\frac{m\omega}{k} - \underline{k}\frac{h}{2}\right) + M\left(\frac{m\omega}{k} + \underline{k}\frac{h}{2}\right)\right] \qquad (5.61)$$

$$= \frac{n}{2}\left(\frac{m\beta}{2\pi}\right)^{1/2}\frac{1}{k}\left[1 + e^{-\beta\hbar\omega}\right]M\left(\frac{m\omega}{k} - \underline{k}\frac{h}{2}\right)$$

From equation (5.5), we obtain the scattering function :

$$S(\underline{k},\omega) = \frac{2}{1+e^{-\beta\hbar\omega}}\, S^{sym}(\underline{k},\omega) \qquad (5.62)$$

$$= \frac{n}{k}\left(\frac{m\beta}{2\pi}\right)^{1/2} M\left(\frac{m\omega}{k} - \frac{k\hbar}{2}\right)$$

which is the correct result for neutron scattering from non-degenerate perfect gases.

5.1.b : THE CLASSICAL LIMIT

The classical limit is obtained by letting $\hbar$ go to zero everywhere in equation (5.55). The result is :

$$s\,\tilde{\Phi}(\underline{k},\underline{p},\underline{p}',s) + i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\tilde{\Phi}(\underline{k},\underline{p},\underline{p}',s) \qquad (5.63)$$

$$-i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right) M(p)\left(\frac{n\hat{h}(k)}{1+n\hat{h}(k)}\right)\int d\underline{p}_2\, \tilde{\Phi}(\underline{k},\underline{p}_2,\underline{p}',s)$$

$$-\tilde{g}(\underline{k},s)\left(\frac{D}{\beta m}\right) M(p)\left[\nabla_p^2 - \frac{\beta}{m}\underline{p}\cdot\nabla_p\right]\frac{\tilde{\Phi}(\underline{k},\underline{p},\underline{p}',s)}{M(p)}$$

$$+ M(p)\,\tilde{g}(\underline{k},s)\,\underline{p}\cdot\left[\frac{\beta^2}{m^2}\frac{\underline{\underline{\zeta}}(k)}{n} + \frac{\underline{k}\,\underline{k}}{m^2}\left(\frac{n\hat{h}(k)}{1+n\hat{h}(k)}\right)\right]\cdot\int d\underline{p}_2\, \underline{p}_2\,\tilde{\Phi}(\underline{k},\underline{p}_2,\underline{p}',s)$$

$$= n\delta(p-p')\,M(p) + n^2\hat{h}(k)\,M(p)\,M(p')$$

This equation can be rewritten as :

$$s\,\tilde{\phi}(\underline{k},p,p',s) + i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\tilde{\phi}(\underline{k},p,p',s) \qquad (5.64)$$

$$-i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\left(\frac{n\,R(\underline{k})}{1+n\,R(\underline{k})}\right)M(p)\int dp_2\,\tilde{\phi}(\underline{k},p_2,p',s)$$

$$-\hat{g}(\underline{k},s)\left(\frac{D}{\beta m}\right)\left[\nabla_p^2 + \frac{\beta}{m}\nabla_p\cdot p\right]\tilde{\phi}(\underline{k},p,p',s)$$

$$+\tilde{g}(\underline{k},s)\,M(p)\,p\cdot\left[\frac{\beta^2}{m^2}\,\frac{\underline{\underline{C}}(\underline{k})}{n} + \frac{\underline{k}\,\underline{k}}{m^2}\left(\frac{n\,R(\underline{k})}{1+n\,R(\underline{k})}\right)\right]\cdot$$

$$\cdot\int dp_2\; p_2\,\tilde{\phi}(\underline{k},p_2,p',s)$$

$$= n\,\delta(p-p')\,M(p) + n^2\,R(\underline{k})\,M(p)\,M(p')$$

It is identical to the equation obtained classically by Aksacu and Duderstadt except for minor differences due to the fact that they used as their dynamical variables

$$f_i(\underline{k},p,t) = \sum_{i=1}^{n} e^{i\,\underline{k}\cdot\underline{r}_i(t)}\,\delta(p-p_i(t)) - \langle f_i(\underline{k},p)\rangle \qquad (5.65)$$

$$f(\underline{k},p,t) = \sum_{i=1}^{n} e^{i\,\underline{k}\cdot\underline{r}_i(t)}\,\delta(p-p_i(t)) - n\,\delta(\underline{k})\,M(p)$$

while we have used essentially the quantum analogue of :

$$f(\underline{k},p,t) = \sum_{i=1}^{n} e^{-i\,\underline{k}\cdot\underline{r}_i(t)}\,\delta(p-p_i(t)) \qquad (5.66)$$

The solution of the classical equation along with the model

$$g(\underline{k},t) = e^{-\alpha(\underline{k})t} \qquad (5.67)$$

where $\alpha(\underline{k})$ is obtained by requiring the scattering function to have the proper form for small and large k, gave good agreement with Rahman's computer experiment. This suggests that the information extracted through equation (5.64) is adequate and compare well with the exact solution of the Liouville equation.

5.1.c : QUANTUM CORRECTIONS TO THE CLASSICAL EQUATION.

Returning to equation (5.55), we see that quantum corrections appear mostly as a displacement of the momentum $\underline{p}$ by $+\hbar\frac{\underline{k}}{2}$ or $-\hbar\frac{\underline{k}}{2}$ and as a factor $e^{\beta\frac{k^2\hbar^2}{m}}$. It is almost impossible to solve this equation exactly for the scattering function. However we shall make the following approximations in order to have an equation that we can solve.

$$\frac{M(p + \frac{k\hbar}{2})}{\frac{1}{2}\left[M(p-\frac{k\hbar}{2}) + M(p+\frac{k\hbar}{2})\right]} \approx 1 \qquad (5.68)$$

and

$$\frac{1}{\frac{1}{2}\left[M(p-\frac{k\hbar}{2}) + M(p+\frac{k\hbar}{2})\right]} \approx \frac{1}{M(p-\frac{k\hbar}{2})} \quad \text{OR} \quad \frac{1}{M(p+\frac{k\hbar}{2})} \qquad (5.69)$$

With these approximations, equation (5.55) becomes after integrating over dp'

$$s\,\tilde{\Phi}(\underline{k},\underline{p},s) + i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\tilde{\Phi}(\underline{k},\underline{p},s) \tag{5.70}$$

$$- i\,\frac{\underline{k}\cdot(\underline{p}-\frac{t_k\underline{k}}{2})}{m}\left(\frac{n\,R(\underline{k})\,G_2(\underline{k})}{1+n\,R(\underline{k})\,G_1(\underline{k})}\right) M(\underline{p}-\tfrac{t_k\underline{k}}{2})\int d\underline{p}_2\,\tilde{\Phi}(\underline{k},\underline{p}_2,s)$$

$$+ i\left(\frac{t_k D}{4n}\right)\frac{\beta}{m}\left[t_k\,\underline{k}\cdot\nabla_p\right]\tilde{\Phi}(\underline{k},\underline{p},s)$$

$$- \tilde{g}(\underline{k},s)\left(\frac{D}{\beta n}\right)\left[\nabla_p^2 + \frac{\beta}{m}\,\nabla_p\cdot\underline{p}\right]\tilde{\Phi}(\underline{k},\underline{p},s)$$

$$+ \tilde{g}(\underline{k},s)\,M(\underline{p}-\tfrac{t_k\underline{k}}{2})\,(\underline{p}-\tfrac{t_k\underline{k}}{2})\cdot\left[\frac{\beta^2}{nm^2}\,\underline{\underline{C}}(\underline{k})\right.$$

$$\left. + \frac{\underline{k}\,\underline{k}}{m^2}\left(\frac{n\,R(\underline{k})}{1+n\,R(\underline{k})\,G_1(\underline{k})}\right) + i\,\frac{\underline{k}\,\underline{k}}{m^2}\,\frac{t_k\beta}{\tilde{g}(\underline{k},s)}\,G_1(\underline{k})\left(\frac{n\,R(\underline{k})}{1+n\,R(\underline{k})\,G_1(\underline{k})}\right)^2\right]\cdot$$

$$\cdot\int d\underline{p}_2\,(\underline{p}_2+\tfrac{t_k\underline{k}}{2})\,\tilde{\Phi}(\underline{k},\underline{p}_2,s)$$

$$= \frac{n}{2}\left[M(\underline{p}-\tfrac{t_k\underline{k}}{2}) + M(\underline{p}+\tfrac{t_k\underline{k}}{2})\right]$$

$$+ n^2\,R(\underline{k})\,M(\underline{p}-\tfrac{t_k\underline{k}}{2})\left[1 - \frac{t_k\beta}{2m}\,\underline{k}\cdot(\underline{p}-\tfrac{t_k\underline{k}}{2})\right]$$

Let us take $\underline{k}$ to be along the z-axis and integrate over dp_x dp_y and let p stand for p_3. After taking the Fourier transform in momentum space:

$$\tilde{Y}(k,\mu,s) = \int_{-\infty}^{\infty} dp\, e^{i\mu p}\, \tilde{\phi}(k,p,s) \tag{5.71}$$

and letting $\mu = \sqrt{\frac{\beta}{m}}\, u$,we get :

$$\frac{d}{du} Y(k,u,s) + \frac{3 + Au + u^2}{K + u} Y(k,u,s) \tag{5.72}$$

$$= \frac{(n/2)\, e^{-u^2/2}}{(D/mn)\,\tilde{g}(k,s)(K+u)} \left\{ e^{-i\frac{u}{2}\left(\beta\frac{k^2h^2}{m}\right)^{1/2}} + e^{i\frac{u}{2}\left(\beta\frac{k^2h^2}{m}\right)^{1/2}} \left[1 + \right.\right.$$

$$\left.\left. + 2\, n R(k) \left(1 - i\frac{u}{2}\sqrt{\beta\frac{k^2h^2}{m}} \right) \right] \right\}$$

$$- \frac{(n/2)\, e^{-u^2/2}\, e^{i\frac{u}{2}\sqrt{\beta\frac{k^2h^2}{m}}}}{(D/mn)\,\tilde{g}(k,s)\,(K+u)} \left\{ R(s)\, u \sqrt{\frac{\beta}{m}} \left(\frac{dY(k,u,s)}{du}\right)_{u=0} \right.$$

$$\left. + \left(2\frac{h\,L(k)}{\beta} + i\frac{kh}{2} R(s) \right) \sqrt{\frac{\beta}{m}}\, u\; Y(k,0,s) \right\}$$

where

$$K = \frac{n}{D}\frac{k}{\tilde{g}(k,s)} \quad ; \quad 3 = \frac{s}{\frac{D}{m}\tilde{g}(k,s)} \tag{5.73}$$

$$R(s) = \frac{m}{\beta}\, g(k,s) \left[\frac{\beta^2}{nm^2} C(k) + \frac{k^2}{m^2} \frac{n R(k)}{1 + n R(k) G_1(k)} \right. \tag{5.74}$$

$$\left. + i\frac{k^2}{m^2}\frac{k\beta}{\tilde{g}(k,s)} G_1(k) \left(\frac{n R(k)}{1 + n R(k) G_1(k)} \right)^2 \right]$$

$$A = \frac{k\beta^2}{4\sqrt{m\beta}} \frac{k_2}{\tilde{g}(k,s)} \quad ; \quad L(k) = \frac{R(k)\,G_2(k)}{1 + n\,R(k)\,G_1(k)} \qquad (5.75)$$

