DEPARTMENT OF NUCLEAR ENGINEERING

UNIVERSITY OF MICHIGAN

THE SCATTERING OF NEUTRONS BY MACROSCOPIC SYSTEMS

By R. K. Osborn
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Section I) Some General Remarks on Neutron Scattering.

The task that we set here for ourselves is that of determining the extent of the information about a given scattering system that is available from a neutron diffraction experiment. The sort of experiment that is here envisaged is characterized schematically in figure (1).
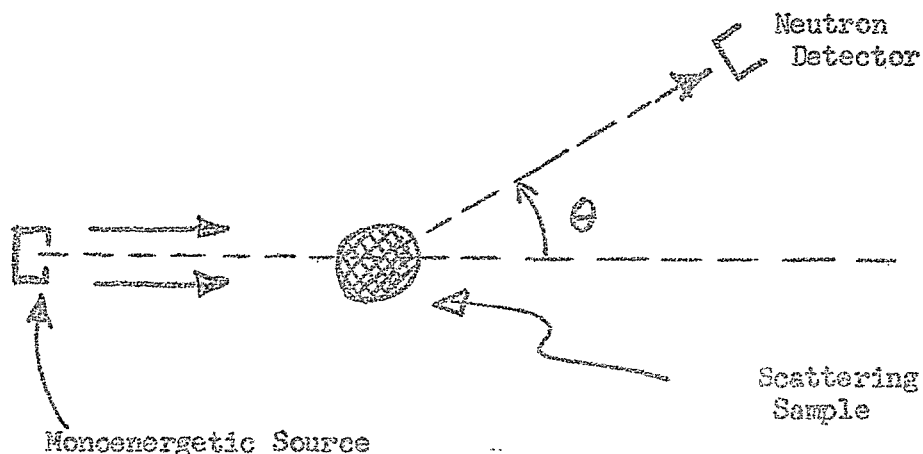

Fig. (1)

Ideally, the incident beam should be monoenergetic though in practice, of course, it is characterized by a finite spread in energy. The sample is presumed small enough that multiple scattering of neutrons is negligible, but yet large enough that the fraction of the neutrons scattered out of the incident beam is appreciable. Again ideally, the detector — which is to be set at various angles, θ — is presumed capable of counting neutrons monoenergetically at all relevant energies. The problems associated with the attempts to achieve approximate realization of these conditions in actual practice will not be entered into here. Our concern is rather to investigate the extent to which such experiments provide useful informa-

tion about the scattering system, i.e., assuming that we can observe under essentially ideal conditions, what do the observations mean.

As some aspects of these experiments - particularily those associated with energy transfer between the neutrons and the scattering system - are quite sensitive to details of the microscopic properties of the neutrons and the target, a quantum mechanical analysis is necessary. One way of visualizing such experiments theoretically is in terms of a steady state situation in which monoenergetic, monodirectional neutrons are incident upon the target at a constant rate, and subsequently pass through the surface of a large conceptual sphere centered at the target at the same rate. [1,2] In such a circumstance, the experiment is presumably described by the steady state Schroedinger equation,

$$H \Psi = E \Psi \qquad (I,1)$$

In this equation, E is the total energy of the scattering system plus that of the neutron;

$$H = \frac{p^2}{2m} + H_s + V_{Sn} \qquad (I,2)$$

where $p^2/2m$ is the kinetic energy of the neutron, H_S the energy of the system, and V_{Sn} the energy of the interactions of the neutrons with the system; and Ψ is the wave function for the system plus neutron. Clearly, in general H_S and Ψ are exceedingly complex and in fact usually unknown. Nevertheless, we may proceed formally (and usefully) a considerable way before seeking explicit, approximate representations of these quantities. This follows be-

cause we have every reason to expect that there exists a complete orthornormal set of functions $\{\bar{\Phi}_n\}$ such that

$$H_s \bar{\Phi}_n = \mathcal{E}_n \bar{\Phi}_n \qquad (I,3)$$

The symbol n stands for a sufficiently large set of numbers to distinguish all the members of the indicated set (usually 4 N numbers for a system of N particles with fixed spins). The functions $\bar{\Phi}_n$ are the energy eigenstates of the scattering system, and the $\mathcal{E}_n$ are their corresponding energy eigenvalues. It is convenient to add to the set $\{\bar{\Phi}_n\}$ the functions describing the neutron spin states. Designating this set by $\{X_s\}$, we construct the expanded set $\{\bar{\Phi}_n X_s\}$.

Because the set $\{\bar{\Phi}_n \cdot X_s\}$ is presumed complete in the domain of variables required to specify the scattering system and the spin states of the neutron, it follows that we may exhibit

$$\bar{\Psi} = \sum_{n,s} \psi_{ns}(\underline{r}) \bar{\Phi}_n X_s \qquad (I,4)$$

where $\psi_{ns}(\underline{r})$ is a neutron state corresponding to the nth state of the system and the sth spin state of the neutron and depends only upon the position $(\underline{r})$ of the neutron. We may now rewrite equation (I,1) as

$$\frac{p^2}{2m}\psi_{ns} + \mathcal{E}_n \psi_{ns} + \sum_{n',s'}(\bar{\Phi}_n X_s, V_{sn} \bar{\Phi}_{n'} X_{s'})\psi_{n's'} \qquad (I,5)$$

$$= E \psi_{ns}$$

or

$$\frac{p^2}{2m}\psi_{ns} + \sum_{n's'}(\bar{\Phi}_n X_s, V_{sn} \bar{\Phi}_{n'} X_{s'})\psi_{n's'} = (E - \mathcal{E}_n)\psi_{ns} \qquad (I,6)$$

Letting $\epsilon_n = E - \xi_n$ and then $k_n^2 = 2m\,\epsilon_n/\hbar^2$, (I,6) may be exhibited as

$$(\nabla^2 + k_n^2)\,\psi_{ns} = \frac{2m}{\hbar^2}\sum_{n's'}(\Phi_n \chi_s,\, V_{sn}\,\Phi_{n'}\chi_{s'})\,\psi_{n's'} \qquad (I,7)$$

It is convenient to reformulate this system of differential equations as a system of integral equations by defining the Green's functions, $G_n\ (r,\ r')$, by

$$(\nabla^2 + k_n^2)\,G_n\,(r,r') = -\,\delta(r-r') \qquad (I,8)$$

and then observing that

$$\psi_{ns} = \psi_n^0 - \frac{2m}{\hbar^2}\sum_{n's'}\int_{r'} d^3r'\,G_n(r,r')(\Phi_n\chi_s,\, V_{sn}\,\Phi_{n'}\chi_{s'})\,\psi_{n's'} \qquad (I,9)$$

In (I,9), the function ψ_n^0 is simply a solution of the homogeneous equation,

$$(\nabla^2 + k_n^2)\,\psi_n^0 = 0 \qquad (I,10)$$

For the Green's function employed here, as defined by (I,8), we have

$$G_n\,(r,r') = \frac{e^{ik_n|r-r'|}}{4\pi|r-r'|} \qquad (I,11)$$

The source term of the integral equation (I,9) is to be chosen so that the equation describes a wave function ψ_{ns} which corresponds to a scattering experiment. But in such an experiment, if the interaction between the incident neutrons and the nuclei of the target system were zero, one would expect that $\psi_{ns} = 0$,

unless (ns) corresponded to the actual state of the target system
and to the spin state of the neutrons in the incident beam; and

$$\psi_{n_0 s_0} = e^{i \underline{k}_0 \cdot \underline{r}} \qquad (I,12)$$

if $(n_0 \ s_0)$ were the system and neutron spin state at that in-
stant. Thus in the general case in which the neutron-system inter-
action does not vanish, we have

$$\psi_{ns} = \delta_{nn_0} \delta_{ss_0} e^{i \underline{k}_0 \cdot \underline{r}} \qquad (I,13)$$

$$- \frac{2m}{\hbar^2} \sum_{n's'} \int d^3r' G_n(r,r') (\overline{\Phi}_n \chi_s, V_{sn} \overline{\Phi}_n, \chi_s) \psi_{n's'}$$

To achieve a "first approximation" solution to this equation
we iterate once to obtain

$$\psi_{ns} = \delta_{nn_0} \delta_{ss_0} e^{i \underline{k}_0 \cdot \underline{r}} \qquad (I,14)$$

$$- \frac{2m}{\hbar^2} \int d^3r' G_n(r,r') (\overline{\Phi}_n \chi_s, V_{sn} \overline{\Phi}_{n_0} \chi_{s_0}) e^{i \underline{k}_0 \cdot \underline{r}'}$$

In these expressions, $\underline{k}_0$ is a vector whose magnitude is the inverse
of the wave length associated with the neutrons in the incident beam,
i.e., $k_0 = m v_0 / \hbar$. W $\underline{\Theta}$ are primarily interested in this solution
when evaluated on the surface of a large sphere centered in the scat-
tering system which is presumably confined to a region whose least
linear dimension is very small compared to the radius of the sphere.
In such circumstances we have in the integrand of (I,14), $r/r' \gg 1$.

Hence

$$G_n \xrightarrow[r/r' \gg 1]{} \frac{e^{ik_n r - ik_n \cdot r'}}{4\pi r} + \mathcal{O}(r^{-2}) \qquad (I,15)$$

and we may ignore the terms of $O(r^{-2})$ as they can contribute nothing to a current at "infinity". Hence at large distances from the scattering system our approximate solution assumes the form

$$\psi_{ns} \sim \delta_{nn_0} \delta_{ss_0} e^{ik_0 \cdot r}$$

$$- \frac{2m}{4\pi\hbar^2} \frac{e^{ik_n r}}{r} \int d^3r' e^{ir' \cdot (k_0 - k_n)} (\Phi_n \chi_s, V_{sn} \Phi_{n_0} \chi_{s_0}) \qquad (I,16)$$

Letting $f_{n_0 s_0}^{ns}(\Omega)$ represent the amplitude of the scattered waves associated with the transition $(n_0 s_0) \longrightarrow (ns)$, i.e.

$$f_{n_0 s_0}^{ns}(\Omega) = - \frac{2m}{4\pi\hbar^2} \int d^3r' e^{ir' \cdot (k_0 - k_n)} (\Phi_n \chi_s, V_{sn}' \Phi_{n_0} \chi_{s_0}) \qquad (I,17)$$

we have for our "scattering states",

$$\psi_{ns} \sim \delta_{nn_0} \delta_{ss_0} e^{ik_0 \cdot r} + f_{n_0 s_0}^{ns}(\Omega) \frac{e^{ik_n r}}{r} \qquad (I,18)$$

Section II) The Cross Section

The results of scattering experiments are generally presented in terms of the differential cross section which is usually defined by

$$\sigma d\Omega \equiv \frac{n^{\circ} \text{ of particles into } d \quad \text{per sec. per atom}}{n^{\circ} \text{ of incident particles per sec per } cm^2}$$

$$dA = R^2 d\Omega$$
$$= R^2 \sin\theta \, d\theta \, d\Phi$$

Scattering Sample

R

Incident beam of intensity

fig. (2)
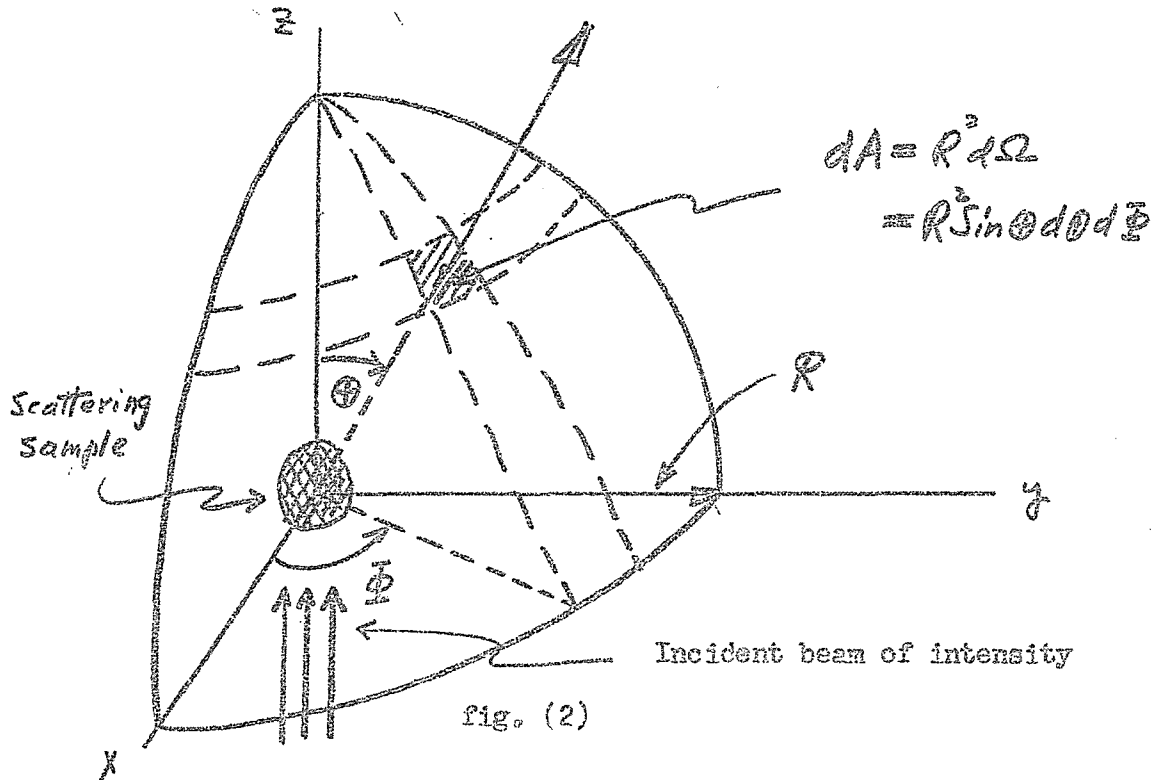
In figure (2) we have presented a conceptualization of the experiment and a specification of most of the quantities appropriate to the definition of the cross section. To proceed further, we define $\underline{J}(\underline{R}, \underline{\Omega})$ to be the current of scattered particles passing through the surface of the sphere of radius R going in direction $\underline{\Omega}$. Then if $\underline{R}$ is a radial unit vector, $\underline{J} \cdot \hat{\underline{R}} \ R^2 d\underline{\Omega}$ is the number of scattered particles passing through the element of area $dA = R^2 d\underline{\Omega}$ per sec. Hence

$$\sigma d\underline{\Omega} \equiv \frac{\underline{J} \cdot \hat{\underline{R}} \ R^2 d\underline{\Omega}}{N I} \tag{II,1}$$

where as indicated in figure (2), I is the intensity of the incident beam and N is the number of scatterers in the sample.