After noting that:

$$\left(\frac{dY(k,u,s)}{du}\right)_{u=0} = -\frac{\beta}{k} Y(k,0,s) + \frac{m\,n}{k}\left(1 + n\,R(k)\right)$$

the solution of this first order differential equation is just (for u=0 only)

$$Y(k,0,s) = \frac{(n/2)\quad e^{(k-A)k}}{\left[1 + I(k,s)\right]\left[k\right]^{\beta + k^2 - Ak}} \int_0^k dy\, e^{-(k-A)y} \qquad (5.76)$$

$$(*) \quad \left[y\right]^{\beta + k^2 - Ak - 1} \; Q(y-k,s)$$

where

$$Q(u,s) = \frac{1}{(D/m_n)\,\tilde{g}(k,s)} \left\{ e^{-i\frac{u}{2}\sqrt{\beta \frac{k_1^2 k^2}{m}}} + e^{i\frac{u}{2}\sqrt{\beta \frac{k_1^2 k^2}{m}}} \left[1 + \right. \right. \qquad (5.77)$$

$$\left. \left. + \; 2\,n\,R(k)\left(1 - i\,\frac{u}{2}\sqrt{\beta \frac{k_1^2 k^2}{m}}\right)\right]\right\}$$

$$I(k,s) = \frac{(n/2)\quad e^{k(k-A)}}{(D/m_n)\,\tilde{g}(k,s)\left[k\right]^{\beta + k^2 - Ak}} \int_0^k dy\; e^{-(k-A)y} \qquad (5.78)$$

$$(*) \left[y\right]^{\beta + k^2 - Ak - 1} \; (y-k)\sqrt{\frac{\beta}{m}} \left\{ R(s)\,\frac{n\,m}{k}\left(1 + n\,R(k)\right) \right.$$

$$\left. + \left[\frac{2\,k_2\,L(k)}{\beta} - R(s)\left(\frac{\beta}{k} - i\,\frac{k_1 k_2}{2}\right)\right]\right\}$$

The total scattering function is then

$$S(k,\omega) = \frac{(n/\pi)}{1 + e^{-\beta\hbar\omega}} \operatorname{Re} \lim_{s \to -i\omega} \frac{1}{[1 + I(k,s)]}(*) \quad (5.79)$$

$$(*)\ \frac{e^{k(k-A)}}{[k]^{3+k^2-Ak}} \int_0^k dy\, e^{-(k-A)y} [y]^{3+k^2-Ak-1} Q(y-k,s)$$

It is this equation that should be compared to the results of neutron scattering experiments.But we still have to say more about the function g(k,t). Several models have been proposed for this function, but the model that seems to give the best fit to the computer experiment is due to Akcasu and Duderstadt:

$$g(k,t) = e^{-\alpha(k)t} . \quad (5.80)$$

$\alpha(k)$ is determined by requiring, for $\omega = 0$

$$S(k,0) = \frac{n}{k}\left(\frac{m\beta}{2\pi}\right)^{1/2} e^{-\beta\frac{k^2\hbar^2}{8m}} \quad \text{for large } k \quad (5.81)$$

$$S(k,0) = \frac{n}{D\pi k^2} \quad \text{for small } k \quad 5.82)$$

where

D = the diffusion coefficient

5.2 THE HYDRODYNAMIC APPROACH

Any set of microscopic density operators in configu-

ration space, which includes the number density, can be taken to form a vector $\underline{A}(t)$ whose time evolution can be studied via the projection operator technique of section (3.2). However, for reasons which will be clear very shortly we shall choose a vector $\underline{A}(t)$ with the following three components :

$$\hat{a}_1(t) = \hat{\rho}(\underline{k},t) = \sum_{i=1}^{n} e^{-i\,\underline{k}\cdot\underline{r}_i(t)} \tag{5.83}$$

$$\hat{a}_2(t) = \underline{k}\cdot\hat{\underline{J}}(\underline{k},t) = \underline{k}\cdot\sum_{i=1}^{n}\left(\underline{p}_i(t)\, e^{-i\underline{k}\cdot\underline{r}_i(t)} + e^{-i\underline{k}\cdot\underline{r}_i(t)}\,\underline{p}_i(t)\right) \tag{5.84}$$

$$\hat{a}_3(t) = \hat{E}(\underline{k},t) - \frac{\langle \hat{E}(\underline{k},t)\,\hat{\rho}^{+}(\underline{k})\rangle_{+}}{\langle \hat{\rho}(\underline{k})\,\hat{\rho}^{+}(\underline{k})\rangle_{+}}\,\hat{\rho}(\underline{k},t) \tag{5.85}$$

with

$$\hat{E}(\underline{k},t) = \frac{1}{8m}\sum_{i=1}^{n}\left\{\hat{\underline{p}}_i^{\,2}\, e^{-i\underline{k}\cdot\underline{r}_i} + 2i\,\hat{\underline{p}}_i\cdot e^{-i\underline{k}\cdot\underline{r}_i}\cdot\hat{\underline{p}}_i + e^{-i\underline{k}\cdot\underline{r}_i}\,\hat{\underline{p}}_i^{\,2}\right\} + \frac{1}{2}\sum_{i=1}^{n}\sum_{\alpha=1}^{N}\sum_{\gamma\neq\alpha}^{n} V(\underline{r}_\alpha - \underline{r}_\gamma)\, e^{-i\underline{k}\cdot\underline{r}_i} \tag{5.86}$$

$\hat{a}_1(\underline{k}t)$, $\hat{a}_2(\underline{k}t)$, $\hat{E}(\underline{k},t)$ represent respectively the number density, the current density along the vector $\underline{k}$ and the energy density of the system.

Note that all of $\hat{a}_1(\underline{k},t)$, $\hat{a}_2(\underline{k},t)$ and $\hat{a}_3(\underline{k},t)$ are Fourier components of hermitian operators.

$$\hat{\underline{A}}(\underline{k},t) = \begin{pmatrix} \hat{a}_1(\underline{k},t) \\ \hat{a}_2(\underline{k},t) \\ \hat{a}_3(\underline{k},t) \end{pmatrix} \tag{5.87}$$

A property of these operators and their thermal average which will be used extensively in the subsequent calculation is their sign change under time reversal. Since the Hamiltonian of our system is spin independent, any operator Q is transformed into an operator Q' under time reversal by the following operation[62-63]

$$Q' = K\, Q^{+}\, K^{-1} \tag{5.88}$$

where

K = the complex conjugation operator

Q^{+} = the hermitian adjoint of Q

Under the above transformation, each of the three components of $\underline{A}$ transforms like :

$$\hat{a}_1(\underline{k}) = +\hat{a}_1(\underline{k}) \tag{5.89}$$

$$\hat{a}_2(\underline{k}) = -\hat{a}_2(\underline{k}) \tag{5.90}$$

$$\hat{a}_3(\underline{k}) = +\hat{a}_3(\underline{k}) \tag{5.91}$$

$\hat{a}_1(\underline{k})$ and $\hat{a}_3(\underline{k})$ are said to be even with respect to time reversal while $a_2(\underline{k})$ is said to be odd. We will denote this change of sign by :

$$\hat{a}_i(\underline{k}) = \epsilon_i\, a_i(\underline{k}) \tag{5.92}$$

where

$$\epsilon_i = +1 \quad \text{for even variable}$$

$$= -1 \quad \text{for odd variable}$$

The thermal average of two dynamical variables $\hat{a}_i$ and $\hat{a}_j$ has the following property :

$$\begin{aligned} \langle \hat{a}_i \hat{a}_j^{\dagger} \rangle &= \langle \hat{a}_i(t) \hat{a}_j(t) \rangle \\ &= \langle \hat{a}_i(-t) \hat{a}_j^{\dagger}(-t) \rangle \end{aligned} \tag{5.93}$$

The Hamiltonian of the system is invariant with respect to time reversal (there are no external parameters odd with respect to time reversal in H) so that,

$$\begin{aligned} \langle \hat{a}_i \hat{a}_j \rangle_+ &= \langle (\hat{a}_i \hat{a}_j)' \rangle_+ \\ &= \epsilon_i \epsilon_j \langle a_i a_j \rangle_+ \\ &= 0 \quad \text{if} \quad \epsilon_i \epsilon_j = -1 \end{aligned} \tag{5.94}$$

Because the liquid is isotropic, $\langle a_i(k,t)\, a_j(k) \rangle_+$ is invariant with respect to the inversion of $k \rightarrow -k$ and turns out to be real.[24]

It is clear now why we had to choose a symmetrized thermal average for our correlation functions.

$$\begin{aligned} \langle (\hat{a}_i(k)\, a_j^{\dagger}(k))' \rangle_+ &= \tfrac{1}{2} \langle (\hat{a}_i(k)\, \hat{a}_j^{\dagger}(k))' + (\hat{a}_j^{\dagger}(k)\, \hat{a}_i(k))' \rangle \\ &= \tfrac{1}{2} \epsilon_i \epsilon_j \langle K \hat{a}_j(-k) \hat{a}_i^{\dagger}(-k) K^{-1} + K \hat{a}_i^{\dagger}(-k) \hat{a}_j(-k) K^{-1} \rangle \end{aligned} \tag{5.95}$$

$$= \epsilon_i \epsilon_j \; \langle \hat{a}_i(\underline{k}) a_j(\underline{k}) \rangle_+$$

Had we not symmetrized the thermal average, we would not have been able to utilize its time reversal invariance property. From equation (5.94), we have :

$$\begin{aligned} \langle \dot{\hat{a}}_2(\underline{k}) \hat{a}_2^+ \rangle_+ &= \langle \dot{\hat{a}}_1(\underline{k}) \hat{a}_3^+(\underline{k}) \rangle_+ \\ &= \langle \dot{\hat{a}}_3(\underline{k}) \hat{a}_3(\underline{k}) \rangle_+ = \langle \hat{a}_1(\underline{k}) \hat{a}_2(\underline{k}) \rangle_+ \\ &= \langle \hat{a}_2(\underline{k}) \hat{a}_3(\underline{k}) \rangle_+ = 0 \end{aligned} \tag{5.96}$$

The reason for choosing $a_3(\underline{k},t)$ in the form given by (5.85) is obvious when we note that :

$$\langle \hat{a}_1(\underline{k}) \hat{a}_3^+(\underline{k}) \rangle_+ = \langle \hat{\rho}(\underline{k}) \hat{E}^+(\underline{k}) \rangle_+ - \frac{\langle \hat{\rho}(\underline{k}) E^+(\underline{k}) \rangle_+}{\langle \hat{\rho}(\underline{k}) \hat{\rho}^+(\underline{k}) \rangle_+} \langle \hat{\rho}(\underline{k}) \hat{\rho}^+(\underline{k}) \rangle_+ \tag{5.97}$$

Since $= 0$

$$\langle \hat{a}_2(\underline{k}) \hat{a}_1^+(\underline{k}) \rangle = 0 \tag{5.98}$$

the three components $\hat{a}_1(\underline{k})$, $\hat{a}_2(\underline{k})$, $\hat{a}_3(\underline{k})$ are said to be orthogonal to each other.

The time evolution of the correlation matrix

$$\underline{\underline{\Phi}}(t) = \begin{pmatrix} \langle \hat{a}_1(\underline{k},t) \hat{a}_1^+(\underline{k}) \rangle_+ & \langle \hat{a}_1(\underline{k},t) \hat{a}_2^+(\underline{k}) \rangle_+ & \langle \hat{a}_1(\underline{k},t) \hat{a}_3^+(\underline{k}) \rangle_+ \\ \langle \hat{a}_2(\underline{k},t) \hat{a}_1^+(\underline{k}) \rangle_+ & \langle \hat{a}_2(\underline{k},t) \hat{a}_2^+(\underline{k}) \rangle_+ & \langle \hat{a}_2(\underline{k},t) \hat{a}_3^+(\underline{k}) \rangle_+ \\ \langle \hat{a}_3(\underline{k},t) \hat{a}_1^+(\underline{k}) \rangle_+ & \langle \hat{a}_3(\underline{k},t) \hat{a}_2^+(\underline{k}) \rangle_+ & \langle \hat{a}_3(\underline{k},t) \hat{a}_3^+(\underline{k}) \rangle_+ \end{pmatrix} \tag{5.99}$$

is given by equation (3.53). The static correlation matrix is just :

$$\underline{\underline{\Phi}} = \begin{pmatrix} \langle \hat{a}_1(k)\hat{a}_1^{+}(k)\rangle_{+} & 0 & 0 \\ 0 & \langle \hat{a}_2(k)\hat{a}_2^{+}(k)\rangle_{+} & 0 \\ 0 & 0 & \langle \hat{a}_3(k)\hat{a}_3^{+}(k)\rangle_{+} \end{pmatrix} \tag{5.100}$$

where we have utilized properties (5.96) and (5.97), while its inverse is :

$$\underline{\underline{\Phi}}^{-1} = \begin{pmatrix} \frac{1}{\langle \hat{a}_1(k)\hat{a}_1^{+}(k)\rangle_{+}} & 0 & 0 \\ 0 & \frac{1}{\langle \hat{a}_2(k)\hat{a}_2^{+}(k)\rangle_{+}} & 0 \\ 0 & 0 & \frac{1}{\langle \hat{a}_3(k)\hat{a}_3^{+}(k)\rangle_{+}} \end{pmatrix} \tag{5.101}$$

the frequency matrix

$$\underline{\underline{\Omega}} = \underline{\underline{\Phi}}^{-1} \cdot \underline{\underline{\Lambda}} \tag{5.102}$$

becomes, after using the hermition property of the operator L and the fact that

$$\dot{\hat{a}}_1(t) = -\hat{a}_2(t), \tag{5.103}$$

$$\underline{\underline{\Omega}} = \begin{pmatrix} 0 & i\,\dfrac{\langle \hat{a}_2(k)\hat{a}_2^{+}(k)\rangle_{+}}{\langle \hat{a}_1(k)\hat{a}_1^{+}(k)\rangle_{+}} & 0 \\ i & 0 & i\left[\dfrac{\langle \dot{\hat{a}}_2(k)\hat{a}_3^{+}(k)\rangle_{+}}{i\langle \hat{a}_2(k)\hat{a}_2^{+}(k)\rangle_{+}}\right] \\ 0 & i\left[\dfrac{\langle \dot{\hat{a}}_3(k)\hat{a}_2^{+}(k)\rangle_{+}}{i\langle \hat{a}_3(k)\hat{a}_3^{+}(k)\rangle_{+}}\right] & 0 \end{pmatrix} \tag{5.104}$$

The damping term has to be approximated. We shall choose the Markovian approximation, i.e.,

$$\int_0^t dt\ \underline{\underline{\Phi}}(t-t')\cdot\underline{\underline{\Psi}}(t') \cong \underline{\underline{\Phi}}(t)\cdot\underline{\underline{\varpi}} \tag{5.105}$$

where

$$\underline{\underline{\varpi}} = \underline{\underline{\Phi}}^{-1}\cdot\int_0^{\infty}\underline{\underline{\Psi}}(t')\,dt' \tag{5.106}$$

Equation (5.105) was arrived at by expanding $\underline{\underline{\Phi}}(t-t')$ about t and keeping the first term, then letting the limits of the time integration go from 0 to ∞ instead of 0 to t. Because of the fact that

$$\hat{f}_1(0) = (1-P)\dot{\hat{a}}_1 = 0, \tag{5.107}$$

$$\underline{\underline{B}} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \dfrac{\varphi_{22}}{\langle \hat{a}_2(\underline{k})\, \hat{a}_2^{+}(\underline{k}) \rangle_{+}} & 0 \\ 0 & 0 & \dfrac{\varphi_{33}}{\langle \hat{a}_3(\underline{k}) \hat{a}_3^{+}(\underline{k}) \rangle_{+}} \end{pmatrix} \tag{5.108}$$

with

$$\varphi_{ij} = \int_0^{\infty} \varphi_{ij}(t)\, dt' \tag{5.109}$$

φ_{23} and φ_{32} have been set equal to zero because if we assume $\varphi_{ij}(t) = e^{-\alpha(\underline{k})t} \varphi_{ij}$

$$\varphi_{23} = \frac{1}{\alpha(\underline{k})} \left\langle \left\{ (1-P)\, \dot{\hat{a}}_2(\underline{k}) \right\} (1-P)\, \dot{\hat{a}}_3 \right\rangle_{+} = 0 \tag{5.110}$$

The equation of motion for the correlation matrix, being

$$\frac{d}{dt}\, \underline{\underline{\phi}}(t) = \underline{\underline{\phi}}(t) \cdot \underline{\underline{\Omega}} - \underline{\underline{\phi}}(t) \cdot \underline{\underline{\varpi}} \tag{5.111}$$

its Laplace transform is :

$$\underline{\underline{\phi}}(\underline{k}, s) = \underline{\underline{\phi}}(\underline{k}) \cdot \frac{\underline{\underline{I}}}{s\underline{\underline{I}} - \underline{\underline{\Omega}} + \underline{\underline{\varpi}}} \tag{5.112}$$

The relation between $\underline{\underline{\phi}}(s)$ and $S(\underline{k},\omega)$ is simply :

$$S(\underline{k},\omega) = \frac{Re}{2\pi} \lim_{s \to -i\omega} \phi_{11}(\underline{k},s) \frac{2}{1+e^{-\beta\hbar\omega}} \qquad (5.113)$$

With the help of equations (5.111), (5.112), (5.108) and (5.104) we obtain

$$S(\underline{k},\omega) = \frac{\left(\frac{1}{\pi}\right) < \hat{a}_1(\underline{k})\, \hat{a}_1^{+}(\underline{k}) >_{+}}{1+e^{-\beta\hbar\omega}} \qquad (*) \qquad (5.114)$$

$$(*)\ \omega^2 \frac{\varphi_{22}}{<\hat{a}_2(\underline{k})\hat{a}_2^{+}(\underline{k})>_{+}} + \frac{<\hat{a}_2(\underline{k})\hat{a}_2^{+}(\underline{k})>_{+}}{<\hat{a}_1(\underline{k})\hat{a}_1^{+}(\underline{k})>_{+}} \frac{\varphi_{33}}{<\hat{a}_3(\underline{k})\hat{a}_3^{+}(\underline{k})>_{+}} \left(\frac{\varphi_{22}\varphi_{33}}{<\hat{a}_2\hat{a}_2^{+}>_{+}<\hat{a}_3\hat{a}_3^{+}>_{+}} - \frac{<\hat{a}_2\hat{a}_3^{+}><\hat{a}_3\hat{a}_2^{+}>}{<\hat{a}_2\hat{a}_2^{+}>_{+}<\hat{a}_3\hat{a}_3^{+}>_{+}} \right)$$

$$\left[\omega^2 \left(\frac{\varphi_{22}}{<\hat{a}_2\hat{a}_2^{+}>_{+}} + \frac{\varphi_{33}}{<a_3 a_3^{+}>_{+}} \right) - \frac{<\hat{a}_2\hat{a}_2^{+}>_{+}}{<\hat{a}_1\hat{a}_1^{+}>_{+}} \frac{\varphi_{33}}{<\hat{a}_3\hat{a}_3^{+}>_{+}} \right]^2 + \omega^2 \left[\omega^2 - \frac{\varphi_{22}\varphi_{33}}{<\hat{a}_2\hat{a}_2^{+}>_{+}<\hat{a}_3\hat{a}_3^{+}>_{+}} - \frac{<\hat{a}_2\hat{a}_2^{+}>_{+}}{<\hat{a}_1\hat{a}_1^{+}>_{+}} + \frac{<\hat{a}_2\hat{a}_3^{+}>_{+}<\hat{a}_3\hat{a}_2^{+}>_{+}}{<\hat{a}_2\hat{a}_2^{+}>_{+}<\hat{a}_3\hat{a}_3^{+}>_{+}} \right]^2$$

From assumption (5.110), φ_{22} and φ_{33} are completely determined except for the factor $\alpha(\underline{k})$ which can be evaluated by looking at the behavior of $S(\underline{k}, \omega)$ for large and small values of $\underline{k}$. (equations (5.81) and (5.82)).

The quantum corrections to the classical $S^{classical}(\underline{k},\omega)$ are contained in the evaluation of the thermal average and in $(\underline{k})$. If we compare equation (5.114) with $S^{classical}(\underline{k},\omega)$, we would find them to be identical except for the definition of the thermal average and the factor $(1+e^{-\beta\hbar\omega})^{-1}$. It is also interesting to note that all the thermal averages entering our equations can be related to the usual transport

coefficients with a $\underline{k}$ dependence. These thermal averages can be easily calculated by the expansion method of Chapter III, and the quantum corrections so obtained are indeed in agreement with the corrections to the transport coefficients calculated by Pietrass.[64]

CHAPTER VI

THE INCOHERENT NEUTRON SCATTERING FUNCTION

Just like in the previous chapter, we shall proceed to calculate the symmetrized incoherent scattering function.

$$S_s^{sym}(k,\omega) = \frac{1}{(2\pi)}\int dt\, e^{i\omega t}\, \frac{1}{2}\sum_{i=1}^{n} \langle e^{-i k\cdot r_i(t)} e^{i k\cdot r_i} + e^{i k\cdot r_i} e^{-i k\cdot r_i(t)} \rangle \tag{6.1}$$

both via the kinetic and the hydrodynamic routes. The relation between $S_s^{sym}(\underline{k},\omega)$ and $S_s(\underline{k},\omega)$ is the same as the relation between $S^{sym}(\underline{k},\omega)$ and $S(\underline{k},\omega)$.

6.1 THE KINETIC APPROACH

We shall take as our dynamical variable the operator $\hat{f}_i(\underline{k},p)$ defined by equation (2.66) and look for the equation of motion of the time correlation function

$$\Phi_s(k,p,p',t) = \frac{1}{2}\langle \hat{f}_i(k,p,t)\hat{f}_i^{+}(k,p') + \hat{f}_i^{+}(k,p')\hat{f}_i(k,p,t)\rangle \tag{6.2}$$

It is given by equation (3.42)

$$\frac{d}{dt}\,\Phi_s(\underline{k},p,p',t) \;-\int dp_2\,\Omega_s(\underline{k},p,p_2)\,\Phi_s(\underline{k},p_2,p',t) \qquad (6.3)$$

$$+\int_0^t dt'\int dp_2\;\mathcal{G}_s(\underline{k},p,p_2,t-t')\,\Phi_s(\underline{k},p_2,p',t')=0$$

with

$$\Omega_s(\underline{k},p,p_2)=\int dp_3 \left\langle \dot{\hat{f}}_i(\underline{k},p)\,\hat{f}_i^{+}(\underline{k},p_3)\right\rangle_{+}\Phi_s^{-1}(\underline{k},p_3,p') \qquad (6.4)$$

$$\mathcal{G}_s(\underline{k},p,p_2,\tau)=\int dp_3 \left\langle \hat{F}_s(\underline{k},p,t)\,\dot{\hat{f}}_i^{+}(\underline{k},p_3)\right\rangle_{+}\Phi_s^{-1}(\underline{k},p_3,p') \qquad (6.5)$$

$$\hat{F}_s(\underline{k},p,\tau)= e^{i\tau(1-P)L}\,(1-P)\,\dot{\hat{f}}_i(\underline{k},p) \qquad (6.6)$$

and

$$\int dp_2\;\Phi_s(\underline{k},p,p_2)\,\Phi_s^{-1}(\underline{k},p_2,p')=\delta(p-p') \qquad (6.7)$$

Here again we shall assume the time dependence of the random force $\hat{F}_s(\underline{k},\underline{p},t)$ to be of the form

$$\hat{F}_s(\underline{k},p,t)= g_s(\underline{k},t)\,(1-P)\,\dot{\hat{f}}_i(\underline{k},p) \qquad (6.8)$$

$g_s(\underline{k},t)$ will have to be modeled if we want to get numbers out of our formulas; and again we shall take

$$g_s(\underline{k},t) = e^{-\alpha_s(\underline{k})t} \qquad (6.9)$$

Note that $\alpha_s(\underline{k})$ is different from the $\alpha(\underline{k})$ of the previous section. But its modeling will consist of looking at $S_s(\underline{k},\omega)$ for small and large values of $\underline{k}$.