Now recall that the particle current in a system described by

the state vector ψ is given by

$$\underline{S} = \frac{i}{2m\hbar} \left[(\psi \underline{\nabla} \psi^\dagger) - (\psi^\dagger \underline{\nabla} \psi) \right] \tag{II,2}$$

Evidently we may now calculate the incident beam intensity, I, and the scattered current, $\underline{J}$. Recalling equation (I,18) and figure (2) we see first of all that

$$I \doteq \hat{\underline{z}} \cdot \underline{S} = \frac{k_0}{m\hbar} \tag{II,3}$$

where we have recognized $e^{i \underline{k_0} \cdot \underline{r}}$ as the wave function for the incident beam. Similarily, interpreting $f^{ns}_{n_0 s_0} e^{iknr}/r$ as the scattered wave, we have for the relevant outgoing current,

$$\underline{J} \cdot \hat{\underline{R}} R^2 d\Omega = \frac{k_n}{m\hbar} \left| f^{ns}_{n_0 s_0} \right|^2 d\Omega \tag{II,4}$$

Thus now we have for a differential cross-section,

$$\sigma^{ns}_{n_0 s_0} d\Omega = \frac{k_n}{N k_0} \left| f^{ns}_{n_0 s_0} \right|^2 d\Omega \tag{II,5}$$

This cross-section is still, in general, not measurable, as neither the initial nor the final states of the scattering system (characterized by the sets of numbers n_0 and n respectively) are usually observable. Furthermore the initial and final spin states of the neutron (s_0, s) may or may not be prepared in some definite way. Thus in order to calculate a measurable quantity from (II,5) we define $p n_0 s_0$ to be the probability of finding the scattering system in the initial state n_0 and the neutrons in the incident beam in the initial spin state s_0, and then compute

$$\sigma^{ns} d\Omega = \sum_{n_0 s_0} P_{n_0 s_0} \sigma^{ns}_{n_0 s_0} d\Omega \quad , \tag{II,6}$$

where the sum runs over all possible system and neutron spin states.
Lastly we sum over all of the unobservable final states of the scattering system to obtain

$$\sigma^s d\Omega = \sum_{n n_o s_o} P_{n_o s_o} \sigma_{n_o s_o}^{ns} d\Omega \qquad (II,7)$$

This differential cross-section is measurable provided that only neutrons of a definite spin orientation are counted in the scattered beam. If all scattered neutrons are counted, regardless of orientation, then the observed quantity is (II,7) summed over all s.

Recalling equation (II,5), we write (II,7) as

$$\sigma^s d\Omega = \frac{1}{N} d\Omega \sum_{n n_o s_o} P_{n_o s_o} \frac{k_n}{k_o} \left| f_{n_o s_o}^{ns} \right|^2 \qquad (II,8)$$

Further reduction of this expression toward interpretable terms requires that at least some of the sums indicated in (II,8) must be performed. Progress in this direction may be at least partially accomplished in accordance with the following arguments.[3] First we note that by equations (I,6) and (I,7) we have the relations

$$\frac{\hbar^2 k_n^2}{2m} = E - \mathcal{E}_n \quad , \qquad \frac{\hbar^2 k_o^2}{2m} = E - \mathcal{E}_{n_o} \quad ,$$

so that

$$\frac{\hbar^2 k_n^2}{2m} + \mathcal{E}_n = \frac{\hbar^2 k_o^2}{2m} + \mathcal{E}_{n_o} \qquad (II,9)$$

Recalling that $\mathcal{E}_n$ was defined to be the energy of the scattering system when in the state, n, we see that (II,9) is merely a state-

ment of conservation of energy. Note that (II,9) may be also written as

$$\epsilon_n + \mathcal{E}_n = \epsilon_o + \mathcal{E}_{n_o} \qquad (II,10)$$

in accordance with notation previously introduced.

Now k_o (or equivalently, ϵ_o - the energy of the neutrons in the incident beam) is prepared experimentally, and k_n (or ϵ_n) is an <u>observed</u> quantity appropriate to the neutrons in the scattered beam. Designate this latter quantity by k_f (or ϵ_f). We may then introduce a new differential cross-section defined by

$$\sigma^s d\Omega d\epsilon_f \qquad (II,11)$$

$$= \frac{d\Omega}{N} \sum_{n n_o s_o} P_{n_o s_o} \frac{k_f}{k_o} \left| f_{n_o s_o}^{ns} \right|^2 \delta(\epsilon_f + \mathcal{E}_n - \epsilon_o - \mathcal{E}_{n_o}) d\epsilon_f$$

where evidently

$$\int_{\epsilon_f} \sigma^s d\Omega d\epsilon_f = \sigma^s d\Omega$$

as exhibited in equation (II,8). Employing as a representation of the delta-function

$$\delta(\epsilon_f + \mathcal{E}_n - \epsilon_o - \mathcal{E}_{n_o}) = \frac{1}{(2\pi)} \int_{-\infty}^{\infty} \frac{dt}{\hbar} e^{it(\epsilon_f + \mathcal{E}_n - \epsilon_o - \mathcal{E}_{n_o})/\hbar} \qquad (II,12)$$

we see that we may write (II,11) as

$$* \quad \sigma^s d\Omega d\epsilon_f = \frac{d\Omega d\epsilon_f}{2\pi N} \frac{k_f}{k_o} \sum_{n n_o s} \int \frac{dt}{\hbar} e^{it(\epsilon_f - \epsilon_o)/\hbar}$$

$$\times P_{n_o s_o} e^{it(\mathcal{E}_n - \mathcal{E}_{n_o})/\hbar} \left| f_{n_o s_o}^{ns} \right|^2$$

$$* = \frac{d\Omega \, d\epsilon_f}{2\pi N} \frac{k_n}{k_o} \int \frac{dt}{\hbar} e^{it(\epsilon_f - \epsilon_o)/\hbar} \qquad (II,13)$$

$$\times \sum_{n n_o s_o} P_{n_o s_o} \, e^{it(E_n - E_{n_o})/\hbar} \left| f_{n_o s_o}^{ns} \right|^2$$

It should be emphasized that the quantity presented in (II,13) is not an observable, as it is essentially a sum of delta functions. However, it does provide us with a quantity that by integration is directly related to observables, and is furthermore in a convenient form for further manipulation in that now the sum over n (final system states) can be performed. The principal advantage gained, of course, is the removal of the factor k_n/k_o from the summand.

Now consider the sum

$$\sum_n e^{it(E_n - E_{n_o})/\hbar} \left| f_{n_o s_o}^{ns} \right|^2 \qquad (II,14)$$

Recalling (I,17) rewrite $f_{n_o s_o}^{ns}$ as $\qquad (II,15)$

$$f_{n_o s_o}^{ns} = - \left(\Phi_n \chi_s, \left\{ \frac{2m}{4\pi\hbar^2} \int d\vec{r}' e^{i \vec{k}' \cdot (\vec{k}_o - \vec{k}_f)} V_{sn}' \right\} \Phi_{n_o} \chi_{s_o} \right)$$

(Remember that $\vec{\Phi}_\eta$ depends only upon system variables, not the position of the neutron, and X_s depends only upon the neutron spin state.) To proceed further, it is necessary to give some explicit consideration to the interaction energy, V_{Sn}. Keeping in mind that we are concerned here only with the scattering of slow neutrons (neutrons with energies of the order of or less than a few electron volts), and observing that usually the scattering of such neutrons by isolated nuclei is isotropic in the center of mass coordinate system and independent of the neutron energy (effectively as if the neutron and the target nuclei were hard spheres) we choose our potential so as to reproduce these observations in an adequate fashion in the sense of the approximation, (I,14). A choice which accomplishes these objectives and simultaneously provides considerable simplification for the subsequent analysis is the "Fermi pseudo-potential," i.e., a potential describing the interaction between a neutron and a particular nucleus which is zero unless the two particles coincide, in which case it becomes infinite. Since the potential energy, V_{Sn}, is the sum of the potential energies of interaction between the incident neutron and all the nuclei of the target system, we exhibit

$$V_{SN} = \frac{4\pi\hbar^2}{2m} \sum_j a(\underline{S}, \underline{\mathcal{L}}_j) \delta(\underline{r} - \underline{R}_j) \qquad (II,16)$$

In this expression, $\underline{R}_j$ is the position vector to the jth nucleus, $\underline{S}$ is the angular momentum of the neutron, and $\underline{\mathcal{L}}_j$ is the angular momentum of the jth nucleus. The quantity, $a(\underline{S}, \underline{\mathcal{L}}_j) = a_j$ is the scattering length of the jth nucleus and is - as indicated -

generally a function of the angular momentum of the neutron and the nucleus.

With this particular choice for the potential characterizing the interaction between a neutron and a nucleus, we see that (II,15) becomes

$$f_{n_0 s_0}^{ns} = -\sum_j (\Phi_n \chi_s, q_j e^{i R_j \cdot (k_0 - k_f)} \Phi_{n_0} \chi_{s_0}) \qquad (II,17)$$

It is convenient at this point to introduce further compression in our notation. This we do by rewriting (II,17) as

$$f_{n_0 s_0}^{ns} = -\sum_j \langle ns | U_j | n_0 s_0 \rangle \qquad (II,18)$$

where we have introduced the symbol

$$U_j = q_j e^{i R_j \cdot (k_0 - k_f)}$$

We now return to our consideration of the sum (II,14) which we may write as

$$(II,19)$$

$$\sum_n \sum_{i j} e^{i t (\varepsilon_n - \varepsilon_{n_0})/\hbar} \langle ns | U_i | n_0 s_0 \rangle^* \langle ns | U_j | n_0 s_0 \rangle$$

This may be further rewritten as

$$(II,20)$$

$$\sum_{i j} \sum_n \langle n_0 s_0 | U_i^\dagger | ns \rangle \langle ns | e^{i \varepsilon_n t/\hbar} U_j e^{-i \varepsilon_{n_0} t/\hbar} | n_0 s_0 \rangle$$

$$= \sum_{i j} \sum_n \langle n_0 s_0 | U_i^\dagger | ns \rangle \langle ns | e^{i H_s t/\hbar} U_j e^{-i H_s t/\hbar} | n_0 s_0 \rangle$$

It is now desirable to exhibit

where
$$U_i = a_i \Lambda_i \, ,$$
$$\Lambda_i = e^{i \underline{R}_i \cdot (\underline{k}_0 - \underline{k}_f)}$$

and note that H_S (the Hamiltonian for the target system is ~ to good approximation ~ not a function of the spins of the nuclei of that system. Then (II,20) may be rewritten as

$$
(II,21)
$$

$$
\sum_{ijM} \langle S_0 M_0 | a_i^\dagger | S M \rangle \langle S M | a_j | S_0 M_0 \rangle
$$

$$
\times \sum_{n} \langle n_0 | \Lambda_i^\dagger | n \rangle \langle n | e^{i H_S t / \hbar} \Lambda_j \, e^{-i H_S t / \hbar} | n_0 \rangle
$$

Note that here we have separated out from the states $| n \rangle$ their dependence upon the projection states of the nuclei in the target system, and then again labeled the target states in configuration space by the set of numbers $\{ n \}$ ~ now only 3N of them for N nuclei, i.e.,

$$
| n \rangle \longrightarrow | n \rangle | M \rangle
$$

It should be pointed out that this assumed separation of the space and spin dependence of the target system precludes investigation of such interesting phenomena as the scattering from the ortho and para hydrogen states in liquid hydrogen.

Introducing the notation,

$$
(II,22)
$$

$$
\Lambda(t) = e^{i H_S t / \hbar} \Lambda_j \, e^{-i H_S t / \hbar}
$$

we see that we may finally exhibit our sum as

$$\sum_{ij\,M} \langle S_0 M_0 | a_i^\dagger | SM \rangle \langle SM | a_j | S_0 M_0 \rangle \langle n_0 | A_i^\dagger A_j(t) | n_0 \rangle \qquad \text{(II,23)}$$

The differential cross-section (II,13) may now be written as,

$$\sigma\, d\Omega\, d\epsilon_f = \frac{d\Omega\, d\epsilon_f}{2\pi N} \frac{k_f}{k_0} \int \frac{dt}{\hbar} e^{it(\epsilon_f - \epsilon_0)/\hbar} \qquad \text{(II,24)}$$

$$x \sum_{ij} \sum_{n_0 S_0 M_0} P_{n_0 S_0 M_0} \langle S_0 M_0 | a_i^\dagger | SM \rangle \langle SM | a_j | S_0 M_0 \rangle$$

$$x \langle n_0 | A_i^\dagger A_j(t) | n_0 \rangle$$

Finally, we introduce the new variable $\omega = (\epsilon_f - \epsilon_0)/\hbar$ and note that quite generally the probability of finding the scattering system in an initial state in configuration space n_0 and the neutron and nuclei in the initial spin state $s_0\, m_0$ is simply the product of the two indicated probabilities, i.e.,

$$P_{n_0 S_0 M_0} = P_{n_0} P_{S_0 M_0}\,, \qquad \text{(II,25)}$$

so that now we have

$$\sigma\, d\Omega\, d\omega = \frac{d\Omega\, d\omega}{2\pi N} \frac{k_f}{k_0} \int dt\, e^{i\omega t} \qquad \text{(II,26)}$$

$$x \sum_{ij} \sum_{S_0 M_0} P_{S_0 M_0} \langle S_0 M_0 | a_i^\dagger | SM \rangle \langle SM | a_j | S_0 M_0 \rangle$$

$$x \sum_{n_0} P_{n_0} \langle n_0 | A_i^\dagger A_j(t) | n_0 \rangle$$

This is the form of the scattering cross-section that we
shall employ as a starting point for the analysis of specific ex-
periments in the subsequent sections. This expression is actually
quite general, and will be employed in an investigation of the scat-
tering from gases, crystals, and liquids. Furthermore, it holds for
a considerable range of incident neutron energies provided the scat-
tering of neutrons from isolated nuclei of the type found in the
sample is actually isotropic in the center of mass coordinate system
and independent of the neutron energy.

Section III) The Scattering of Neutrons by Dilute, Monatomic Gases

As a first illustration of the utility of the formula $(II,26)$,
we consider the scattering of neutrons by a dilute, monatomic gas. (3)
As we shall see, the experiment envisaged in this analysis is actually
the appropriate one for the measurement of the scattering of neutrons
by the individual nuclei that comprise the gas; as the interference of
scattered waves associated with neutrons scattered by different nuclei.
(terms in the sum over i and j for i different from j) may be consid-
ered negligible if the dilution is sufficiently great. In fact, we
shall here define a dilute, monatomic gas to be one for which the in-
terference contributions to the scattering cross-section may be ignored.
In such an event, our expression for the cross-section reduces to

$$\bar{\sigma}\, d\Omega\, d\omega = \frac{d\Omega\, d\omega}{2\pi}\, \frac{k_f}{k_0}\int dt\, e^{i\omega t} \sum_{S_0 M_0} P_{S M_0}\, \left| \langle SM|\alpha|S_0 M_0\rangle \right|^2 \qquad (III,1)$$

$$\times \sum_{n_0} P_{n_0}\, \langle n_0|\Lambda^t \Lambda(t)|n_0\rangle$$

We are, of course, also assuming here that our scattering gas
consists of but a single nuclear component. The sum over i and j
has disappeared since, after setting equal to j and summing over
j we found a sum of N identical terms -- hence also the disappearance
of the factor N^{-1}.

At this point it is desirable to become somewhat more explicit
about the spin-dependent scattering lengths, a. Recall that they
were effective by introduced according to the definition,

$$V(r, S, R_j, \theta_j) = \frac{4\pi\hbar^2}{2m} a(S, \theta_j) \delta(r - R_j) \quad (III,2)$$

Hence it is evident that we must make some sort of a guess as to
the potential, V, characterizing the interaction of a neutron with
a given nucleus. That we can only guess about the nature of this
interaction follows firstly from the fact that at present the law
of force governing the interaction between nucleons is not known;
and secondly from the fact that even if the force law for such in-
teractions were known, it is doubtful if the precise character of
the interaction between a neutron and a given nucleus comprised of
several nucleons could be deduced therefrom. Hence we lead from
ignorance with an appeal to simplicity and choose a potential of
the form

$$V(r, S, R, \theta) = V_0(|r-R|) + S \cdot \theta V_1(|r-R|) \quad (III,3)$$

Such a choice, plus the definition (III,2), implies that

$$a(S, \theta_j) = a_{0j} + S \cdot \theta_j a_{1j}, \quad (III,4)$$

where a_{oj} is to be interpreted as the scattering length for the spin-independent part of the interaction of a neutron with the jth type nucleus, and a_{1j}' is the scattering length for the spin-dependent part of same - and are to be regarded as empirical constants to be determined experimentally.

The quantity that here concerns us is the factor in the expression for the cross-section,

$$\sum_{S_o M_o M} P_{S_o M_o} \left| \langle S M | a | S_o M_o \rangle \right|^2 \qquad \text{(III,5)}$$

$$= \sum_{S_o M_o M} P_{S_o M_o} \left| \langle S M | a_o + \vec{S} \cdot \vec{\sigma} a_1 | S_o M_o \rangle \right|^2$$

If we let $\underline{J} = \underline{S} + \underline{I}$, then the matrix element in (III,5) may be conveniently rewritten as

$$\langle S M | a_o + a_1 \frac{J^2 - I^2 - S^2}{2} | S_o M_o \rangle \qquad \text{(III,6)}$$

We now assume that our neutron detector in no way distinguishes between neutrons in different spin states, i.e., every neutron entering the detector is counted regardless of its spin orientation. In such an event, (III,5) should be summed over all final neutron spin states and we obtain

$$\qquad \text{(III,7)}$$

$$\sum_{S_o M_o} P_{S_o M_o} \langle S_o M_o | \left(a_o + a_1 \frac{J^2 - I^2 - S^2}{2} \right) \left(a_o + a_1 \frac{J^2 - I^2 - S^2}{2} \right) | S_o M_o \rangle$$

To perform the sum in (III,7), it is first necessary to evaluate explicitly the indicated matrix elements. But this is not readily accomplished in the representation chosen above as it does not diagonalize J^2. The representation in which J^2 (as well as $\mathcal{G}^2$ and S^2) is diagonal is the one in which $\mathcal{G}$ and $\underline{S}$ add to form a $\underline{J}$ of fixed magnitude and in which further the projection states of $\underline{J}$ along the z-axis say are also constant in time. The labels for such states would hence be (j m) where

$$\vec{J}^2 |jm\rangle = j(j+1)|jm\rangle \qquad (\text{III},8)$$

$$\text{and } J_z |jm\rangle = m|jm\rangle$$

In this representation, (III,7) becomes

$$(\text{III},9)$$

$$\sum_{jm} P_{jm} \langle jm|(a_0 + a_1 \frac{\vec{J}^2 - \mathcal{G}^2 - S^2}{2})(a_0 + a_1 \frac{\vec{J}^2 - \mathcal{G}^2 - S^2}{2})|jm\rangle$$

$$= \sum_{jm} P_{jm} \left(a_0 + a_1 \frac{j(j+1) - I(I+1) - \frac{3}{4}}{2}\right)^2$$

In (III,9), P_{jm} is the probability of finding the neutron and nucleus before collision in a state having total angular momentum j and z-component m. Since the magnitude of the neutron spin is 1/2, it follows that there are but two values that j can take on; j = I+1/2 and j = I-1/2. As the total number of states that can be formed from a nucleus of spin I and a neutron of spin 1/2 is 2 (2I + 1)

(2I + 1 nuclear orientations and 2 neutron orientations for each nuclear one), we find that (III,9) becomes

$$\sum_{m=-(I+\frac{1}{2})}^{(I+\frac{1}{2})} \frac{m}{2(2I+1)}\left[a_0 + a_1\frac{I}{2}\right]^2 + \sum_{m=-(I-\frac{1}{2})}^{(I-\frac{1}{2})} \frac{m}{2(2I+1)}\left[a_0 - a_1\frac{I+1}{2}\right]^2 \quad (III,10)$$

$$= \frac{I+1}{2I+1}\left(a_0 + \frac{I}{2}a_1\right)^2 + \frac{I}{2I+1}\left(a_0 - \frac{I+1}{2}a_1\right)^2$$

It is conventional to introduce new scattering lengths

$$a_+ = a_0 + \frac{I}{2}a_1 , \qquad (III,11)$$

$$a_- = a_0 - \frac{I+1}{2}a_1 ,$$

so that we obtain for the cross-section (III,1) the form

$$\qquad\qquad\qquad (III,12)$$

$$\sigma\, d\Omega\, d\omega$$

$$= \frac{d\Omega\, d\omega}{2\pi}\left[\frac{I+1}{2I+1}a_+^2 + \frac{I}{2I+1}a_-^2\right]\frac{k_f}{k_i}\int dt\, e^{i\omega t}$$

$$\times \sum_{n_0} P_{n_0}\langle n_0|\Lambda^\dagger\Lambda(t)|n_0\rangle$$

In order to complete the explicit development of this cross-section, a considerable, but straight-forward, manipulation is required. To sketch it most briefly we note that

$$\Lambda(t) = e^{\frac{iHt}{\hbar}}e^{i\vec{R}\cdot\vec{k}}e^{-\frac{iHt}{\hbar}} = e^{i\vec{R}(t)\cdot\vec{k}} \qquad (III,13)$$

where $K = k_0 - k_f$ and

$$R(t) = e^{\frac{iHt}{\hbar}} R e^{-\frac{iHt}{\hbar}} \qquad \text{(III,14)}$$

Since, in this case, $H = P^2/2M$, we have

$$R(t) = R(0) + \frac{t}{M} P \qquad \text{(III,15)}$$

which is just what would be expected from strictly classical con-
siderations. Now employing the formula,

$$e^A e^B = e^{A+B+\frac{1}{2}[A,B]} \qquad \text{(III,16)}$$

for those A and B such that A and B commute with $[A,B]$, we
obtain

$$\Lambda^+ \Lambda(t) = e^{\frac{it}{M} P \cdot K + \frac{it\hbar}{2M} K^2} \qquad \text{(III,17)}$$

The thermal average of (III,17) is then readily computed in the
classical limit, i.e.,

$$\text{(III,18)}$$

$$\sum_n P_n \langle n | \Lambda^+ \Lambda(t) | n \rangle$$

$$\longrightarrow \left(\frac{M}{2\pi kT} \right)^{\frac{3}{2}} \int d^3 v \, e^{-\frac{Mv^2}{2kT} + it\, v \cdot K + \frac{it\hbar}{2M} K^2}$$

$$= e^{K^2(it\hbar - kTt^2)/2M}$$

It is now a straight forward matter to carry through the time - integration indicated in (III,12). After considerable manipulation one obtains [3,4]

(III,19)

$$\sigma d^3 v = \left[\frac{I+1}{2I+1} a_+^2 + \frac{I}{2I+1} a_-^2 \right] \sqrt{\frac{M}{2\pi kT}} \; \frac{e^{-\frac{M}{2kT} X}}{v' |v - v'|}$$

where

(III,20)

$$X = \frac{|v - v'|^2}{(2\beta)^2} + \frac{v' \cdot (v - v')}{\beta} + \left[\frac{v' \cdot (v - v')}{|v - v'|} \right]^2,$$

and we have introduced

(III,21)

$$\beta = \frac{M}{m + M}$$

This formula has been employed extensively in investigations of neutron thermalization in reactors. [5]

Section IV)   The Scattering of Neutrons by Monatomic Crystals

A)   In the previous section we considered in some detail the
scattering of neutrons from a macroscopic system idealized as an
ideal, monatomic gas.   In consequence, the only macroscopic char-
acteristic of the system that entered into the final expression for
the cross-section was the system temperature.   Specifically, the
assumptions that the target system was an ideal, monatomic gas pre-
cluded the possibility of a dependence of the cross-section upon
the dynamical details of the interactions between the particles com-
prising the scattering system.   Thus, as a second illustration we
choose as a target system one which also may be conveniently sim-
plified by idealization, but which at the same time leads to a cru-
cial dependence of the cross-section upon the existence of inter-
actions between the particles of the target system.   In this case,
we consider the scattering of neutrons from a monatomic crystal (a
crystal comprised of atoms rather than molecules at the lattice sites).
Hence, in this instance, we assume that the target particles inter-
act so strongly that a given particle merely executes oscillations
about a well-defined position of equilibrium.