The static autocorrelation function $\phi_s(\underline{k},\underline{p},\underline{p}';0)$ is :

$$\phi_s(k,p,p') = \frac{1}{2}\int \frac{d\underline{\ell}\,d\underline{\ell}'}{(2\pi)^6} e^{i\underline{\ell}\cdot\underline{p} + i\frac{t}{2}\underline{k}\cdot\underline{\ell}} e^{i\underline{\ell}'\cdot\underline{p}' - i\frac{t}{2}\underline{k}\cdot\underline{\ell}'}_{(*)} \qquad (6.10)$$

$$(*) < e^{-i\underline{k}\cdot\hat{\underline{r}}_i} e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i} e^{i\underline{k}\cdot\hat{\underline{r}}_i} e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_i} >$$

$$+ \frac{1}{2}\int \frac{d\underline{\ell}\,d\underline{\ell}'}{(2\pi)^6} e^{i\underline{\ell}'\cdot\underline{p}' - i\frac{t}{2}\underline{k}\cdot\underline{\ell}'} e^{i\underline{\ell}\cdot\underline{p} + i\frac{t}{2}\underline{k}\cdot\underline{\ell}}_{(*)}$$

$$(*) < e^{i\underline{k}\cdot\hat{\underline{r}}_i} e^{-i\underline{\ell}'\cdot\hat{\underline{p}}_i} e^{-i\underline{k}\cdot\hat{\underline{r}}_i} e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i} >$$

This is just the first two terms of equation (5.20) without the summation over all the particles in the system. Hence, from (5.23), we obtain

$$\Phi_s(\underline{k},p,p') = \frac{1}{2}\delta(p-p')\Big\{M(p-\tfrac{k_1\hbar}{2})\Big[1-\frac{k_1^2\beta^2 D}{8nm} + \frac{k_1^2\beta^3 D}{24nm^2}(p-k_1\hbar)^2\Big] + M(p+\tfrac{k_1\hbar}{2})\Big[1-\frac{k_1^2\beta^2 D}{8nm} + \frac{k_1^2\beta^3 D}{24nm^2}(p+\tfrac{k_1\hbar}{2})^2\Big]\Big\} \tag{6.11}$$

The inverse function $\Phi_s^{-1}(\underline{k},\underline{p},\underline{p}')$ is immediately obtained from (6.7) :

$$\frac{1}{2}\Big\{M(p-\tfrac{k_1\hbar}{2})\Big[1-\frac{k_1^2\beta^2 D}{8nm}+\frac{k_1^2\beta^3 D}{24nm^2}(p-\tfrac{k_1\hbar}{2})^2\Big] + M(p+\tfrac{k_1\hbar}{2})\Big[1-\frac{k_1^2\beta^2 D}{8nm}+\frac{k_1^2\beta^3 D}{24nm^2}(p+\tfrac{k_1\hbar}{2})^2\Big]\Big\}\Phi_s^{-1}(\hbar,p,p') = \delta(p-p') \tag{6.12}$$

or

$$\Phi_s^{-1}(\hbar,p,p') = \frac{\delta(p-p')}{\frac{1}{2}\big[M(p-\tfrac{k_1\hbar}{2})+M(p+\tfrac{k_1\hbar}{2})\big]} - \frac{\delta(p-p')\frac{1}{2}\Big\{M(p-\tfrac{k_1\hbar}{2})\Big[-\frac{k_1^2\beta^2 D}{8nm}+\frac{k_1^2\beta^3 D}{24nm^2}(p-\tfrac{k_1\hbar}{2})^2\Big]\Big\}}{\frac{1}{4}\big[M(p-\tfrac{k_1\hbar}{2})+M(p+\tfrac{k_1\hbar}{2})\big]^2} - \frac{\delta(p-p')\frac{1}{2}M(p+\tfrac{k_1\hbar}{2})\Big[-\frac{k_1^2\beta^2 D}{8nm}+\frac{k_1^2\beta^3 D}{24nm^2}(p+\tfrac{k_1\hbar}{2})^2\Big]}{\frac{1}{4}\big[M(p-\tfrac{k_1\hbar}{2})+M(p+\tfrac{k_1\hbar}{2})\big]^2} \tag{6.13}$$

$\langle \hat{f}_i(\underline{k},\underline{p})\ \hat{f}_i^{+}(\underline{k},\underline{p}')\rangle_{+}$ is obtained from equation (5.38) by keeping the term i=j and dropping the sum over i.

$$< \dot{\hat{f}}_i(\underline{k}, p)\, \hat{f}_i^+(\underline{k}, p_3) >_+ = -i \left(\frac{\underline{k}\cdot\underline{p}}{m}\right) \phi_s(\underline{k}, p, p_3) \qquad (6.14)$$

$$+ i \left(\frac{kD}{4n}\right) \Bigg\{ M\left(p - \tfrac{k}{2}\right) \left[\nabla_p^2 - \frac{\beta}{m}\left(p - \tfrac{k}{2}\right)\cdot\nabla_p\right]$$

$$- M\left(p + \tfrac{k}{2}\right) \left[\nabla_p^2 - \frac{\beta}{m}\left(p + \tfrac{k}{2}\right)\cdot\nabla_p\right] \Bigg\} \delta(p - p_3)$$

The frequency function is:

$$\Omega_s(\underline{k}, p, p_2) = -i \left(\frac{\underline{k}\cdot\underline{p}}{m}\right) \delta(p - p_2) \qquad (6.15)$$

$$+ i \left(\frac{kD}{4n}\right) \Bigg\{ M\left(p - \tfrac{k}{2}\right) \left[\nabla_p^2 - \frac{\beta}{m}\left(p - \tfrac{k}{2}\right)\cdot\nabla_p\right]$$

$$- M\left(p + \tfrac{k}{2}\right) \left[\nabla_p^2 - \frac{\beta}{m}\left(p + \tfrac{k}{2}\right)\cdot\nabla_p\right] \Bigg\} (*)$$

$$(*) \frac{\delta(p - p_2)}{\frac{1}{2}\left[M\left(p_2 - \tfrac{k}{2}\right) + M\left(p_2 + \tfrac{k}{2}\right)\right]}$$

For the damping term, let us evaluate

$$< \left\{ (1 - P)\, \dot{\hat{f}}_i(\underline{k}, p) \right\} \dot{\hat{f}}_i^+(\underline{k}, p_3) >_+ = \qquad (6.16)$$

$$= -\frac{1}{h^2} < [U, \hat{f}_i(\underline{k}, p)][U, \hat{f}_i^+(\underline{k}, p_3)] >_+$$

$$+ \frac{1}{h^2}\int dp_1 dp_2 < \left[U, \hat{f}_i(\underline{k}, p)\right] \hat{f}_i^+(\underline{k}, p_1) >_+ \Phi_s^{-1}(\underline{k}, p_1, p_2)(*)$$

$$(*) < \hat{f}_i(\underline{k}, p_2)\left[U, \hat{f}_i^+(\underline{k}, p')\right] >_+$$

The second term is of order $\hbar^2$ as can be seen from equation (6.14) and is proportional to $(\hbar D)^2$. So we shall neglect it. The only contribution comes from the first term which has been evaluated in equation (5.46).

$$< \left\{(1-P)\,\dot{\hat{f}}_i(\underline{k}, p)\right\} \dot{\hat{f}}_i^+(\underline{k}, p_3) >_+ \qquad (6.17)$$

$$= \frac{D}{2\beta n}\left\{ M(p - \tfrac{\underline{k}\hbar}{2})\left[\nabla_p^2 - \frac{\beta}{m}(p - \tfrac{\underline{k}\hbar}{2})\cdot\nabla_p\right] \right.$$

$$\left. + M(p + \tfrac{\underline{k}\hbar}{2})\left[\nabla_p^2 - \frac{\beta}{m}(p + \tfrac{\underline{k}\hbar}{2})\cdot\nabla_p\right]\right\} \delta(p - p_3)$$

The function $\varphi_s(\underline{k}, \underline{p}, \underline{p}_2, t)$ is calculated to be

$$\varphi(\underline{k}, p_3, p_2, t) = g_s(\underline{k}, t)\int dp_3 < \hat{F}_i(\underline{k}, p)\, \dot{\hat{f}}_i^+(\underline{k}, p_3) >_+ \Phi_s^{-1}(\underline{k}, p_3, p_2) \qquad (6.18)$$

$$= g_s(\underline{k},t)\left(\frac{D}{2n\beta}\right)\left\{M(p_- - \tfrac{k_-h}{2})\left[\nabla_p^2 - \frac{\beta}{m}(p_- - \tfrac{k_-h}{2})\cdot\nabla_p\right]\right.$$

$$\left. + M(p_- + \tfrac{k_-h}{2})\left[\nabla_p^2 - \frac{\beta}{m}(p_- + \tfrac{k_-h}{2})\cdot\nabla_p\right]\right\} \delta(p_- - p_{2-}) \quad (*)$$

$$(*)\left\{\frac{1}{\frac{1}{2}\left[M(p_{2-} - \frac{k_-h}{2}) + M(p_{2-} + \frac{k_-h}{2})\right]} - \frac{\frac{1}{2}M(p_{2-} - \frac{k_-h}{2})\left[-\frac{k^2\beta^2 D}{8nm} + \frac{k^2\beta^3 D}{24nm^2}(p_{2-} - \frac{k_-h}{2})^2\right]}{\frac{1}{4}\left[M(p_{2-} - \frac{k_-h}{2}) + M(p_{2-} + \frac{k_-h}{2})\right]^2}\right.$$

$$\left. - \frac{\frac{1}{2}M(p_{2-} + \frac{k_-h}{2})\left[-\frac{k^2\beta^2 D}{8nm} + \frac{k^2\beta^3 D}{24nm^2}(p_{2-} - \frac{k_-h}{2})^2\right]}{\frac{1}{4}\left[M(p_{2-} - \frac{k_-h}{2}) + M(p_{2-} + \frac{k_-h}{2})\right]^2}\right\}$$

The time evolution of the autocorrelation function is :

$$\frac{d}{dt}\Phi_s(\underline{k},p_-,p'_-,t) + i\left(\frac{\underline{k}\cdot p_-}{m}\right)\Phi_s(\underline{k},p_-,p'_-,t) \qquad (6.19)$$

$$- i\left(\frac{kD}{4n}\right)\left\{M(p_- - \frac{k_-h}{2})\left[\nabla_p^2 - \frac{\beta}{m}(p_- - \tfrac{k_-h}{2})\cdot\nabla_p\right]\right.$$

$$\left. - M(p_- + \tfrac{k_-h}{2})\left[\nabla_p^2 - \frac{\beta}{m}(p_- + \tfrac{k_-h}{2})\cdot\nabla_p\right]\frac{\Phi_s(\underline{k},p_-,p'_-,t)}{\frac{1}{2}\left[M(p_- - \frac{k_-h}{2}) + M(p_- + \frac{k_-h}{2})\right]}\right\}$$

$$- \int_0^t g_s(\underline{k},t-t')\left(\frac{D}{2n\beta}\right)\left\{M(p_- - \tfrac{k_-h}{2})\left[\nabla_p^2 - \frac{\beta}{m}(p_- - \tfrac{k_-h}{2})\cdot\nabla_p\right] + \right.$$

$$+ M\left(p + \frac{k\hbar}{2}\right)\left[\nabla_p^2 - \frac{\beta}{m}\left(p+\frac{k\hbar}{2}\right)\cdot\nabla_p\right]\Bigg\}\phi(k, p, p', t)\,(*)$$

$$(*)\Bigg\{\frac{1}{\frac{1}{2}\left[M\left(p-\frac{k\hbar}{2}\right) + M\left(p+\frac{k\hbar}{2}\right)\right]}$$

$$- \frac{\frac{1}{2}\left(M\left(p-\frac{k\hbar}{2}\right)\left[-\frac{k^2\beta^2 D}{8nm} + \frac{k^2\beta^3 D}{24nm^2}\left(p-\frac{k\hbar}{2}\right)^2\right] + M\left(p+\frac{k\hbar}{2}\right)\left[-\frac{k^2\beta^2 D}{8nm} + \frac{k^2\beta^3 D}{24nm^2}\left(p+\frac{k\hbar}{2}\right)^2\right]\right)}{\frac{1}{4}\left[M\left(p-\frac{k\hbar}{2}\right) + M\left(p+\frac{k\hbar}{2}\right)\right]^2}\Bigg\}$$

The solution of this equation would give us the incoherent neutron scattering function.