Returning to equation (II,26) we have for this case

$$\sigma = \sigma_d + \sigma_o \qquad (IV,1)$$

where

$$\sigma_d = \frac{1}{2\pi N} \frac{k}{k_0} \sum_j \sum_{S_0, M} P_{S_0, M_0} \left| \langle S, M | a_j | S_0, M_0 \rangle \right|^2 \qquad (IV,2)$$

$$\times \int dt \, e^{i\omega t} \sum_{n_0} P_{n_0} \langle n_0 | A_j^\dagger A_j(t) | n_0 \rangle ,$$

and

$$\sigma_o = \frac{1}{2\pi N} \frac{k_f}{k_o} \sum_{ij}' \sum_{S_o M} P_{S_o M_o} \langle S_o M_o | a_i^\dagger | S M \rangle \langle S M | a_j | S_o M_o \rangle$$

$$\times \int dt \, e^{i\omega t} \sum_{n_o} P_{n_o} \langle n_o | A_i^\dagger A_j(t) | n_o \rangle$$

The prime on the summation symbol means delete terms for which $i = j$. This particular subdivision of the cross-section is more than merely convenient, for the two terms represent contributions that are often sensitive to quite different physical aspects of the scattering system. In particular, σ_d, the direct scattering part, is usually more dependent upon the dynamical details of the target, whereas the second term, σ_o, the interference scattering, is more sensitive to macroscopic symmetry properties of the scattering system. The example under consideration in this and the succeeding section will illustrate this point.

We consider first the evaluation of the spin dependent factors appearing in equations (IV,2) and (IV,3). We make here the same assumptions as in the previous section regarding the preparation and observation of neutron and nuclear spin states. Hence the factor in (IV,2) reduces exactly as in the previous section to

$$\sum_{S,M} P_{S_o M_o} | \langle S M | a_j | S_o M_o \rangle |^2 \qquad\qquad (IV,4)$$

$$\longrightarrow \sum_{S_o M_o S M} P_{S_o M_o} | \langle S M | a_j | S_o M_o \rangle |^2$$

$$= \sum_{S_o M_o} P_{S_o M_o} \langle S_o M_o | a_j^\dagger a_j | S_o M_o \rangle$$

$$= \frac{I+1}{2I+1} a_+^2 + \frac{I}{2I+1} a_-^2$$

Employing similar arguments, the spin factor in (IV,3) may be evaluated as

$$\sum_{S_o M} P_{S_o M_o} \langle S_o M_o | a_i^\dagger | S M \rangle \langle S M | a_j | S_o M_o \rangle \qquad \text{(IV,5)}$$

$$\longrightarrow \sum_{S_o M_o, S M} P_{S_o M_o} \langle S_o M_o | a_i^\dagger | S M \rangle \langle S M | a_j | S_o M_o \rangle$$

$$= \sum_{S_o M_o} P_{S_o M_o} \langle S_o M_o | a_i^\dagger a_j | S_o M_o \rangle$$

$$= \sum_{S_o M_o} P_{S_o M_o} \langle S_o M_o | (a_{oi} + \underline{S} \cdot \underline{q}_i a_{1i})(a_{oj} + \underline{S} \cdot \underline{q}_j a_{1j}) S_o M_o \rangle$$

$$= a_{oi} a_{oj} + \sum_{S_o M_o} P_{S_o M_o} a_{oi} a_{1j} \langle S_o M_o | \underline{S} \cdot \underline{q}_j | S_o M_o \rangle$$

$$+ \sum_{S_o M_o} P_{S_o M_o} a_{oj} a_{1i} \langle S_o M_o | \underline{S} \cdot \underline{q}_i | S_o M_o \rangle$$

$$+ \sum_{S_o M_o} P_{S_o M_o} a_{1i} a_{1j} \langle S_o M_o | \underline{S} \cdot \underline{q}_i \underline{S} \cdot \underline{q}_j | S_o M_o \rangle$$

Noting that the last three terms of (IV,5) are all proportional to a
factor of the form,

$$\sum_{M} P_M \langle M | \vec{g} | M \rangle \qquad (IV,6)$$

which corresponds to the average of a vector in a system in which
the vectors are randomly oriented and hence is zero, we find that
the spin factor in (IV,3) is simply a_0^2 - assuming, of course,
that our crystal is composed of but a single kind of atom. It is
of interest to note that

$$a_0 = \frac{I+1}{2I+1} a_+ + \frac{I}{2I+1} a_- \qquad (IV,7)$$

where a_+ and a_- have been defined by equation (III,11). It is
also worth pointing out that the interference scattering contribu-
tion to the cross-section depends only upon the spin-independent
part of the neutron-nuclear interaction. We may now rewrite (IV,2)
and (IV,3) respectively as,

$$\sigma_d = \frac{1}{2\pi N} \frac{k_f}{k_0} \left[\frac{I+1}{2I+1} a_+^2 + \frac{I}{2I+1} a_-^2 \right] \qquad (IV,8)$$

$$\times \sum_{j} \int dt\, e^{i\omega t} \sum_{n_0} P_{n_0} \langle n_0 | A_j^\dagger A_j(t) | n_0 \rangle,$$

$$\sigma_0 = \frac{1}{2\pi N} \frac{k_f}{k_0} \left[\frac{I+1}{2I+1} a_+ + \frac{I}{2I+1} a_- \right]^2 \qquad (IV,9)$$

$$\times \sum_{i,j}' \int dt\, e^{i\omega t} \sum_{n_0} P_{n_0} \langle n_0 | A_i^\dagger A_j(t) | n_0 \rangle,$$

At this point assumptions sufficient to characterize the dynamical properties of the crystal must be invoked. The simplest such assumption (the zeroth approximation to the real crystal as it were) is that all crystal atoms are rigid by fixed to their lattice sites. In such an event

$$\Lambda_i^+ \Lambda_j(-t) \longrightarrow e^{i \underline{K} \cdot (\underline{R}_j - \underline{R}_i)} \qquad (IV,10)$$

where $\underline{K} = \underline{k}_o - \underline{k}_f$ and $\underline{R}_i, (\underline{R}_j)$ are the positions of the ith and j^{th} lattice sites. In this instance, the integral over t yields $\delta(\omega)$ so that now we have

$$\sigma_d = \left[\frac{I+1}{2I+1} a_+^2 + \frac{I}{2I+1} a_-^2 \right] \delta(\omega) \qquad (IV,11)$$

$$\sigma_o = \frac{1}{N} \left[\frac{I+1}{2I+1} a_+ + \frac{I}{2I+1} \right] \delta(\omega) \sum_{ij}' e^{i \underline{K} \cdot (\underline{R}_j - \underline{R}_i)} \qquad (IV,12)$$

Recalling that $\omega = (\epsilon_o - \epsilon_f)/\hbar$, we see that the proportionality of the cross-section to $\delta(\omega)$ merely implies that the target (in this approximation) can neither receive nor give energy to the neutrons by the scattering process. That this should be so is an obvious consequence of the assumption that the scattering atoms are rigidly bound to their lattice sites clearly now our only interest in the cross-section is for the information it contains about the angular distributions of the scattered neutrons, hence we integrate (IV,11) and (IV,12) over ω obtaining,

$$\qquad (IV,13)$$

$$\sigma_d = \left[\frac{I+1}{2I+1} a_+^2 + \frac{I}{2I+1} a_-^2 \right]$$

$$\sigma_o = \frac{1}{N}\left[\frac{I+1}{2I+1}a_+ + \frac{I}{2I+1}a_-\right]\overset{\sim}{\underset{ij}{\sum}}' e^{iK\cdot(R_j - R_i)} \qquad (IV,14)$$

There finally remains the calculation of the sum in the interference scattering term. To accomplish this we first rewrite it explicitly as,

$$\qquad\qquad\qquad\qquad\qquad (IV,15)$$

$$\underset{ij}{\sum}' \longrightarrow \overset{N}{\underset{j=1}{\sum}}\ \underset{\substack{i=1\\i\neq j}}{\overset{N}{\sum}} e^{iK\cdot(R_j - R_i)}$$

Then consider first the sum over i for a randomly selected j. Assume that the crystal is such that the displacement of the ith scattering center relative to that of the jth is given by the vector

$$N_{ij} = \left[n_{ij}a_1 e_1 + m_{ij}a_2 e_2 + \ell_{ij}a_3 e_3\right], \qquad (IV,16)$$

i.e.,

$$\qquad\qquad\qquad\qquad\qquad (IV,17)$$

$$R_i = R_j + N_{ij}$$

where the $(n_{ij}, m_{ij}, \ell_{ij})$ are, for a particular $R_j - R_i$, appropriate integers, the (a_1, a_2, a_3) are the primitive lattice parameters of a rectangular lattice, and the (e_1, e_2, e_3) are the base vectors in a Cartesian coordinate system. Then the sum over 'i' becomes

$$\qquad\qquad\qquad\qquad\qquad (IV,18)$$

$$\underset{\substack{i=1\\i\neq j}}{\overset{N}{\sum}} \longrightarrow \underset{\substack{i=1\\i\neq j}}{\overset{N}{\sum}} e^{-iK\cdot N_{ij}}$$

$$= \underset{\substack{i=1\\j\neq i}}{\overset{N}{\sum}} e^{-[iK_1 a_1 n_{ij} + iK_2 a_2 m_{ij} + iK_3 a_3 \ell_{ij}]}$$

Now for an overwhelming majority of selections of particular sites located by $\underline{R}_j$, the sum in (IV,18) is essentially equivalent to a sum of the integers $(n_{ij}, m_{ij}, \ell_{ij}) \to (n, m, \ell)$ over all possible values from $-\infty$ to $+\infty$, excluding $n = m = \ell = 0$. Hence

$$(IV,19)$$

$$\sum_{\substack{i=1 \\ i \neq j}}^{N} \to \left[\sum_{n=-\infty}^{\infty} e^{-ia_1 k_1 n} \sum_{m=-\infty}^{\infty} e^{-ia_2 k_2 m} \sum_{\ell=-\infty}^{\infty} e^{-ia_3 k_3 \ell} - 1 \right]$$

The subtraction of unity from the sums on the right in (IV,19) accounts for the requirement in the sum on the left that i must not equal j.

Let a representative factor on the right above define a function according to

$$f_N(x) = \sum_{n=-N}^{N} e^{-inx} \qquad (IV,20)$$

Note that $f_N(x - 2\pi m)$ where m is any integer is defined by the same sum, i.e.,

$$(IV,21)$$

$$f_N(x - 2\pi m) = \sum_{n=-N}^{N} e^{-i(x-2\pi m)n} = \sum_{n=-N}^{N} e^{-inx} = f_N(x),$$

since $e^{-2\pi i\, m\, n} = 1$ so long as m and n are integers.

The sum in (IV, 20) is readily performed, yielding

$$f_N(x) = \frac{\sin(N+\frac{1}{2})x}{\sin\frac{x}{2}} \tag{IV,22}$$

Thus recalling (IV,21) we see that (IV,19) may be written as

$$\sum_{\substack{i=1 \\ i\neq j}}^{N} \longrightarrow \lim_{\substack{N_1\to\infty \\ N_2\to\infty \\ N_3\to\infty}} \left\{ \frac{\sin\left[(N_1+\frac{1}{2})(a_1 K_1 - 2\pi n)\right]}{\sin\frac{a_1 K_1}{2}} \right. \tag{IV,23}$$

$$\times \frac{\sin\left[(N_2+\frac{1}{2})(a_2 K_2 - 2\pi m)\right]}{\sin\frac{a_2 K_2}{2}} \frac{\sin\left[(N_3+\frac{1}{2})(a_3 K_3 - 2\pi \ell)\right]}{\sin\frac{a_3 K_3}{2}} \left. - 1 \right\}$$

We are primarily interested in this expression only when

$A_1 \ K_1 \quad \ll \quad$ 1, i.e. only when the De Broglie wave lengths
of the incident neutrons is large compared to the spacings be-
tween lattice sites.   In that instance we find that recall ng
that

$$\lim_{N\to\infty} \frac{\sin Nx}{\pi x} \longrightarrow \delta(x) \tag{IV,24}$$

(IV,25) may be effectively reduced to

$$\sum_{\substack{i=1 \\ i\neq j}}^{N} \longrightarrow 8\pi^3 \delta(a_1 K_1 - 2\pi n)\,\delta(a_2 K_2 - 2\pi m)\,\delta(a_3 K_3 - 2\pi \ell), \tag{IV,24}$$

where n, m and ℓ are any integers or zero. Summing
(IV,24) over all atoms of the target, we obtain finally
as our expression for the cross-section in this example,

$$(IV,25)$$

$$\sigma = \left[\frac{I+1}{2I+1} a_+^2 + \frac{I}{2I+1} a_-^2 \right]$$

$$+ 8\pi^3 \left[\frac{I+1}{2I+1} a_+ + \frac{I}{2I+1} a_- \right]^2$$

$$\times \delta(a_1 K_1 - 2\pi n) \, \delta(a_2 K_2 - 2\pi m) \, \delta(a_3 K_3 - 2\pi \ell)$$

Evidently, unless in a given case the spin-dependent part
of the neutron-nuclear interaction were enormously greater
than the spin-independent part - the cross-section in (IV,25)
is predominantly determined by the interference scattering
characterized by the delta functions in the second term. In
such an event we may simply note that

$$\sigma \propto \delta(a_1 K_1 - 2\pi n) \, \delta(a_2 K_2 - 2\pi m) \, \delta(a_3 K_3 - 2\pi \ell) \quad (IV,26)$$

The implication of (IV,26) is that the scattered beam in-
tensity is negligible unless

$$(IV,27)$$

$$K_1 = \frac{2\pi n}{a_1} \,,$$

$$K_2 = \frac{2\pi m}{a_2} \,,$$

$$K_3 = \frac{2\pi \ell}{a_3} \,,$$

or, more compactly,

$$(IV,28)$$

$$K = 2\pi \left(\frac{n}{a_1} e_1 + \frac{m}{a_2} e_2 + \frac{\ell}{a_3} e_3 \right)$$

For the cubic lattice ($a_1 = a_2 = a_3$) this becomes

$$K = \frac{2\pi}{a}(n\,\underline{e}_1 + m\,\underline{e}_2 + \ell\,\underline{e}_3) \qquad \text{(IV,29)}$$

which may be rewritten as

$$\underline{K} = \frac{2\pi n'}{a}\left(\frac{n}{n'}\underline{e}_1 + \frac{m}{n'}\underline{e}_2 + \frac{\ell}{n'}\underline{e}_3\right) \qquad \text{(IV,30)}$$

where n' is yet another integer. Finally, defining

$$\underline{\tau} = \frac{1}{a}\left(\frac{n}{n'}\underline{e}_1 + \frac{m}{n'}\underline{e}_2 + \frac{\ell}{n'}\underline{e}_3\right), \qquad \text{(IV,31)}$$

we have (recalling the definition of K),

$$\qquad \text{(IV,32)}$$

$$\underline{k}_0 - \underline{k}_f = 2\pi n'\,\underline{\tau}$$

Squaring (and remembering that $k_0 = k_f$), one finds that

$$2(k_0^2 - \underline{k}_0 \cdot \underline{k}_f) = 4\pi^2 n'^2 \tau^2, \qquad \text{(IV,33)}$$

$$2k_0^2(1 - \cos\theta) = 4\pi^2 n'^2 \tau^2,$$

$$4k_0^2 \sin^2\frac{\theta}{2} = 4\pi^2 n'^2 \tau^2,$$

But $k_0^2 = 4\pi^2/\lambda^2$, where $\lambda = h/mv_0$ is the De Broglie wavelength of the incident neutrons, so we have

$$\qquad \text{(IV,34)}$$

$$\frac{2}{\lambda}\sin\frac{\theta}{2} = n'\,\tau$$

This is essentially the Bragg equation originally proposed for the description of X-Ray scattering from crystals.

B. It is desirable that, in this section, one of the extreme limitations imposed on the immediately preceding calculation be removed. The restriction here referred to is the one that followed from the assumption that the crystal atoms were rigidly fixed in their lattice positions. This restriction was imposed just following the development of equations (IV,8) and (IV,9). Thus we return to these

equations as a starting point for the presently envisaged
generalization.

The problem, of course, with which we are presently
faced is that of calculating the quantity,

$$\sum_{ij} \int dt \, e^{i\omega t} \sum_n P_n \langle n | A_i^\dagger A_j(t) | n \rangle \qquad (IV,35)$$

Here we have dropped the subscript on the quantum label n.
The sum is to be evaluated separately for two different
situations, one in which $i = j$ and the other in which $i \neq j$.

However, before we can proceed to the evaluation of
(IV,35) we must calculate the matrix elements,

$$\langle n | A_i^\dagger A_j(t) | n \rangle \qquad (IV,36)$$

Evidently before we can compute these matrix elements we
must first determine in some detail the nature of the eigen-
states, $|n\rangle$. In order to accomplish the latter, we must
propose a dynamical model for the representation of a crystal.

The model that we shall select for purposes of present
illustration is one of the simplest that yet retains many
useful qualitative features of the true crystal - the so-
called Einstein model of a crystal.[6] This model is based
upon the assumption that each atom in the crystal oscillates
about its lattice site as an equilibrium position. The
restoring force acting on each atom is presumed to obey
Hooke's Law, and the force constant is presumed to be the

same for all atoms. As a consequence of these assumptions,
the energy of the crystal may be written as

$$H = \sum_{i=1}^{N} \frac{P_i^2}{2m} + \frac{1}{2} k R_i^2, \quad \text{where} \qquad \text{(IV,37)}$$

R_i is the displacement of the ith particle from equilibrium.
Since the energy of the system can be written as a sum of
the energies of the component parts, the wave function for
the system may be written as a product of functions – one
for each individual atom. Hence, if we find the eigenstates
of the equation,

$$\left(\frac{P^2}{2m} + \frac{1}{2} k R^2 \right) \psi = E \psi \qquad \text{(IV,38)}$$

we will have effectively obtained the eigenstates of the
whole crystal.

It is not our intention to enter into elaborate analytical detail here, hence we simply clarify some notation, indicate the eigenvalues of the particle energy, and present a few properties of the eigenstates. The eigenstates and eigenvalues may be defined by

$$\left(\frac{P^2}{2m} + \frac{1}{2}kR^2\right)|n_x n_y n_z\rangle = \hbar\Omega\left(n_x + n_y + n_z + \frac{3}{2}\right)|n_x n_y n_z\rangle \qquad (IV,39)$$

The quantities (n_x, n_y, n_z) are positive integers or zero, and $\Omega = 2\pi\sqrt{\frac{k}{m}}$

Two important (and subsequently useful) properties of these eigenstates are that the diagonal elements of P^2 and X^2 are

$$\langle n_x n_y n_z | \frac{P^2}{2m} | n_x n_y n_z \rangle = \frac{\hbar\Omega}{2}\left(n_x + n_y + n_z + \frac{3}{2}\right)$$

and

$$\langle n_x n_y n_z | \frac{1}{2}kR^2 | n_x n_y n_z \rangle = \frac{\hbar\Omega}{2}\left(n_x + n_y + n_z + \frac{3}{2}\right) \qquad (IV,40)$$

This is sufficient information for us to undertake the calculation of the matrix elements in (IV,36). (Note that in (IV,36) the symbol $|n\rangle$ stands for $|n_{x_1} n_{y_1} n_{z_1} \cdots n_{x_N} n_{y_N} n_{z_N}\rangle$ i.e., it is an eigenstate of the whole system).

We turn our attention first to the evaluation of

$$\langle n | \Lambda_i^\dagger \Lambda_j(t) | n \rangle \qquad (IV,41)$$

when $i \neq j$. These are the matrix elements needed for the calculation of the interference scattering contribution to the cross-section in this case. Employing a more explicit notation, we note that we may write (IV,41) as

$$\langle n | \Lambda_i^\dagger \Lambda_j(t) | n \rangle$$
$$= \langle n_i n_j | \Lambda_i^\dagger \Lambda_j(t) | n_i n_j \rangle$$
$$= \langle n_i | \Lambda_i^\dagger | n_i \rangle \langle n_j | \Lambda_j(t) | n_j \rangle \qquad (IV,42)$$

This particular decomposition is a direct consequence of the fact that Λ_i and Λ_j depend on the dynamical variables of different particles and that the model assumed that the behavior of a given particle was completely independent of the others. Recalling that

$$\Lambda_j(t) = e^{\frac{iHt}{\hbar}} e^{i(R_j + b_j)\cdot K} e^{-\frac{iHt}{\hbar}} \qquad (IV,43)$$
$$= e^{\frac{iHt}{\hbar}} e^{i(R_j + b_j)\cdot K} e^{-\frac{H_j t}{\hbar}}$$

where

$$H_j = \frac{P_j^2}{2m} + \frac{1}{2} k R_j^2 \quad,$$

(IV,44)

and that the states $|n_j\rangle$ diagonalize H_j, we find that (IV,42) becomes

$$|\langle n|e^{i\underline{K}\cdot\underline{R}}|n\rangle|^2 \, e^{i\underline{K}\cdot(\underline{b}_j-\underline{b}_i)} \quad,$$

(IV,45)

The vectors $\underline{b}_i$ and $\underline{b}_j$ in (IV,43) and (IV,45) are the position coordinates of the equilibrium positions of the ith and j^{th} atoms in the crystal respectively. Thus, the second factor in (IV,45) is exactly the same as the individual terms in (IV,15) obtained for the case of the rigidly fixed atoms in the crystal.

In the present instance, the sums in (IV,35) for $i \neq j$ become

$$\sum_{ij}' \sum_{n} P_n \langle n|A_i^\dagger A_j^{(i)}|n\rangle$$

$$= \sum_{ij}' \sum_{n_i n_j} P_{n_i} P_{n_j} \langle n_i|A_i^\dagger|n_i\rangle\langle n_j|A_j|n_j\rangle$$

$$= \sum_{n} P_n \langle n|e^{i\underline{K}\cdot\underline{R}}|n\rangle|^2 \sum_{ij}' e^{i\underline{K}\cdot(\underline{b}_j-\underline{b}_i)}$$

(IV,46)

In view of the remarks above, the sum over i and j in (IV,46) is the same as (IV,15), hence the subsequent comments on the contribution of (IV,15) to the cross-section in sub-section (IV,14) above apply with equal force here.

Thus, we see that in this case we obtain again the characteristic Bragg interference scattering pattern modified simply by a multiplicative factor which tends to lower and broaden the individual peaks in the pattern. This smearing of the interference scattering pattern is a direct consequence of the effective smearing of the particles over a volume centered at their equilibrium positions by their thermal motions.

That the inclusion of the dynamics of the target system provides little modification of the interference scattering may be understood in intuitive terms. In order that the waves representing neutrons scattered from different atoms be capable of interfering it is necessary that the propagation vectors of the two waves be the same. Since the propagation vectors of the neutrons in the incident beam are all the same, it follows that in order that they be

the same after the scattering both neutrons must have been scattered without energy change or both must have received from or transferred to the scattering nuclei exactly the same amount of energy. The latter of these alternatives is by far the less probable, hence interference scattering is almost entirely due to neutrons scattered without energy change, and is thus quite insensitive to target dynamics – but conversely quite sensitive to target symmetry.

Evidently we may anticipate that the direct scattering will reflect the dynamical characteristics of the target. To realize this anticipation we turn now to the evaluation of the matrix element for $i = j$ (IV,41). Here again, the first task is the calculation of

$$\Lambda(t) = e^{\frac{iH_j t}{\hbar}} e^{i\vec{K}\cdot\vec{R}_j} e^{-\frac{iH_j t}{\hbar}} \qquad (IV,47).$$

(Of course, in this case, in which $i = j$, we must compute the dependence of this quantity upon dynamical variables explicitly, since

$$\Lambda_j^\dagger e^{\frac{iH_j t}{\hbar}} \neq e^{\frac{iH_j t}{\hbar}} \Lambda_j$$

It is a straight-forward, but somewhat tedious, matter to show that (IV,47) becomes,

$$e^{i\vec{K}\cdot[\vec{R}_j\cos\Omega t + \vec{P}_j \frac{1}{m\Omega}\sin\Omega t]} \qquad (IV,48)$$

Thus now (IV,41) becomes

$$\langle n| e^{-i\vec{K}\cdot\vec{R}_j} e^{i\vec{K}\cdot[\vec{R}_j\cos\Omega t + \frac{1}{m\Omega}\vec{P}_j\sin\Omega t]} |n\rangle \qquad (IV,49)$$

Making use of the formula,

$$e^A e^B = e^{A+B+\frac{1}{2}[A,B]} \qquad (IV,50)$$

which holds so long as A and B commute with $[A,B]$, we find that we may write the matrix element (IV,49) as

$$e^{\frac{i\hbar K^2 \sin\Omega t}{2m\Omega}} \langle n| e^{-i\vec{K}\cdot[(1-\cos\Omega t)\vec{R} - \frac{\sin\Omega t}{m\Omega}\vec{P}]} |n\rangle \qquad (IV,51)$$

The thermal average in (IV,35) can now be exhibited for $i = j$ as

$$\sum_n P_n \langle n| \Lambda^\dagger \Lambda(t) |n\rangle \qquad (IV,52)$$

$$= e^{\frac{i\hbar K^2 \sin\Omega t}{2m\Omega}} \sum_n P_n \langle n| e^{-i\vec{K}\cdot[(1-\cos\Omega t)\vec{R} - \frac{\sin\Omega t}{m\Omega}\vec{P}]} |n\rangle.$$

In this case we may compute the sum in (IV,52) by an application of a theorem which states that

$$\sum_n P_n \langle n | e(Q) | n \rangle = e\left[\frac{1}{2}\sum_n P_n \langle n | Q^2 | n \rangle\right], \tag{IV,53}$$

provided that Q is a harmonic oscillator variable (either the displacement or the corresponding conjugate momentum) and that the states $|n\rangle$ are harmonic oscillator states. We find, after considerable manipulation, that (IV,52) becomes

$$e^{-AK^2}\left[I_0(BK^2) + \sum_{m=1}^{\infty} I_m(BK^2)\left\{e^{im\left(\Omega t - \frac{\langle \hbar \Omega \rangle}{2kT}\right)} + e^{-im\left(\Omega t - \frac{\hbar \Omega}{2kT}\right)}\right\}\right] \tag{IV,54}$$

where

$$A = \frac{\hbar}{2m\Omega} \coth \frac{\hbar\Omega}{2kT} ,$$

$$B = \frac{\hbar}{2m\Omega} \operatorname{csch} \frac{\hbar\Omega}{2kT} ,$$

I_m is the modified Bessel function of the first kind of order m, and the m's are integers.