6.1.a. THE IDEAL GAS LIMIT

In the limit as the potential goes to zero, equation (6.19) reduces to just :

$$\frac{d}{dt}\phi_s(k, p, p', t) + i\left(\frac{k\cdot p}{m}\right)\phi_s(k, p, p', t) = 0 \qquad (6.20)$$

After taking the Laplace transform and integrating over dp' we obtain :

$$s\,\phi_s(k, p, t) + i\,\frac{k\cdot p}{m}\,\phi(k, p, t) = \frac{1}{2}\left[M\left(p-\frac{k\hbar}{2}\right) + M\left(p+\frac{k\hbar}{2}\right)\right] \qquad (6.21)$$

This equation is identical to equation (5.57) except for a factor of n missing on the right hand side. Remember that we have to sum over all particles in the system to get $S(\underline{k},\omega)$. Equation (6.21) has been solved in Chapter V and we saw that it gives the correct quantum non-degenerate ideal gas limit .

6.1.b. THE CLASSICAL LIMIT

Letting $\hbar \longrightarrow 0$, we immediately get :

$$\frac{d}{dt}\phi_s(\underline{k},\underline{p},\underline{p}',t) + i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\phi_s(\underline{k},\underline{p},\underline{p}',t) \qquad (6.22)$$

$$+\int_0^t dt'\, g_s(\underline{k},t-t')\left(\frac{D}{n\beta}\right) M(\underline{p})\left[\nabla_{\underline{p}}^2 - \frac{\beta}{m}\underline{p}\cdot\nabla_{\underline{p}}\right]\frac{\phi_s(\underline{k},\underline{p},\underline{p}',t)}{M(\underline{p})}$$

$$= 0$$

which is exactly the equation obtained classically by Akcasu, Corngold and Duderstadt[57]. They solved this equation exactly for $S_s^{\text{classical}}(\underline{k},\omega)$ by the Fourier transform method.

6.1.c. QUANTUM CORRECTIONS TO THE CLASSICAL EQUATION

The solution of (6.19) contains quantum corrections to the solution of (6.22). We can solve (6.19) under appro-

ximation (5.69) by letting

$$\phi_s(\underline{k}, p, p', t) = \phi_s^{(1)}(\underline{k}, p, p', t) + k^2 \phi_s^{(2)}(\underline{k}, p, p', t) \quad (6.23)$$

After integrating over dp', dp_x, dp_y, ($p_z \to p$) assuming $\underline{k}$ to be along the z axis, and taking the Laplace transform, we get the following equation :

$$s\,\phi_s^{(1)}(k, p, s) + i\left(\frac{kp}{m}\right)\phi_s^{(1)}(k, p, s) \quad (6.24)$$

$$+ i\,\frac{kD}{4n}\,\frac{\beta}{m}\left(kh\,\frac{d}{dp}\,\phi_s^{(1)}(k, p, s)\right)$$

$$- \tilde{g}_s(k, s)\left(\frac{D}{\beta n}\right)\left[\frac{d^2}{dp^2} + \frac{\beta}{m}\frac{d}{dp}p\right]\phi_s^{(1)}(k, p, s)$$

$$= \frac{1}{2}\left[M\left(p - \frac{kh}{2}\right) + M\left(p + kh/2\right)\right]$$

and

$$\left\{s + i\left(\frac{kp}{m}\right) + i\,\frac{kD}{4n}\,\frac{\beta}{m}\,kh\,\frac{d}{dp}\right. \quad (6.25)$$

$$\left. - \tilde{g}_s(k, s)\left(\frac{D}{\beta n}\right)\left(\frac{d^2}{dp^2} + \frac{\beta}{m}\frac{d}{dp}p\right)\right\}\phi_s^{(2)}(k, p, s) =$$

$$= \frac{1}{2}\left\{ M(p - \tfrac{k_1 h}{2})\left[-\frac{\beta^2 D}{8nm} + \frac{\beta^3 D}{24nm^2}(p - \tfrac{k_1 h}{2})^2 \right] + M(p + \tfrac{k_1 h}{2})\left[-\frac{\beta^2 D}{8nm} + \frac{\beta^3 D}{24nm^2}(p + \tfrac{k_1 h}{2})^2 \right] \right\}$$

$$- \tilde{q}_s(h,s)\left(\frac{D}{n\beta}\right)\left[\frac{d^2}{dp^2} + \frac{d}{dp}p\right]\phi_s^{(0)}(h,p,s)\left\{ \frac{1}{2}M(p - \tfrac{k_1 h}{2})\left[-\frac{\beta^2 D}{8nm} + \frac{\beta^3 D}{24nm^2}(p - \tfrac{k_1 h}{2})^2 \right] + \frac{1}{2}M(p + \tfrac{k_1 h}{2})\left[-\frac{\beta^2 D}{8nm} + \frac{\beta^3 D}{24nm^2}(p + \tfrac{k_1 h}{2})^2 \right] \right\} \Big/ \frac{1}{4}\left[M(p - \tfrac{k_1 h}{2}) + M(p + \tfrac{k_1 h}{2}) \right]^2$$

Let us look at the solution of equation (6.24). Define the Fourier transform

$$Y_s(h,\mu,s) = \int_{-\infty}^{\infty} dp\, e^{i\mu p}\, \phi_s(h,\mu,s) \qquad (6.26)$$

After taking the Fourier transform of equation (6.24), we obtain

$$\frac{d\,\tilde{Y}_s(h,u,s)}{du} + \frac{\beta_s + A_s u + u^2}{\mathcal{H}_s(h) + u}\,\tilde{Y}_s(h,u,s) = \cos\left\{ \frac{k_1}{2}\sqrt{\frac{\beta k_2}{m}}\,u \right\} \frac{e^{-u^2/2}}{\frac{D}{mn}\tilde{q}_s(s)\left[\mathcal{H}(h) + u\right]} \qquad (6.27)$$

where $u = \sqrt{\frac{m}{\beta}}\,\mu$

$$\mathcal{H}_s(h) = \frac{n}{D}\,\frac{h}{\tilde{q}_s(h,s)} \qquad (6.28)$$

$$A_s = \frac{k\beta^2}{4\sqrt{m\beta}} \frac{k}{\tilde{g}_s(k,s)} \tag{6.29}$$

$$\beta_s = \frac{s}{\frac{D}{m}\tilde{g}_s(k,s)} \tag{6.30}$$

This first order equation is solved to give

$$\tilde{Y}_s(k,u,s) = \frac{e^{-u^2/2}\, e^{(K_s - A)(K_s+u)}}{[K_s+u]^{\beta_s + K_s^2 - A_s K_s}} \int_0^{K_s+u} dy \cos\left\{\sqrt{\frac{\beta k^2 k^2}{m}}\left(\frac{y-k}{2}\right)\right\} [y]^{\beta_s + K_s^2 - A_s K_s - 1} \; (*) \tag{6.31}$$

Using $(*)\ \dfrac{e^{-(K_s - A_s)y}}{\frac{D}{mn}\tilde{g}_s(k,s)}$

$$S_s^{sym}(k,\omega) = \frac{Re}{2\pi} \lim_{s \to -i\omega} Y_s(k,0,s) \tag{6.32}$$

we get

$$S_s^{sym}(k,\omega) = \frac{Re}{2\pi} \lim_{s\to -i\omega} (*) \tag{6.33}$$

$$(*)\ \frac{e^{(K_s(k) - A_s(k))K_s(k)}}{[K_s(k)]^{\beta_s + K_s^2(k) - A_s K_s(k)}} \int_0^{K_s(k)} dy \cos\left\{\frac{y-k}{2}\sqrt{\beta \frac{k^2 k^2}{m}}\right\} (*)$$

$$(*)\ [y]^{\beta_s + K_s^2(k) - A_s K_s(k) - 1} \frac{e^{-(K_s(k) - A_s)y}}{(D/mn)\tilde{g}_s(k,s)}$$

and

$$S_s(k,\omega) = \frac{n/\pi}{1+e^{-\beta k\omega}} (*)\ Re \lim_{s\to -i\omega} \tag{6.34}$$

$$(*)\frac{e^{(K_s(k)-A_s)K_s(k)}}{[K_s(k)]^{3s}+K_s^2(k)-A_sK_s(k)}\int_0^{K_s(k)}dy\,\cos\left\{\frac{y-k}{2}\sqrt{\beta\frac{k^2h^2}{m}}\right\}(*)$$

$$(*)[y]^{3s}+K_s^2(k)-A_sK_s(k)-1\quad\frac{e^{-(K_s(k)-A)y}}{(D/mn)\,\tilde{g}_s(k,s)}$$

More corrections can be obtained by solving equation (6.25) and adding the result to (6.34). However, because of the fact that $\frac{k^2k^2\beta^3D}{8nm}\chi\,10^{-3}$, the corrections due to this term are rather small.

6.2. THE HYDRODYNAMIC APPROACH

To obtain the incoherent scattering approach from the hydrodynamic approach, all we have to do is define a vector $\hat{\underline{B}}(\underline{k},t)$

$$\hat{\underline{B}}(\underline{k},t) = \begin{pmatrix} \hat{b}_1(\underline{k},t) \\ \hat{b}_2(\underline{k},t) \\ \hat{b}_3(\underline{k},t) \end{pmatrix} \tag{6.35}$$

whose components are :

$$\hat{b}_1(t) = e^{-i\underline{k}\cdot\hat{\underline{x}}_i(t)} \tag{6.36}$$

$$\hat{b}_2(t) = \underline{k}\cdot\left(\hat{\underline{p}}_i(t)\,e^{-i\underline{k}\cdot\hat{\underline{x}}_i(t)} + e^{-i\underline{k}\cdot\hat{\underline{x}}_i(t)}\,\hat{\underline{p}}_i(t)\right) \tag{6.37}$$

$$\hat{b}_3(t) = \hat{E}_i(\underline{k},t) - \frac{\langle \hat{E}_i(\underline{k},t)\, \hat{b}_1^{\dagger}(\underline{k}) \rangle_t}{\langle \hat{b}_1(\underline{k})\, \hat{b}_1^{\dagger}(\underline{k}) \rangle_t}\, \hat{b}_1(\underline{k}) \qquad (6.38)$$

with

$$\hat{E}_i(\underline{k},t) = \frac{1}{8m}\left\{ \hat{p}_i^2(t)\, e^{-i\underline{k}\cdot\underline{r}_i(t)} + 2\,\hat{p}_i(t)\cdot e^{-i\underline{k}\cdot\underline{r}_i(t)}\cdot \hat{p}_i(t) + e^{-i\underline{k}\cdot\underline{r}_i(t)}\, \hat{p}_i^2(t) \right\} \qquad (6.39)$$

$$+ \frac{1}{2}\sum_{\alpha=1}^{n}\sum_{\gamma\neq\alpha} V(\underline{r}_\alpha - \underline{r}_\gamma)\, e^{-i\underline{k}\cdot\underline{r}_i(t)}$$

$\hat{b}_1(\underline{k},t)$, $\hat{b}_2(\underline{k},t)$ and $\hat{b}_3(\underline{k},t)$ are just the $\hat{a}_1(\underline{k},t)$, $\hat{a}_2(\underline{k},t)$ $\hat{a}_3(\underline{k},t)$ without the summation over all the particles in the system.