By another application of the formula (IV,53), we find that (IV,46) may be exhibited as

$$e^{-AK^2} \sum_{i,j}' e^{i\vec{K}\cdot(\vec{b}_j - \vec{b}_i)} \tag{IV,55}$$

Thus now, recalling (IV,2) and (IV,3) for the direct and interference scattering respectively and the discussion in sub-section (IV,A) about the evaluation of the spin factors, we find that we may now write

$$\sigma_d = \frac{k}{k_o}\left[\frac{I+1}{2I+1}a_+^2 + \frac{I}{2I+1}a_-^2\right]e^{-AK^2}\left[I_0(BK^2)\,\delta(\omega)\right.$$

$$+ \sum_{m=1}^{\infty} I_m(BK^2) e^{\frac{m\hbar\Omega}{2kT}} \delta(\omega+m\Omega) \tag{IV,56}$$

$$\left. + \sum_{m=1}^{\infty} I_m(BK^2) e^{-\frac{m\hbar\Omega}{2kT}} \delta(\omega-m\Omega)\right] .$$

and

$$\sigma_o = \frac{\delta(\omega)}{N} e^{-AK^2}\left[\frac{I+1}{2I+1}a_+ + \frac{I}{2I+1}a_-\right]^2 \sum_{i,j}' e^{i\vec{K}\cdot(\vec{b}_j - \vec{b}_i)} \tag{IV,57}$$

These formulae for the description of slow neutron scattering from monatomic crystals have sufficient qualitative validity to warrant a brief discussion of

some of their implications. In the first place we note that (IV,56) and (IV,57)
contain (IV,11) and (IV,12) respectively (as they should). Recalling that the
latter relations were obtained for the model of a crystal in which it was
assumed that the atoms of the crystal were rigidly fixed at their respective
lattice sites, and surmising that this should correspond to the case in which
the force binding the oscillating atoms in the Einstein model becomes infinitely
great; we investigate (IV,56 and 57) in the limit as (since $\Omega = \sqrt{\frac{k}{m}}$,
k being the Hooke's low force constant) approaches infinity. We note that

$$A \xrightarrow[\Omega \to \infty]{} O ,$$

$$B \xrightarrow[\Omega \to \infty]{} \frac{\hbar}{m\Omega} e^{-\frac{\hbar\Omega}{2kT}} \longrightarrow O , \qquad (IV,58)$$

Thus, we see immediately that (IV,57) goes to (IV,12) in this limit; and further
noting that

$$I_m (x) \xrightarrow[x \to 0]{} x^m \qquad (IV,59)$$

we see that (IV,56) goes to (IV,11) also.

In this instance - as in the previous one - we note the proportionality
of the interference scattering (σ_b) to the square of the average of the singlet
(a_-) and triplet (a_+) scattering lengths characteristic of the nuclei that
comprise the crystal. The presence of this factor suggests that under special
circumstances a peculiarly nuclear property can profoundly influence the
character of a diffraction pattern. An example would be provided by the scatter-
ing from crystallive hydrogen, since for neutron-proton scattering,

$$a_- \cong -2.35 \times 10^{-12} \; cms$$

$$a_+ \cong .592 \times 10^{-12} \; cms$$

so that the ratio of the spin dependent factors for interference versus direct
scattering respectively is $\frac{(\frac{3}{4}a_+ - \frac{1}{4}a_-)^2}{(\frac{3}{4}a_+^2 + \frac{1}{4}a_-^2)} \cong 3 \times 10^{-3}$,

Evidently the peaks in the angular distribution of the scattered neutrons which

reflect macroscopic symmetries of the system and are due solely to interference scattering would be probably unobservable above the diffuse background of direct scattering. We note also that there is a further smoothing of the interference scattering (though not relative to the direct scattering) due to the presence of the factor,

$$e^{-AK^2}$$

which tends to zero as $\hbar\Omega/kT$ tends to zero. Since for interference scattering $K^2 \propto \sin^2\frac{\Theta}{2}$, it is seen that this latter effect will be most pronounced in the angular range in the vicinity of $45°$.

Finally, we note that the several sets of terms characterizing the direct scattering have a satisfying intuitive interpretation. Recalling that $\hbar\omega = \epsilon_f - \epsilon_i$, we see that the various delta functions occuring in these terms are merly embodiments of the requirement of energy conservation. In particular, the first term - proportional to $\delta(\omega)$ as is also the interference scattering - describes the angular distribution of neutrons which have been scattered without energy transfer. This is possible, since these neutrons have effectively transferred an unobservable amount of their energy to the crystal as a whole in order to accomplish an observable momentum change. The situation is precisely analogous to the "reflection" of a tennis ball from a brick wall. The terms containing $\delta(\omega + m\Omega)$ are non-vanishing only when $\epsilon_f = \epsilon_i - m\hbar\Omega$, ie., they describe scattering in which the neutron transfers energy in the amount of $m\hbar\Omega$ to the atoms in the crystal. We note that if $\epsilon_i < \hbar\Omega$, such processes cannot take place. Conversely, the terms containing $\delta(\omega - m\Omega)$ vanish unless $\epsilon_f = \epsilon_i + \hbar m\Omega$. Hence, these terms describe scattering events in which oscillator quanta have been transferred to the neutron. It is interesting to note that these terms are proportional to $e^{-m\hbar\Omega/2kT}$ which is a measure of the probability of finding

an oscillator in the mth excitation state. If the oscillator level spacings in the crystal are neither too large nor too small, it is expected that one might observe a discreteness in the spectrum of the neutrons which have gained energy upon scattering and that the level separation in such a spectrum would correspond to the oscillator level spacing in the crystal. Thus, we see clearly the sense of the earlier assertion that the direct scattering is sensitive to the dynamics of crystal structure, whereas the interference scattering reflects the macroscopic symmetries of the crystal lattice.

Section V)   The Scattering of Neutrons by Monatomic Liquids

A)   In the previous section we have skirted the sub-
ject of the utility of the neutron as a probe for the revela-
tion of macroscopic and microscopic detail of crystal struc-
ture.   In actuality, we have merely developed some of the
basic formulae in terms of which experiments may - after con-
siderable more labor than has been expended here in - be use-
fully interpreted to shed light upon crystal structure.   How-
ever, the application of the previous results to specific
cases proceeds - for a reasonably large and interesting class
of experiments - straightforwardly without undue complication
in principle.

The same cannot be said for the class of experiments
presently envisaged, i.e., the scattering of neutrons from
liquids.   This is largely because the liquid state of matter
is the least understood of the gas, solid, and liquid states.
In fact, the above (somewhat oversimplified) treatments of
the ideal monatomic gas and the monatomic crystal provide a
theoretical basis of quantitative utility for the interpreta-
tion of neutron scattering experiments in terms of details of
the structure of the states of matter involved.   But the same
claim has yet to be asserted convincingly for comparable ex-
periments on the liquid state.   Hence it is perhaps not sur-
prising that we approach the immediate topic somewhat gingerly.

The initial attack on the subject shall be coached in
terms of the development of a specific model purporting to
characterize some aspects of a certain class of liquids.[7] Re-
calling that we are presently restricting our attention to

consideration of monatomic liquids, we exhibit the energy of
a collection of N such atoms as

$$(V,1)$$

$$H = \sum_{j=1}^{N} T(\underline{R}_j) + \sum_{j=1}^{N} T(\underline{\xi}_j) + \sum_{j=1}^{N} V(\underline{\xi}_j)$$

$$+ \sum_{i<j}^{N} V(\underline{\xi}_i, \underline{\xi}_j, \underline{R}_{ij})$$

where $T(\underline{R}_j)$ is the kinetic energy of the center of mass motion
of the jth atom, $T(\underline{\xi}_j)$ is the kinetic energy of the
internal degrees of freedom (3M of them if there are M elec-
trons in the atom) of the jth atom, $V(\underline{\xi}_j)$ is the
potential energy, resulting from the interactions of the elec-
trons with each other and with the nucleus of the jth atom
and $V(\underline{\xi}_i, \underline{\xi}_j, \underline{R}_{ij})$ is the potential energy of
interaction between the electrons and nucleus of the ith
atom and those of the jth atom. An approach to a simplified treatment of the liquid
might proceed in terms of an attempt to find (or guess) effect-
ive bi-atom potentials in terms of the interdistances of the
mass centers of pairs of atoms. Of course, one could proceed
from this point by simply asserting that some such potentials
exist and then on some empirical grounds or other guess a
functional form for the dependence of these potentials upon
interatomic distance. However, it is more desirable to develop
an argument for the introduction of such potentials in some-
what more logical terms.

Thus consider the energy of any pair of atoms comprising
our system, i.e.,

$$H_{ij} = T(\rho_{ij}) + T(R_{ij}) + T(\xi_i) + T(\xi_j)$$

$$+ V(\xi_i) + V(\xi_j) + V(\xi_i, \xi_j, R_{ij})$$

where we have explicitly introduced the coordinates of the
center of mass of the pair, ρ_{ij} . Since we shall not be
interested in the motion of the center of mass, we ignore $T(\rho_{ij})$
henceforth. Defining $H'_{ij} = H_{ij} - T(\rho_{ij})$, we look
for bi-atom steady states defined by the equation

$$H'_{ij} \Psi(\xi_i, \xi_j, R_{ij}) = E \Psi(\xi_i, \xi_j, R_{ij})$$

In some sense, we wish to accomplish a separation of
the dynamics of the internal (electronic) degrees of freedom
from those of inter-atomic displacement (R_{ij}). This may
be accomplished formally and illuminatingly(and conventionally)
by defining a complete set of bi-atomic electronic states which
depend parametrically upon the atomic interdistance by

$$\left[T(\xi_i) + T(\xi_j) + V(\xi_i) + V(\xi_j) + V(\xi_i, \xi_j, R_{ij}) \right] \Phi_{a_{ij}} (\xi_i, \xi_j, R_{ij})$$

$$= E_{a_{ij}}(R_{ij}) \Phi_{a_{ij}} (\xi_i, \xi_j, R_{ij})$$

As asserted, the $\overline{\Phi}_{aij}$ are expected to be a complete, orthonormal set of base vectors in $\overline{\xi}$ -space depending parametrically (as do their eigenvalues $\mathcal{E}_{aij}(R_{ij})$) upon the relative displacement of the atomic mass centers. The collection of numbers, a_{ij} , are sufficient to completely designate an individual member of the set, $\{\overline{\Phi}_{aij}\}$.

Recalling (V, 3), we expand the functions $\overline{\Psi}$ as

$$\overline{\Psi}(\overline{\xi}_i, \overline{\xi}_j, R_{ij}) = \sum_{aij} \chi_{aij}(R_{ij}) \overline{\Phi}_{aij}(\overline{\xi}_i, \overline{\xi}_j, R_{ij}) \quad (V,5)$$

The coefficients , χ , in the expansion of $\overline{\Psi}$ are independent of $(\overline{\xi}_i, \overline{\xi}_j)$ because of the presumed completeness of the set $\overline{\Phi}$ in $\overline{\xi}$ -space. Substituting (V,5) into (V,3) we obtain

$$(V,6)$$

$$\sum_{bij} (\overline{\Phi}_{aij}, T(R_{ij}) \overline{\Phi}_{bij}) \chi_{bij}$$

$$+ \mathcal{E}_{aij} \chi_{aij} = E \chi_{aij}$$

Henceforth we drop the subscripts i and j. Noting that

$$T(R) = - \frac{\hbar^2}{2\mu} \nabla_R^2 , \qquad (V,7)$$

where μ is the reduced mass of the pair of atoms, we find that (V,6) becomes

$$(V,8)$$

$$\sum_b \chi_b \left(\overline{\Phi_a}, -\frac{\hbar^2}{2\mu} \nabla_R^2 \overline{\Phi_b} \right) + \sum_b \nabla_R \chi_b \cdot \left(\overline{\Phi_a}, -\frac{\hbar^2}{\mu} \nabla_R \Phi_b \right)$$

$$-\frac{\hbar^2}{2\mu} \nabla_R^2 \chi_a + \mathscr{E}_a \chi_a = E \chi_a.$$

The matrix elements in the sums on the left-hand side are generally small compared to the rest of (V,8), hence to good approximation we have

$$(V,9)$$

$$-\frac{\hbar^2}{2\mu} \nabla_R^2 \chi_R + \mathscr{E}_a \chi_a = E \chi_a$$

Thus for a given electronic state (the a th state) we find that the wave-functions characterizing the states of relative displacement are defined by a Hamiltonian depending only on these displacements. Furthermore, for each such electronic configuration there is a potential function, .