The analysis is exactly the same as the one in section (5.2), and the result has the same form, namely :

$$S_s^{sym}(k,\omega) = \qquad (6.40)$$

$$\frac{\omega^2 \dfrac{\varphi^s_{22}}{\langle \hat{b}_2 \hat{b}_2^{\dagger}\rangle_t} + \dfrac{\langle \hat{b}_2 \hat{b}_2^{\dagger}\rangle_t \varphi^s_{33}}{\langle \hat{b}_3 \hat{b}_3^{\dagger}\rangle_t}\left(\dfrac{\varphi^s_{22}\varphi^s_{33}}{\langle \hat{b}_2 \hat{b}_2^{\dagger}\rangle_t \langle \hat{b}_3 \hat{b}_3^{\dagger}\rangle_t} - \dfrac{\langle \dot{\hat{b}}_2 \hat{b}_3^{\dagger}\rangle \langle \dot{\hat{b}}_3 \hat{b}_2^{\dagger}\rangle_t}{\langle \hat{b}_2 \hat{b}_2^{\dagger}\rangle_t \langle \hat{b}_3 \hat{b}_3^{\dagger}\rangle_t} \right)}{\left[\omega^2\left(\dfrac{\varphi^s_{22}}{\langle \hat{b}_2 \hat{b}_2^{\dagger}\rangle_t} + \dfrac{\varphi^s_{33}}{\langle \hat{b}_3 \hat{b}_3^{\dagger}\rangle_t}\right) - \dfrac{\langle \hat{b}_2 \hat{b}_2^{\dagger}\rangle \varphi_{33}}{\langle \hat{b}_3 \hat{b}_3^{\dagger}\rangle_t}\right]^2 + \omega^2\left[\omega^2 - \dfrac{\varphi^s_{22}\varphi^s_{33}}{\langle \hat{b}_2 \hat{b}_2^{\dagger}\rangle_t \langle \hat{b}_3 \hat{b}_3^{\dagger}\rangle_t} - \langle \hat{b}_2 \hat{b}_2^{\dagger}\rangle_t + \dfrac{\langle \dot{\hat{b}}_2 \hat{b}_3^{\dagger}\rangle_t \langle \dot{\hat{b}}_3 \hat{b}_2^{\dagger}\rangle_t}{\langle \hat{b}_2 \hat{b}_2^{\dagger}\rangle_t \langle \hat{b}_3 \hat{b}_3^{\dagger}\rangle_t} \right]^2}$$

where we have put

$$\frac{1}{2} < \hat{b}_1 \hat{b}_1^{+} + \hat{b}_1^{+} \hat{b}_1 > = 1 \tag{6.41}$$

The incoherent scattering function is then :

$$S_s(k,\omega) = \frac{n/\pi}{1 + e^{-\beta\hbar\omega}} \; (*) \tag{6.42}$$

$$(*)_2 \; \frac{\omega^2 \dfrac{\varphi_{22}^s}{<\hat{b}_2 \hat{b}_2^{+}>_+} + \dfrac{<\hat{b}_2 \hat{b}_2^{+}>_+}{<\hat{b}_3 \hat{b}_3^{+}>_+} \varphi_{33}^s \left(\dfrac{\varphi_{22}^s \varphi_{33}^s}{<\hat{b}_2 \hat{b}_2^{+}>_+ <\hat{b}_3 \hat{b}_3^{+}>_+} - \dfrac{<\dot{\hat{b}}_2 \hat{b}_3^{+}> <\dot{\hat{b}}_3 \hat{b}_2^{+}>_+}{<\hat{b}_2 \hat{b}_2^{+}>_+ <\hat{b}_3 \hat{b}_3^{+}>_+} \right)}{\left[\omega^2 \left(\dfrac{\varphi_{22}^s}{<\hat{b}_2 \hat{b}_2^{+}>_+} + \dfrac{\varphi_{33}^s}{<\hat{b}_3 \hat{b}_3^{+}>_+} \right) - \dfrac{<\hat{b}_2 \hat{b}_2^{+}> \varphi_{33}}{<\hat{b}_3 \hat{b}_3^{+}>_+} \right]^2 + \omega^2 \left[\omega^2 - \dfrac{\varphi_{22}^s \varphi_{33}^s}{<\hat{b}_2 \hat{b}_2^{+}>_+ <\hat{b}_3 \hat{b}_3^{+}>_+} - <\hat{b}_2 \hat{b}_2^{+}>_+ + \dfrac{<\dot{\hat{b}}_2 \hat{b}_3^{+}>_+ <\dot{\hat{b}}_3 \hat{b}_2^{+}>_+}{<\hat{b}_2 \hat{b}_2^{+}>_+ <\hat{b}_3 \hat{b}_3^{+}>_+} \right]^2}$$

the evaluation of φ_{22}^s and φ_{33}^s, proceeds in the same way as indicated in Chapter V.

CHAPTER VII

DISCUSSION AND CONCLUSION

We have been able to obtain in Chapter V and VI a closed form for both the total and incoherent scattering functions using two different approaches (the kinetic and the hydrodynamic approaches).

From the kinetic approach to the problem, we could obtain both the correct quantum non-degenerate ideal gas limit and the classical limit for the scattering functions. However the hydrodynamic approach can give us only the correct classical limit (it is valid for $\frac{\beta\hbar^2k^2}{8m} \ll 1$). It is not clear that the final form of the scattering functions can be put in the form of a factor multiplying the classically calculated functions like many authors have suggested. That is, $S(\underline{k},\omega)$ is not in the form $S(\underline{k},\omega) = e^{-\frac{\beta\hbar\omega}{2}} e^{-\beta\frac{\hbar^2k^2}{8m}} S^{class}(\underline{k},\omega)$. Quantum corrections enter everywhere in the formulas and cannot be separeted out. Rosenbaum has shown that the incoherent scattering can be put in the above form, while Shaibly[65] has demonstrated this to be true for the total scattering function in the sense of the "Random Phase Approximation". If we were to neglect the so called "memory term" completely, it would be possible for us to display the final form as $e^{-\frac{\beta\hbar\omega}{2}} e^{-\beta\frac{\hbar^2k^2}{8m}} S^{class}(\underline{k},\omega)$ plus other quantum corrections of order $\hbar$ and higher. But neglecting the "memory term"

would amount to solving essentially a Vlasov like equation, and this is in essence the Randum Phase Approximation. Nelkin has shown[32] that the solution of a Vlasov like equation is not at all adequate for interpreting neutron scattering experiments. He in fact solved the so called Zwanzig equation (a modified Vlasov equation) and found the calculated scattering function not to display the proper features of the experimental scattering function. Therefore the effects of the "damping term", both classical and quantum have to be included.

Even though the classical scattering functions calculated by Akcasu and Duderstadt via the projection operator technique compared well with Rahman's computer experiment, it is not at all certain that these same classical scattering functions would interpret real neutron scattering experiments. Our calculations as an expansion of certain factors, not all,in powers of h , have shown that the quantum corrections are at best of the order of 10 to 13% for large values of the neutron momentum transfer $\underline{k}$. The formulas we have given are expected to give a good fit for small as well as large values of $\underline{k}$, while the classical formulas are expected to be good in the small $\underline{k}$ region. At any rate the total and incoherent scattering functions obtained here have to be compared against neutron scattering experiments to find out whether our equations are

correct or not, and what kind of improvement they give over the classical total and incoherent scattering functions.

So far we have calculated time correlation functions for non-degenerate systems at high and normal temperatures. An immediate extension of this work would be the calculation of time correlation functions for degenerate systems at low and high temperature. A knowledge of how to evaluate thermal averages for such systems is required before making any progress. It would be then possible to evaluate the differential cross section for neutron scattering by superfluid, as well as the electric conductivity and dielectric functions of degenerate electron gases.

APPENDIX A

PROPERTIES OF $\hat{f}_1(\underline{r},\underline{p})$

From the definition of $\hat{f}_1(\underline{r},\underline{p})$, we have

$$\hat{f}_1(\underline{r},\underline{p}) = \frac{1}{(2\pi)^6}\sum_{i=1}^{m}\int d\underline{k}\,d\underline{l}\; e^{i\underline{k}\cdot(\underline{r}-\hat{\underline{r}}_i)} e^{i\underline{l}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{l}} e^{-i\underline{l}\cdot\hat{\underline{p}}_i} \qquad (A.1)$$

i) $\hat{f}_1(\underline{r},\underline{p})$ is hermitian

Let us take the hermitian conjugate of equation (A.1)

$$\hat{f}_1^{+}(\underline{r},\underline{p}) = \frac{1}{(2\pi)^6}\sum_{i=1}^{m}\int d\underline{k}\,d\underline{l}\; e^{-i\underline{l}\cdot\underline{p}-i\frac{\hbar}{2}\underline{k}\cdot\underline{l}} e^{-i\underline{k}\cdot\underline{r}} e^{i\underline{l}\cdot\hat{\underline{p}}_i} e^{i\underline{k}\cdot\hat{\underline{r}}_i} \qquad (A.2)$$

Since

$$e^{i\underline{l}\cdot\hat{\underline{p}}_i} e^{i\underline{k}\cdot\hat{\underline{r}}_i} = e^{i\underline{l}\cdot\hat{\underline{p}}_i} e^{i\underline{k}\cdot\hat{\underline{r}}_i} e^{-i\underline{l}\cdot\hat{\underline{p}}_i} e^{i\underline{l}\cdot\hat{\underline{p}}_i} \qquad (A.3)$$

$$= e^{i\underline{k}\cdot(\hat{\underline{r}}_i - \hbar\underline{l})} e^{i\underline{l}\cdot\hat{\underline{p}}_i}$$

we get

$$\hat{f}_1^{+}(\underline{r},\underline{p}) = \frac{1}{(2\pi)^6}\sum_{i=1}^{m}\int d\underline{k}\,d\underline{l}\; e^{-i\underline{l}\cdot\underline{p}-i\frac{\hbar}{2}\underline{k}\cdot\underline{l}} e^{-i\underline{k}\cdot\underline{r}} e^{i\underline{k}\cdot(\hat{\underline{r}}_i-\hbar\underline{l})} e^{i\underline{l}\cdot\hat{\underline{p}}_i} \qquad (A.4)$$

Let $\underline{K} \longrightarrow -\underline{K}$, and $\underline{l} \longrightarrow -\underline{l}$; we obtain then

$$= \frac{1}{(2\pi)^6}\sum_{i=1}^{m}\int d\underline{k}\,d\underline{l}\; e^{i\underline{l}\cdot\underline{p}} e^{i\underline{k}\cdot\underline{r}} e^{i\frac{\hbar}{2}\underline{k}\cdot\underline{l}} e^{-i\hbar\underline{l}\cdot\hat{\underline{r}}_i} e^{-i\underline{l}\cdot\hat{\underline{p}}_i} \qquad (A.5)$$

Comparing equations (A.1) and (A.5), we see that

$$\hat{f}_1^{+}(\underline{r},\underline{p}) = \hat{f}_1(\underline{r},\underline{p})$$

ii) $\hat{f}_1^{+}(\underline{k},\underline{p}) = \hat{f}_1(-\underline{k},\underline{p})$

$\hat{f}_1(\underline{k},\underline{p})$, by definition, is

$$\hat{f}_1(\underline{k},\underline{p}) = \frac{1}{(2\pi)^3}\sum_{i=1}^{m}\int d\underline{\ell}\; e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\, e^{-i\underline{k}\cdot\hat{\underline{r}}_i}\, e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i} \qquad (A.7)$$