    Note, however, that $\mathscr{E}_a$ is not necessarily a function only of the <u>magnitude</u> of <u>R</u>. In general the electronic config-urations about their respective atoms may be non-spherically symmetric, and hence the interaction energy between such charge clouds would be expected to depend upon the relative

orientations of the assymetric charge distributions. But
if the widely separated atoms were characterized by quite
tightly bound spherically symmetric charge clouds, one might
expect that to good approximation the potentials describing
the atomic interactions will depend only on the magnitude of
the interdistances. The requirement that the spherically
symmetric charge clouds be tightly bound is invoked so that
assymmetries are not induced appreciably when the atoms are
brought into close association.

Since electronic excitations generally involve energy
inputs large compared to kT, we may reasonably assume that
only that potential corresponding to the electronic ground
state need by considered. Thus we have now formally arrived
at a characterization of the interaction between two atoms
dependent only upon the magnitude of the relative displace-
ments of atomic centers of mass, and hence may exhibit the
energy of those liquids describably in these terms as

$$H = \sum_{j=1}^{N} T(R_j) + \sum_{i<j} V(R_{ij}) , \qquad (V,10)$$

where $V(R_{ij})$ is to be interpreted as $E_o(R_{ij})$ —
the potential generated by the interaction of spherically
symmetric, ground state electronic configurations. Eq. (V,10)
is essentially an operational statement of the nature of the
normal (non-associated) liquid.

It should be noted that the above definition of the
normal liquid carries over to those cases in which the elemen-

tary building blocks of the liquid are molecules instead
of atoms. The only substantial difference is that in this
latter case the total energy must include the internal
energies of nuclear vibration and rotation within the molecules-
but the essential feature of the separation of the dynamics of
the internal degrees of freedom from those characterizing mo-
lecular interdistances is preserved, along with the assumption
that the intermolecular potentials depend only upon the mag-
nitudes of their relative displacements.

Examples of normal liquids are provided by helium,
neon, argon, krypton, and zenon in the liquid state as well
as liquid lead and tin. The classic example of the non-normal
- or associated - liquid is water. The discussion that follows
will be devoted solely to the normal liquids.

The potentials, $V(R_{ij})$, are usually presented ex-
plicitly only in empirical terms, if at all. A representation
that has found widespread use for correlating experimental
data on dense gases and liquids is the Lennard - Jones[7] (L J)
potential,

$$V(R) = \frac{-\mu}{R^6} + \frac{\nu}{R^{12}},$$

(V,11)

where μ and ν are parameters to be determined by
experiments.

Only a little reflection is required for the conviction
that our description of a liquid is still too complicated for
convenient analysis. Hence in order to proceed further in
analytical terms it is necessary to approximate some more.
This next approximation takes explicit cognizance of the

assumption that a short range order exists in a liquid (short range and presumably short time - but for times long compared to a neutron interaction time). This assumption is exploited in order to replace the many-particle Hamiltonian (V,10) by a sum of many single-particle Hamiltonian's - much after the fashion of the above discussed treatment of the crystal. (In fact the present discussion of the normal liquid and the previous one of the crystal are formally substantially identical.)

The crux of the argument may be presented somewhat crudely as follows. Rewrite the potential energy of (V,10) as

(V,12)

$$\sum_{i<j} V(R_{ij}) = \frac{1}{2} \sum_{i,j}{}' V(R_{ij})$$
$$= \sum_{j=1}^{N} \left[\frac{1}{2} \sum_{i=1}^{N}{}' V(R_{ij}) \right]$$
$$= \sum_{j=1}^{N} U_j \quad ,$$

where we have defined

(V,13)

$$U_j = \frac{1}{2} \sum_{i=1}^{N}{}' V(R_{ij})$$

employing the prime on the summation symbol to imply that the term for $i = j$ is to be deleted from the sum. Simplification

of (V,13) may be attempted by the introduction of an appropriate conditional density - defined by

$$f(R_j \mid R) \, d^3R \qquad \equiv \text{The}$$

expected number of particles to be found in d^3R about R, given that there is a particle located at R_j -

$$(V,14)$$

and then replacing the sum by an integral, i.e.

$$(V,15)$$

$$U_j \Rightarrow \frac{1}{2} \int_R V(|R_j - R|) f(R_j \mid R) \, d^3R$$

In order to evaluate the integral in (V,15), let us assume that at any given instant the jth particle (whose potential energy we are presently considering) may be regarded as moving in a potential provided by its interaction with its "nearest neighbors" being presumed to be spatially ordered in some regular way. Let us further assume that, during the interval that a given ordering exists, the jth particle finds itself effectively "bound" to a temporary equilibrium position which is essentially a center of symmetry of the "nearest neighbor" array. For still greater simplification, let us assume that (for the purpose of estimating the change in potential energy of the jth particle as it moves away from its "equilibrium" position) these "nearest neighbors" are smeared over the surface of a sphere centered at the "equilibrium" position. The accompanying sketch of this short-lived ordering is intended to clarify some of these assumptions.

The "nearest neighbors" are to be presumed smeared over a sphere of radius,

Fig.
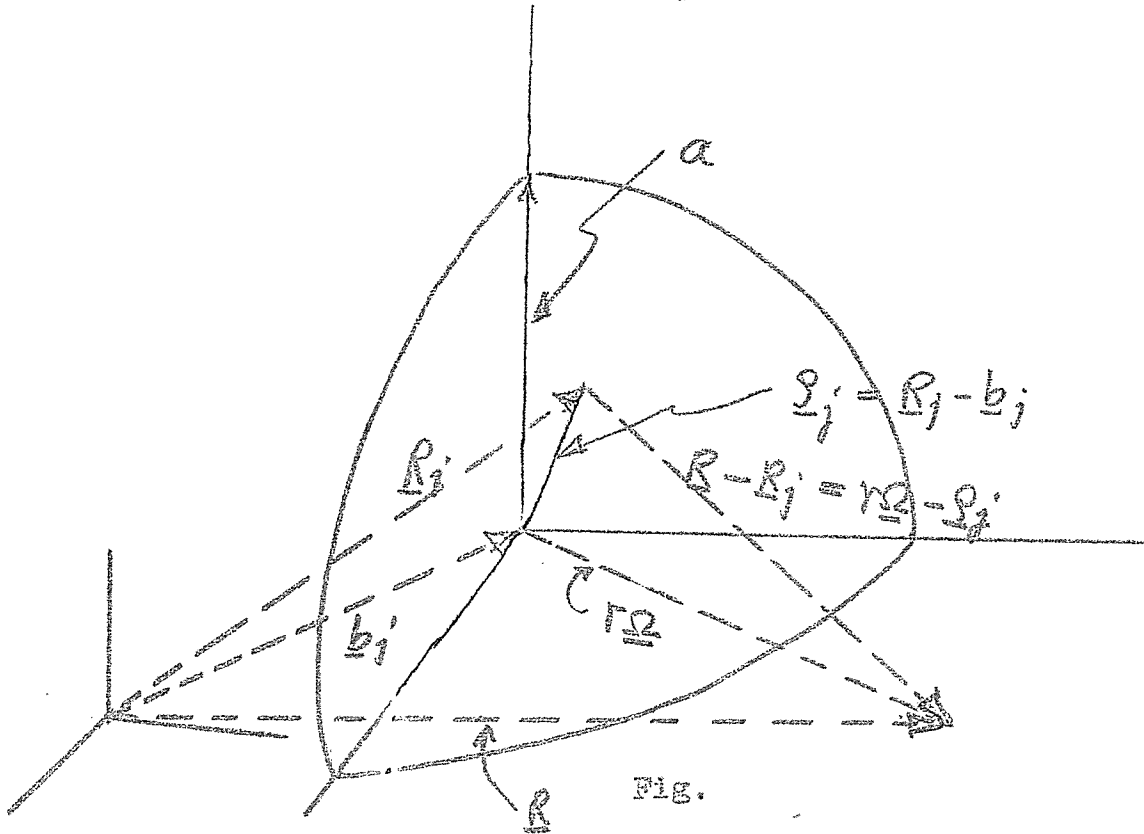
'a' centered at $\underline{b}_j$, the location of the "equilibrium" position of the jth particle as measured in an arbitrary coordinate system. The instantaneous position of the jth particle is $\underline{R}_j$, and $\underline{R}$ is a representative location of one of the contributors to the potential felt by the jth particle.

From the figure, we see that (V, 15) may be written as

$$U_j = \frac{1}{2} \int V(|r\underline{\Omega} - \underline{\rho}_j|) f(\underline{b}_j + \underline{\rho}_j | \underline{b}_j + r\underline{\Omega}) r^2 dr d\underline{\Omega}. \tag{V,16}$$

The above assumptions that for some small time interval the jth particle is effectively bound close to the point $\underline{b}_j$ by particles smeared on a sphere of radius 'a' centered at $\underline{b}_j$

may now be expressed in the approximation

$$f(\underline{b}_j + \underline{\rho}_{j}|\,\underline{b}_j + r\underline{\Omega})\,r^2\,dr\,d\Omega \cong \alpha\,\delta(r-a)\,dr\,d\Omega \qquad (V,17)$$

where α is the number of "nearest neighbors". Now (V,16) becomes

$$U_j = \frac{\alpha}{2}\int V(|a\underline{\Omega} - \underline{\rho}_j|)\,d\Omega \,, \qquad (V,18)$$

and we see that the energy of the liquid (V,10) may be written as

$$H = \sum_{j=1}^{N}\left[\,T(\underline{p}_j) + U(\rho_j)\,\right] = \sum_{j=1}^{N}H_j \,, \qquad (V,19)$$

i.e., as the sum of N single particle energies – each particle moving in the same effective potential ($U(\rho_j)$) as all the others. We note in passing that this effective potential depends upon four empirical parameters; the strengths (μ, ν) of the LJ two-particle potential (V,11) which for some cases have been evaluated from thermodynamic experiments, the radius 'a' of the "sphere of nearest neighbors" which in first approximation may be taken to be simply the average interparticle spacing in the liquid, and the number of "nearest neighbors", α .

The next step in the present development is to find the eigenfunctions of the single-particle Hamiltonian in (V,19) from which by appropriate superposition the eigenstates of the liquid can be constructed. There is no difficulty in

obtaining the explicit functional dependence of U upon ρ as expressed by (V,18) recalling (V,11), but the resulting Hamiltonian is not evidently rigorously diagonalizable. However, a little investigation reveals that, under certain circumstances, this potential exhibits a relatively sharp minimum at $\rho = 0$ and hence might be expected to be adequately represented by a parabola for present purposes. This suggests that we expand U in a Taylor's series about the origin, i.e.,

(V,20)

$$U(\rho) = U(0) + \rho \left.\frac{dU}{d\rho}\right|_{\rho=0} + \frac{1}{2}\rho^2 \left.\frac{d^2U}{d\rho^2}\right|_{\rho=0} + \cdots,$$

This may be most conveniently accomplished by direct consideration of (V,18). One finds that

(V,21)

$$U(0) = 2\pi\alpha \left(\frac{\nu}{a'^2} - \frac{\mu}{a^6} \right),$$

$$\left.\frac{\partial U}{\partial \rho}\right|_{\rho=0} = 0,$$

$$\left.\frac{\partial^2 U}{\partial \rho^2}\right|_{\rho=0} = 2\pi\alpha \left(\frac{44\nu}{a^{14}} - \frac{10\mu}{a^8} \right),$$

In order that the present approximation to the effective potential for a liquid atom be at all reasonable, it is necessary that $U(0)$ be a minimum. The condition that this be so is that

$$(v,22)$$

$$\frac{\partial^2 U}{\partial \rho^2}\bigg|_0 > 0, \qquad i.e.,$$

$$\left(\frac{44\nu}{a^{14}} - \frac{10\mu}{a^8}\right) = \frac{10\mu}{a^8}\left(\frac{22\nu}{5a^6\mu} - 1\right) > 0,$$

$$\text{or} \qquad \frac{22}{5}\frac{\nu/\mu}{a^6} > 1,$$

$$\frac{\nu/\mu}{a^6} > \frac{5}{22} = 0.23.$$

Significantly, for four normal monatomic liquids for which μ and ν are known from independent measurements (Neon, Argon, Krypton, and Xenon), it is found that $\nu/\mu a^6 \gtrsim .46$.

Thus now we have arrived at a description of the energy of monatomic, normal liquids which consists of a sum of the separate energies of the particles comprising the liquid in which the energy of a given particle is

$$(v,23)$$

$$H = -\frac{\hbar^2}{2m}\nabla^2 + U(0) + \frac{1}{2}\kappa\rho^2,$$

where $U(0)$ and K have been evaluated in (V,21). Since the addition of a constant to the energy of a particle in no way affects the subsequent analysis, we ignore $U(0)$ henceforth.

It is now evident that the present approximation to the description of a normal liquid is formally entirely equivalent to the treatment of the crystal developed in the previous section. Thus the form of the cross-section as obtained there applies here equally well-except that in this instance the oscillator frequency is given by

(V,24)

$$\Omega^2 = \frac{K}{m}$$

$$= \frac{2\pi d}{m}\left(\frac{44\nu}{a^{14}} - \frac{10\mu}{a^8}\right)$$

B) In subsection (A) of this section an explicit dynamical model of the normal, monatomic liquid was introduced in order to attempt to predict the angular and energy distribution of the scattered neutrons. The model employed is by no means the only one - though perhaps, it is the simplest conceptually.