Its hermitian adjoint is

$$\hat{f}_1^{+}(\underline{k},\underline{p}) = \frac{1}{(2\pi)^3}\int d\underline{\ell}\sum_{i=1}^{m} e^{-i\underline{\ell}\cdot\underline{p}-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\, e^{i\underline{\ell}\cdot\hat{\underline{p}}_i}\, e^{-i\underline{k}\cdot\hat{\underline{r}}_i} \qquad (A.8)$$

$$= \frac{1}{(2\pi)^3}\int d\underline{\ell}\sum_{i=1}^{m} e^{-i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\, e^{i\underline{k}\cdot\hat{\underline{r}}_i}\, e^{i\underline{\ell}\cdot\hat{\underline{p}}_i}$$

Let $\underline{\ell} \longrightarrow -\underline{\ell}$

$$\hat{f}_1^{+}(\underline{k},\underline{p}) = \frac{1}{(2\pi)^3}\sum_{i=1}^{m}\int d\underline{\ell}\; e^{i\underline{\ell}\cdot\underline{p}-i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\, e^{i\underline{k}\cdot\hat{\underline{r}}_i}\, e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i} \qquad (A.9)$$

Comparing equations (A.7) and (A.9), we get

$$\hat{f}_1^{+}(\underline{k},\underline{p}) = \hat{f}_1(-\underline{k},\underline{p}) \qquad (A.10)$$

iii) The equation of motion of $\hat{f}_1(\underline{k},\underline{p})$

The Heisenberg equation of motion for $f(\underline{k},\underline{p})$ is :

$$\frac{d}{dt}\hat{f}_1(\underline{k},\underline{p}) = \frac{i}{\hbar}\left[H,\ \hat{f}_1(\underline{k},\underline{p})\right] \qquad (A.11)$$

For a system Hamiltonian of the form

$$H = \sum_{i=1}^{m} \frac{\hat{p}_i^2}{2m} + U \tag{A.12}$$

where

$$U = \frac{1}{2} \sum_{i=1}^{m} \sum_{j=1}^{m}{}' V(\underline{r}_i - \underline{r}_j)$$

we have

$$\frac{d}{dt} \hat{f}_1(\underline{k}, \underline{p}) = \frac{i}{\hbar} \sum_{\alpha=1}^{m} \left[\frac{\hat{p}_\alpha^2}{2m}, \hat{f}_1(\underline{k}, \underline{p}) \right] + \frac{i}{\hbar} \left[U, \hat{f}_1(\underline{k}, \underline{p}) \right] \tag{A.13}$$

The kinetic energy term becomes :

$$\frac{i}{\hbar} \sum_{\alpha=1}^{m} \frac{1}{2m} \left[\hat{p}_\alpha^2, \hat{f}_1(\underline{k}, \underline{p}) \right] = \frac{i}{\hbar} \sum_{\alpha=1}^{n} \frac{1}{2m(2\pi)^3} \sum_{i=1}^{m} \int d\underline{\ell} \; (*) \tag{A.14}$$

$$(*)\; e^{i\underline{\ell}\cdot\underline{p} + i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}} \left[\hat{p}_\alpha^2, e^{-i\underline{k}\cdot\hat{\underline{r}}_i} \right] e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}$$

$$= \frac{i}{\hbar} \frac{1}{(2\pi)^3} \frac{1}{2m} \sum_{i=1}^{m} \int d\underline{\ell}\; e^{i\underline{\ell}\cdot\underline{p} + i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}} e^{-i\underline{k}\cdot\hat{\underline{r}}_i} \; (*)$$

$$(*) \left(-2\hbar\underline{k}\cdot\hat{\underline{p}}_i + \hbar^2 k^2 \right) e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}$$

Since

$$\hat{\underline{p}}_i \; e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i} = i \frac{d}{d\underline{\ell}} e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i} \tag{A.15}$$

after an integration by parts, we obtain

$$\frac{i}{\hbar}\sum_{\alpha=1}^{n}\frac{1}{2m}\left[\hat{p}_\alpha^2,\ \hat{f}_1(\underline{k},\underline{p})\right] \qquad (A.16)$$

$$= \frac{i}{\hbar}\frac{1}{(2\pi)^3 2m}\sum_{i=1}^{n}\int d\underline{\ell}\, e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}\left(-2\hbar\underline{k}\cdot\underline{p}\right)e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}$$

$$= -i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\hat{f}_1(\underline{k},\underline{p})$$

The potential energy term becomes, after evaluating the commutator:

$$\frac{i}{\hbar}\left[U,\ \hat{f}_1(\underline{k},\underline{p})\right] = \frac{i}{\hbar}\frac{1}{(2\pi)^3}\sum_{i=1}^{n}\int d\underline{\ell}\, e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}e^{-i\underline{k}\cdot\hat{\underline{r}}_i}\ (*) \qquad (A.17)$$

$$(*)\left[U,\ e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}\right]$$

$$= \frac{i}{\hbar}\frac{1}{(2\pi)^3}\sum_{i=1}^{n}\sum_{\beta\neq i}\int d\underline{\ell}\, e^{i\underline{\ell}\cdot\underline{p}}e^{i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}e^{-i\underline{k}\cdot\hat{\underline{r}}_i}$$

$$(*)\left(V(\underline{r}_i-\underline{r}_\beta)-V(\underline{r}_i-\hbar\underline{\ell}-\underline{r}_\beta)\right)e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}$$

So the final form of the equation of motion is just

$$\frac{d}{dt}\hat{f}_1(\underline{k},\underline{p}) = -i\left(\frac{\underline{k}\cdot\underline{p}}{m}\right)\hat{f}_1(\underline{k},\underline{p}) \qquad (A.18)$$

$$+\frac{i}{\hbar}\sum_{i=1}^{n}\sum_{\beta\neq i}\int\frac{d\underline{\ell}}{(2\pi)^3}e^{i\underline{\ell}\cdot\underline{p}+i\frac{\hbar}{2}\underline{k}\cdot\underline{\ell}}e^{-i\underline{k}\cdot\hat{\underline{r}}_i}\left(V(\underline{r}_i-\underline{r}_\beta)-V(\underline{r}_i-\hbar\underline{\ell}-\underline{r}_\beta)\right)e^{-i\underline{\ell}\cdot\hat{\underline{p}}_i}$$

iv) RELATION BETWEEN $S(\underline{k},\omega)$ and $\phi(\underline{k},\underline{p},\underline{p},t)$

$S(\underline{k},\omega)$, as defined by equation (2.33), is

$$S(\underline{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}dt\, e^{-i\omega t}\sum_{i=1}^{n}\sum_{\delta=1}^{n}\left\langle e^{-i\underline{k}\cdot\underline{r}_\delta}e^{i\underline{k}\cdot\underline{r}_i(t)}\right\rangle \qquad (A.19)$$

From the property of the thermal average,

$$\langle e^{-i\underline{k}\cdot\underline{r}_j} e^{i\underline{k}\cdot\underline{r}_\ell(t)}\rangle = \langle e^{-i\underline{k}\cdot\underline{r}_j(-t)} e^{i\underline{k}\cdot\underline{r}_\ell}\rangle \qquad (A.20)$$

the expression for $S(\underline{k},\omega)$ can be written as

$$S(\underline{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\langle e^{-i\underline{k}\cdot\underline{r}_j(-t)} e^{i\underline{k}\cdot\underline{r}_\ell}\rangle \qquad (A.21)$$

Let $t \to -t$, to obtain

$$S(\underline{k},\omega) = \frac{1}{(2\pi)}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\langle e^{-i\underline{k}\cdot\underline{r}_j(t)} e^{i\underline{k}\cdot\underline{r}_\ell}\rangle \qquad (A.22)$$

From equation (2.66) for $\phi(\underline{k},\underline{p},\underline{p},t)$, we have then

$$S(\underline{k},\omega) = \frac{1}{(2\pi)}\int dt\, e^{i\omega t}\int d\underline{p}\, d\underline{p}'\, \phi(\underline{k},\underline{p},\underline{p}',t) \qquad (A.23)$$

with the inverse Fourier transform in time

$$\int d\underline{p}\, d\underline{p}'\, \phi(\underline{k},\underline{p},\underline{p}',t) = \int_{-\infty}^{\infty} d\omega\, e^{-i\omega t} S(\underline{k},\omega) \qquad (A.24)$$

Similarly, for the incoherent scattering function, we have

$$S_s(\underline{k},\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\, e^{i\omega t}\sum_{i=1}^{m}\int d\underline{p}\, d\underline{p}'\, \phi_s(\underline{k},\underline{p},\underline{p}',t) \qquad (A.25)$$

with the inverse Fourier transform in time

$$\sum_{i=1}^{m}\int d\underline{p}\, d\underline{p}'\, \phi_s(\underline{k},\underline{p},\underline{p}',t) = \int_{-\infty}^{\infty} d\omega\, e^{-i\omega t} S_s(\underline{k},\omega) \qquad (A.26)$$

APPENDIX B

PROPERTIES OF THE PROJECTION OPERATOR P.

The projection operator P is defined by

$$P\cdot = \int dp_1 dp_2 \, \langle \cdot \, A^+(p_1) \rangle_+ \, \Phi^{-1}(p_1, p_2) \, A(p_2) \qquad \text{(B.1)}$$

all the other symbols have been defined in chapter III. We want to show that P is hermitian and that it is equal to its square.

i) HERMITICITY PROPERTY OF P.

Consider the following symmetrized thermal average of two arbitrary operators PB(p) and C(q)

$$\langle \{ PB(p) \} C^+(q) \rangle_+ = \int dp_1 dp_2 \, \langle B(p) \, A^+(p_1) \rangle_+ \qquad \text{(B.2)}$$
$$(*) \; \Phi^{-1}(p_1, p_2) \, \langle A(p_2) \, C^+(q) \rangle_+$$

For P to be hermitian, we must show that (B.2) is equal to $\langle B(p) \{ P C(q) \}^+ \rangle_+$ .Since

$$\langle B(p) \{ PC(q) \}^+ \rangle = \int dp_1 dp_2 \, \langle B(p) \Big\{ \langle C(q) A^+(p_2) \rangle_+ (*) \qquad \text{(B.3)}$$
$$(*) \; \Phi^{-1}(p_1, p_2) \, A(p_2) \Big\}^+ \rangle_+$$

and that

$$\langle C(q) \, A^+(p_1) \rangle_+^* = \tfrac{1}{2} \Big(\mathrm{Tr} \, D \, C(q) \, A^+(p_1) + \mathrm{Tr} \, D \, A^+(p_1) C(q) \Big)^* \qquad \text{(B.4)}$$
$$= \tfrac{1}{2} \Big(\mathrm{Tr} \, D A(p_1) C^+(q) + \mathrm{Tr} \, D C(q) A(p_1) \Big)$$

$$= \langle A(p_1) C^+(q) \rangle_+$$

we get

$$\langle B(q) \{P C(q)\}^+ \rangle_+ = \int dp_1 dp_2 \langle B(p) A^+(p_2) \rangle_+ \phi^{-1*}(p_1, p_2) \qquad (B.5)$$

$$(*) \quad \langle A(p_1) C^+(q) \rangle_+$$

The inverse function $\phi^{-1}(\underline{p}, \underline{p}', o)$, like the function

$$\phi(p_1, p_2) = \langle A(p_1) A^+(p_2) \rangle$$

has the property

$$\phi^{-1*}(p_1, p_2) = \phi^{-1}(p_2, p_1) \qquad (B.6)$$

Hence

$$\langle B(p) \{ P C(q) \}^+ \rangle_+ = \int dp_1 dp_2 \langle B(p) A^+(p_2) \rangle_+ \phi^{-1}(p_2, p_1) \qquad (B.7)$$

$$(*) \quad \langle A(p_1) C^+(q) \rangle_+$$

$$= \langle \{P B(p)\} C^+(q) \rangle_+$$

abd P is indeed hermitian.

ii) P IS A PROJECTOR, i.e. $P^2 = P$

From the definition,

$$P G(p) = \int dp_1 dp_2 \langle G(p) A^+(p_1) \rangle_+ \phi^{-1}(p_1, p_2) A(p_2) \qquad (B.8)$$

where G(p) is an arbitrary operator.Operating on equation

(B.8) with P , we obtain

$$P^2 G(p) = \int dp_3 dp_4 dp_1 dp_2 \, \langle G(p) A^+(p_1) \rangle_+ \phi^{-1}(p_1, p_2) \quad \text{(B.9)}$$

$$(*) \langle A(p_2) A^+(p_3) \rangle_+ \phi^{-1}(p_3, p_4) A(p_4)$$

Using the relation

$$\int dp_3 \, \phi(p_2, p_3) \phi^{-1}(p_3, p_4) = \delta(p_2 - p_4) \quad \text{(B.10)}$$

we get

$$P^2 G(p) = \int dp_1 dp_2 \, \langle G(p) A^+(p_1) \rangle_+ \phi^{-1}(p_1, p_2) A(p_2) \quad \text{(B.11)}$$

$$= P G(p)$$

Thus

$$P^2 = P$$

APPENDIX C

CALCULATION OF $\left\langle \sum_{i=1}^{n} \sum_{j\neq i}^{n} e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \right\rangle_c$

The method developped in section (4.4) will be used to calculate the Fourier transform of the pair distribution function $\left\langle \sum_{i=1}^{n} \sum_{j=1}^{n} e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \right\rangle$ and display it as a classical expression plus quantum corrections.

$$\sum_{i=1}^{n} \sum_{j=1}^{n}{}' \left\langle e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n}{}' \int d[x_N]\, d[p_N] \qquad (C.1)$$

$$(*) \left(\prod_{\rho=1}^{n} e^{-i\frac{p_\rho \cdot x_\rho}{\hbar}} \right) \frac{e^{-\beta H}}{Z_0(\beta)} e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \left(\prod_{\rho=1}^{n} e^{i\frac{p_\rho \cdot x_\rho}{\hbar}} \right)$$

For equation (4.57), we have

$$\sum_{i=1}^{n} \sum_{j=1}^{n}{}' \left\langle e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \right\rangle = \sum_{i=1}^{n} \sum_{j=1}^{n} \int d[x_N]\, d[p_N]\, e^{-i\underline{k}\cdot(\underline{r}_i - \underline{r}_j)} \qquad (C.2)$$

$$(*)\, e^{-\beta \frac{\hbar^2 k^2}{m} + \beta \frac{\hbar \underline{k}}{m}\cdot(p_i - p_j)} \frac{e^{-\beta E(x_i, p_i)}}{Z_c(\beta)} \left[1 + \hbar\lambda_1(\beta) + \hbar^2 \lambda_2(\beta) + \cdots \right]$$

$$\equiv A^{(0)} + \hbar A^{(1)} + \hbar^2 A^{(2)}$$

Note that

$$A^{(0)} = \sum_{i=1}^{n} \sum_{j=1}^{n}{}' \int d[x_N]\, d[p_N]\, e^{-i\, k\cdot(r_i - r_j)} \quad (*) \qquad \text{(C.3)}$$

$$(*)\ \frac{e^{-\beta E(x_i, p_i)}\ e^{-\beta \frac{\hbar^2 k^2}{m}\ +\ \beta \frac{\hbar k}{m}\cdot(p_i - p_j)}}{Z_c^c(\beta)\, Z_c^m(\beta)}$$

$$= \left\langle \sum_{i=1}^{n} \sum_{j=1}^{n} e^{-i\, k\cdot(r_i - r_j)} \right\rangle_c$$

where

$$Z_c^c(\beta) = \int d[x_N]\, e^{-\beta U} \qquad \text{(C.4)}$$

$$Z_c^m(\beta) = \int d[p_N]\, e^{-\beta \sum_i \frac{p_i^2}{2m}} \qquad \text{(C.5)}$$

The term of order $\hbar$ becomes :

$$A^{(1)} = \sum_{i=1}^{n} \sum_{j=1}^{n}{}' \int d[x_N]\, d[p_N]\, e^{-i\, k\cdot(r_i - r_j)}\, \frac{e^{-\beta U}}{Z_c(\beta)}\, e^{-\beta \sum_{\ell} \frac{p_\ell^2}{2m}} \qquad \text{(C.6)}$$

$$(*)\, e^{-\frac{\beta}{2m}\left(p_i - \frac{\hbar k}{2}\right)}\, e^{-\frac{\beta}{2m}\left(p_j + \frac{\hbar k}{2}\right)^2} \left[-i\, \frac{\beta^2}{2} \sum_{\ell=1}^{n} \frac{p_\ell}{m} \cdot \nabla_{x_\ell} U \right.$$

$$\left. +\ i\, \frac{\hbar \beta^2}{2m}\, k \cdot \left(\nabla_{x_i} U - \nabla_{x_j} U \right) \right]$$

$$= \sum_{i=1}^{m} \sum_{j=1}^{i} \int d[\underline{x}_N]\, e^{-i\underline{k}\cdot(\underline{x}_i - \underline{x}_j)} \frac{e^{-\beta U}}{Z_c} \left[-i \frac{\beta^2}{2} \hbar \underline{k} \cdot \underline{\nabla}_{\underline{x}_i} U \right.$$

$$\left. + i \frac{\beta^2}{2m} \hbar \underline{k} \cdot \underline{\nabla}_{\underline{x}_j} U + i \frac{\hbar \beta^2}{2m} \underline{k} \cdot \left(\underline{\nabla}_{\underline{x}_i} U - \underline{\nabla}_{\underline{x}_j} U \right) \right]$$

$$= 0$$

The last term is

$$A^{(2)} = \sum_{i=1}^{m} \sum_{j=1}^{i} \int d[\underline{x}_N]\, d[\underline{p}_N]\, e^{-i\underline{k}\cdot(\underline{x}_i - \underline{x}_j)} \frac{e^{-\beta U}}{Z_c} (*) \qquad \text{(C.7)}$$

$$(*)\; e^{-\beta \sum_{\ell \neq i,j}^{m} \frac{p_\ell^2}{2m}}\, e^{-\frac{\beta}{2m}(\underline{p}_i - \hbar \underline{k})^2}\, e^{-\frac{\beta}{2m}(\underline{p}_j + \hbar \underline{k})^2}$$

$$(*) \left[-\frac{\beta^4}{8} \left(\sum_{\ell=1}^{m} \frac{\underline{p}_\ell}{m} \cdot \underline{\nabla}_{\underline{x}_\ell} U \right)^2 + \frac{\beta^3}{6} \sum_{\ell=1}^{m} \sum_{\lambda=1}^{m} \frac{\underline{p}_\ell \underline{p}_\lambda}{m^2} : \underline{\nabla}_{\underline{x}_\ell} \underline{\nabla}_{\underline{x}_\lambda} U \right.$$

$$+ \frac{\beta^3}{6} \sum_{\ell=1}^{m} \frac{1}{m} \left(\underline{\nabla}_{\underline{x}_\ell} U \right)^2 - \frac{\beta^2}{4} \sum_{\ell=1}^{m} \frac{1}{m} \left(\underline{\nabla}_{\underline{x}_\ell}^2 U \right)$$

$$+ \frac{\beta^3}{24} \sum_{\ell=1}^{m} \frac{1}{m} \left\langle \left(\underline{\nabla}_{\underline{x}_\ell} U \right)^2 \right\rangle_c + \frac{\hbar \beta^4}{8} \left(\underline{\nabla}_{\underline{x}_i} - \underline{\nabla}_{\underline{x}_j} \right) \sum_{\ell=1}^{m} \frac{\underline{p}_\ell}{m} \cdot \left(\underline{\nabla}_{\underline{x}_\ell} U \right)$$

$$- \frac{\hbar \beta^3}{3} \sum_{\ell=1}^{m} \underline{k} \cdot \left(\underline{\nabla}_{\underline{x}_i} - \underline{\nabla}_{\underline{x}_j} \right) \frac{\underline{p}_\ell}{m} \cdot \underline{\nabla}_{\underline{x}_\ell} U$$

$$+ \frac{\hbar \beta^3}{6m} \sum_{\ell=1}^{m} \frac{\underline{p}_\ell}{m} \cdot \underline{\nabla}_{\underline{x}_\ell} U\; \underline{k} \cdot \left(\underline{\nabla}_{\underline{x}_i} U - \underline{\nabla}_{\underline{x}_j} U \right)$$

$$\left. - \frac{\beta^3}{6m} \left\{ \hbar \underline{k} \cdot \left(\underline{\nabla}_{\underline{x}_i} U - \underline{\nabla}_{\underline{x}_j} U \right) \right\}^2 + \right.$$

$$+\frac{\hbar^2\beta^3}{6m^2}\,\underline{h}\cdot\left(\underline{\nabla}_{\underline{x}_i}-\underline{\nabla}_{\underline{x}_j}\right)\underline{h}\cdot\left(\underline{\nabla}_{\underline{x}_i}U-\underline{\nabla}_{\underline{x}_j}U\right)$$

$$=-\frac{\beta^2}{12}\left\langle\sum_{i=1}^{m}\sum_{j=1}^{m}{}'\frac{e^{-i\underline{h}\cdot(\underline{x}_i-\underline{x}_j)}}{m}\left[\nabla^2_{\underline{x}_i}U-\nabla^2_{\underline{x}_j}U\right]\right\rangle_c$$

$$-\frac{\beta^2}{24}\left\langle\sum_{i=1}^{m}\sum_{j=1}^{m}{}'\sum_{\beta\neq i,j}^{m}\frac{e^{-i\underline{h}\cdot(\underline{x}_i-\underline{x}_j)}}{m}\nabla^2_{\underline{x}_\beta}U\right\rangle_c$$

$$+\frac{\beta^2}{24}\sum_{\ell=1}^{m}\left\langle\frac{1}{m}\nabla^2_{\underline{x}_i}U\right\rangle_c P(\underline{h})$$

The function $\left\langle\sum_{i=1}^{m}\sum_{j=1}^{m}e^{-i\underline{h}(\underline{x}_i-\underline{x}_j)}\right\rangle$ is then given by :

$$\left\langle\sum_{i=1}^{m}\sum_{j=1}^{m}{}'e^{-i\underline{h}\cdot(\underline{x}_i-\underline{x}_j)}\right\rangle \tag{C.8}$$

$$=\left\langle\sum_{i=1}^{m}\sum_{j=1}^{m}{}'e^{-i\underline{h}\cdot(\underline{x}_i-\underline{x}_j)}\right\rangle_c$$

$$-\frac{\hbar^2\beta^2}{12}\left\langle\sum_{i=1}^{m}\sum_{j=1}^{m}{}'\frac{e^{-i\underline{h}\cdot(\underline{x}_i-\underline{x}_j)}}{m}\left[\nabla^2_{\underline{x}_i}U-\nabla^2_{\underline{x}_j}U\right]\right\rangle_c$$

$$-\frac{\hbar^2\beta^2}{24}\left\langle\sum_{i=1}^{m}\sum_{j=1}^{m}{}'\sum_{\beta\neq i,j}^{m}\frac{e^{-i\underline{h}\cdot(\underline{x}_i-\underline{x}_j)}}{m}\nabla^2_{\underline{x}_\beta}U\right\rangle_c$$

$$+\frac{\hbar^2\beta^2}{24}\sum_{\ell=1}^{m}\left\langle\frac{1}{m}\nabla^2_{\underline{x}_i}U\right\rangle_c P(\underline{h})$$

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