However, there is a more implicit approach to the analysis of such experiments that is presently given far wider currency than the employment of any specific model. This alternative approach requires, in certain respects, weaker assumptions as to the dynamical description of the liquid under investigation, and hence provides a more rigorous analysis of the experimental data. But conversely, it provides only an indirect (through intuitively interpretable) connection between the microscopic properties of the liquid and experiment.

The essence of this approach resides in a relationship between the cross-section and certain other functions describing the liquid state to which, in turn, the results of other experiments may also be related. Furthermore, these "other functions" have a direct (though intuitive and somewhat subtle) physical interpretation.

To illustrate the principles underlying this attack on the problem, we return to the expression for the cross-section presented in (II,26) after specializing to the case of spinless scatterers, i.e.,

$$(v,25)$$

$$\sigma = \frac{a^2}{2\pi N} \frac{k_f}{k_0} \int dt\, e^{i\omega t} \sum_{ij} \sum_n P_n \langle n | e^{-i\vec{K}\cdot\vec{R}_i} e^{i\vec{K}\cdot\vec{R}_j(t)} | n \rangle.$$

Consider now the function defined by

$$G(R,t) \equiv \frac{1}{(2\pi)^3} \int d^3k \, e^{-iK \cdot R} \sum_{ij\,n} P_n \langle n | e^{-iK \cdot R_i} e^{iK \cdot R_j(t)} | n \rangle ,$$

so that

$$\sum_{ij\,n} P_n \langle n | e^{-iK \cdot R_i} e^{iK \cdot R_j(t)} | n \rangle = \int d^3R \, G(R,t) e^{iK \cdot R}$$

We may present the cross-section (V,25) as

$$\sigma = \frac{a^2}{2\pi N} \frac{k_1}{k_0} \int dt \, d^3R \, e^{i\omega t + iK \cdot R} \, G(R,t) .$$

At first sight, (V,28) seems to be merely a formal
rewriting of (V,25) accomplished by the transformation (V,27),
and as such a profit less manipulation. Indeed, such would
be the conclusion to be drawn if it were not for the fact
that the function, G, introduced according to (V,26) has
much independent significance (independent of the scattering
problem). To establish the significance and examine the
utility of the formula (V,28) in the general case is beyond
the scope of the present discussion. However, we shall in-
vestigate these matters in some detail in the special case
that inelastic scattering is ignorable, i.e., in the limiting
case that we may evaluate G at $t = 0$. In this limit, (V,28)
becomes

$$\sigma = \frac{a^2}{N} \delta(\omega) \int d^3R \, G(R,0) e^{iK \cdot R} ,$$

where

$$G(\underline{R},0) = \frac{1}{(2\pi)^3} \int d^3k \, e^{-i\underline{k}\cdot\underline{R}} \sum_{i,j,n} P_n \langle n | e^{i\underline{k}\cdot(\underline{R}_i'-\underline{R}_j')} | n \rangle \qquad (V,30)$$

$$= N\delta(\underline{R}) + \sum_{i,j}' \sum_n P_n \langle n | \delta(\underline{R}+\underline{R}_i'-\underline{R}_j) | n \rangle \,,$$

and where again we have employed the prime on the summation to imply that terms for which i equals j are not to be included.

We note now a theorem relating the conventional quantum average of a dynamical variable to a phase space average of the classical equivilant of that dynamical variable. We first define a distribution function in the 6 N-dimensional (8) phase space (γ-space) appropriate to an N-particle system — each particle conceived of as a point completely specified by its position in configuration space, i.e.,

$$f^N(\underline{X},\underline{P},t) \qquad (V,31)$$

$$= \left(\frac{1}{\pi}\right)^{3N} \int d^{3N}Z \, e^{-2i\underline{P}\cdot\underline{Z}/\hbar} \, \Psi^\dagger(\underline{X}-\underline{Z},t)\Psi(\underline{X}+\underline{Z},t)$$

In this expression, $\underline{X}$, $\underline{Z}$ and $\underline{P}$ are to be interpreted as 3 N-dimensional vectors whose components are specified by the sets of numbers required to specify the positions ($\underline{X}$, or $\underline{Z}$) or momenta ($\underline{P}$) of the N particles of the syste, $d^{3N}Z$ is a

3-dimensional element of a volume in the configuration space of all the particles, and $\overline{\Psi}$ is the state vector of the N-particle system which satisfies the Schroedinger equation

$$H\overline{\Psi} = i\hbar \frac{\partial \overline{\Psi}}{\partial t} , \qquad (V,32)$$

where H is the Hamiltonian for the whole system. The physical significance of the N-particle distribution defined by (V,31) is perhaps most simply stated (though the statement must be cautiously hedged) as

$$f^N(\underline{X},\underline{P},t) d^{3N}\underline{X} d^{3N}\underline{P} \qquad = \text{the probability}$$

ity of finding the phase points ($\underline{X}$, P) in the element of volume $d^{3N}\underline{X}$ $d^{3N}p$ at time t in the sense that it is the appropriate weight function with respect to which to compute averages of macroscopic observables. (It is not a true probability since it is not everywhere greater than or equal to zero). In the classical limit ($\hbar \rightarrow 0$) it is readily shown that the f^N as defined satisfies the classical Liouville equation. It is our intention here to show (albeit somewhat sketchily) that the cross-section (V,29) can be represented in an intuitively satisfying way in terms of the distribution function f^N.

Our next observation is that if $\Omega(\underline{X},\underline{P},t)$ is any function of its arguments such that it has a power series representation, then the "quantum average",

$$\left(\overline{\Psi}, \Omega(\underline{X},\underline{P},t) \overline{\Psi} \right), \qquad (V,33)$$

is equal to the "classical average",

$$\int d^{3N} \underline{X}\, d^{3N} \underline{P}\, \Omega\left(\underline{X}, \underline{P}, t\right) f^{N},$$

(V,34)

provided that in the quantum expectation non-commutative products of the form,

$$\underline{X}_{j}^{n}\, \underline{P}_{j}^{M}$$

are made hermitian according to the rule

(V,35)

$$\underline{X}_{j}^{n}\, \underline{P}_{j}^{m} \equiv \sum_{k=0}^{n} \frac{n!}{2^{n} k!\,(n-k)!}\, \underline{X}_{j}^{n-k}\, \underline{P}_{j}^{m}\, \underline{X}_{j}^{k}$$

The requirement of this particular recipe for hermitization is a direct consequence of relating the distribution function f^{N} to the system state vector $\underline{\Psi}$ according to (V,31). But neither the recipe (V,35) nor the identification (V,31) is unique.

We now recall that the quantum average (V,33) can be presented in another, more revealing form. Let $\left\{\psi_{n}\left(\underline{X}\right)\right\}$ be a complete, orthornormal set of functions in the space of points, $\underline{X}$. . Then we may expand the state vector $\underline{\Psi}$ as,

$$\underline{\Psi}\left(\underline{X}, t\right) = \sum_{n} C_{n}\left(t\right) \psi_{n}\left(\underline{X}\right)$$

(V,36)

Of course, the symbol 'n' here stands for a collection of 3 N numbers, i.e., a sufficient set to specify the individual base vectors in a 3 N-dimensional space. If $\underline{\Psi}$ is normalized so that

$$\left(\underline{\Psi}, \underline{\Psi}\right) = 1,$$

then the expansion coefficients in (V, 36) have the signif-
icance that $|C_n|^2$ is the probability of finding the system
in the state characterized by the numbers 'n' at time, t. Sub-
stituting (V,36) into (V,33) one finds that

$$(\overline{\Psi}, \Omega \overline{\Psi}) = \sum_{n,m} C_n^* C_m \langle n|\Omega|m\rangle, \qquad (V,37)$$

where we have introduced the notation employed extensively in
the preceeding

$$\langle n|\Omega|m\rangle = (\psi_n, \Omega \psi_m) \qquad (V,38)$$

$$= \int d^{3N}X\, \psi_n^* \,\Omega\, \psi_m$$

Thus now, recalling (V,33) and (V,34), we have

$$\sum_{n,m} C_n^* C_m \langle n|\Omega|m\rangle = \int d^{3N}X\, d^{3N}P\, \Omega\, f^N. \qquad (V,39)$$

Next we note that for systems in thermodynamic equilib-
rium it is usually argued by one pretext or another that the
products $C_n^* C_m$ for $n \neq m$ are negligible with respect to
those for $n = m$, and that $|C_n|^2$ is independent of time.
In fact, in this circumstance the quantities $|C_n|^2$ have
precisely the same significance attached to the symbol, P_n,
introduced previously. Thus for systems in equilibrium we

have

$$(V,40)$$

$$\sum_{n,m} C_n^* C_m \langle n|\Omega|m\rangle$$

$$\equiv \sum_n P_n \langle n|\Omega|m\rangle$$

$$= \int d^{3N}\underline{X}\, d^{3N}P\, \Omega\, f^N$$

Recalling now the expression (V,30) for the function G $(\underline{R},0)$, we see that we may express it as

$$(V,41)$$

$$G(\underline{R},0) = N\delta(\underline{R})$$

$$+ \sum_{i,j}' \int d^{3N}\underline{X}\, d^{3N}P\, \delta(\underline{R}+\underline{R}_i-\underline{R}_j) f^N$$

Consider a typical term in the sum in (V,41) i.e.,

$$\int d^{3N}\underline{X}\, d^{3N}P\, \delta(\underline{R}+\underline{R}_i-\underline{R}_j) f^N$$

Defining a "doublet" probability by

$$f^2(\underline{R}_i, \underline{R}_j, \underline{P}_i, \underline{P}_j)$$

$$= \int d^{3(N-2)}\underline{X}\, d^{3(N-2)}P\, f^N$$

where the integration runs over the coordinates of all of the particles except those of the ith and j^{th} particles, we see that our 'typical term' becomes

$$\int d^3R_i\, d^3R_j\, d^3P_i\, d^3P_j\, \delta(R + R_i - R_j)\, f^2$$

Noting that nothing in this integrand depends upon P_i or P_j except f^2 itself, and further defining

$$n^2(R_i, R_j, t) \equiv \int d^3P_i\, d^3P_j\, f^2(R_i, R_j, P_i, P_j) ,$$

we see that $(V,41)$ becomes

$$(V,42)$$

$$G(R,o) = N\delta(R)$$
$$+ \sum{}' \int d^3R_j\, d^3R_i\, \delta(R + R_i - R_j)\, n^2(R_i, R_j)$$

$$= N\delta(R) + \sum_{ij}{}' \int d^3R_i\, n^2(R_i, R_i + R)$$

$$= N\delta(R) + (N-1)\sum_i \int d^3R_i\, n^2(R_i, R_i + R)$$

Inserting this expression (V,29), we obtain for the cross-section (9)

$$(V,43)$$

$$\sigma = a^2 \delta(\omega)\left[1 + \frac{N-1}{N}\int d^3R\, e^{i \vec{k}\cdot \vec{R}} \sum_i \int d^3R_i\, n^2(R_i, R_i + R)\right]$$

Recalling the original definition of the probability f^N and tracing through the subsequent summations leading to η^2 we observe that

$$\eta^2(\underline{R}_i, \underline{R}_i + \underline{R}) d^3R_i \, d^3R = \text{The prob-}$$

ability of finding the ith particle at $\underline{R}_i$ in d^3R_i and another particle simultaneously in d^3R about $\underline{R}_i + \underline{R}$.

It is conventional to decompose this quantity according to

$$\eta^2(\underline{R}_i, \underline{R}_i + \underline{R}) d^3R_i \, d^3R \qquad (V,44)$$

$$= \eta(\underline{R}_i) d^3R_i \, g(\underline{R}_i | \underline{R}_i + \underline{R}) d^3R ,$$

where

$$\eta(\underline{R}_i) d^3R_i = \text{the probability of finding the th}$$

particle in d^3R_i about $\underline{R}_i$,

and where

$$g(\underline{R}_i | \underline{R}_i + \underline{R}) d^3R = \text{the probability of finding}$$

a particle in d^3R about $\underline{R}$ given that the i th particle is at $\underline{R}_i$. For the equilibrium systems presently under consideration, the latter conditional probability may safely be regarded as independent of the location of the i th particle, i.e.,

$$g(\underline{R}_i | \underline{R}_i + \underline{R}) \longrightarrow g(\underline{R})$$

Furthermore $\sum_i \eta(\underline{R}_i)$ is simply the number density and in these systems is just the constant N/γ, where N is the total number of particles in the sample of volume V. Thus

now (V,43) becomes

$$\sigma = a^2 \delta(\omega)\left[1 + \frac{N}{V}\int d^3R\, e^{i\vec{K}\cdot\vec{R}}\, g(\vec{R})\right],$$

after replacing $(N-1)/N \longrightarrow 1$. This relationship between the cross-section and the two-particle correlation which obtains in the case of purely elastic scattering has been widely exploited in the effort to relate the results of neutron scattering experiments to the results of those thermodynamic experiments which are also theoretically dependent upon this correlation.

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