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SLOW-NEUTRON DIFFRACTION IN NORMAL LIQUIDS

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INTRODUCTION

Extensive studies on the scattering of slow neutrons by a system of atoms have been carried out(1,2,3). However, only for gases and solids has it been possible to make accurate detailed calculations. For the case of liquids the complexity of the interatomic interactions and their time variations make these calculations very difficult and only through the use of several approximations has it been possible to make any progress. Two of the approximations commonly used are the static approximation(4), in which the change of energy of the neutron upon scattering is assumed to be negligible compared with the initial energy of the neutron, and the convolution approximation(5), for which it is difficult to find a physical interpretation, although mathematically it is equivalent to setting the expectation value of a product equal to the product of expectation values.

The static approximation gives no energy spread produced by the scattering; and the diffusion model, which in conjunction with the convolution approximation, predicts too great an energy spread as compared with experiment.

In this work a new approach is attempted. The method consists of introducing a well known liquid potential function, limited to normal liquids, due to Lennard-Jones and Devonshire(6), into the scattering formulae. The energy spread predicted by this model is in better agreement with experiment for the cases studied than the previously mentioned theories.

In Chapter I we have used the quantum mechanical theory of scattering in order to obtain the basic formula (1.14) for the differential cross-section (in angle and energy) of slow-neutrons. The Lennard-Jones and Devonshire liquid theory together with some thermodynamic properties of normal liquids are reviewed in Chapter II. In Chapter III an approximation to the Lennard-Jones and Devonshire potential function (2.9) is used in order to obtain the differential cross-section for monatomic normal liquids (3.20). The parameters used for several monatomic normal liquids are discussed in Chapter IV and exhibited in Table I. The results obtained for the angular cross-section, (4.7) and (4.8), for these liquids together with experimental data available are shown in Figures 5 through 9 at the end of Chapter IV. Some of the existent theories are discussed in Chapter V. The resulting formulae, (5.18) through (5.20), are compared with the model introduced in this dissertation. Table II, at the end of Chapter V, shows experimental as well as theoretical results obtained for the broadening of the neutron final energy spectrum width at half-height for liquid Lead at different temperatures. A generalization to diatomic normal liquids and the introduction of spin dependence into the scattering formulae are made in Chapter VI. The results are applied to liquid Nitrogen, and the angular cross-section thus obtained for liquid Nitrogen is compared to the experimental cross-section in Figure 11.

CHAPTER I

QUANTUM MECHANICAL THEORY OF SCATTERING

In what follows we will derive the basic scattering formulae to which all the foregoing theories are applied.

We want to consider a system of N bodies being bombarded by monoenergetic slow neutrons of incident energy ϵ_o, and we want to calculate the number of neutrons scattered by this system into θ, φ and ϵ (See Figure 1).

We can show that the number of particles scattered per unit time into the solid angle $d\Omega$ by atoms undergoing a transition from initial state α to final state η, per unit incident flux, is given by (Appendix A.1)

$$\sigma_\eta^\alpha (\theta)d\Omega = \frac{k_\eta}{k_o} \mid f_\eta^\alpha(\theta) \mid^2 \tag{1.1}$$

where $\underline{k}_\eta$ and $\underline{k}_o$ are the neutron wave vectors for the final and the initial state respectively, and $f_\eta^\alpha(\theta)$ is the amplitude of the η-th spherically scattered wave.

If we now define p_α as the probability of finding the system in the initial state α $(\sum_\alpha p_\alpha = 1)$

$$\sigma(\theta)d\Omega = \sum_\alpha \sum_\eta p_\alpha \sigma_\eta^\alpha(\theta)d\Omega \tag{1.2}$$

would give us the angular cross-section due to transitions between all final and initial states of the system.

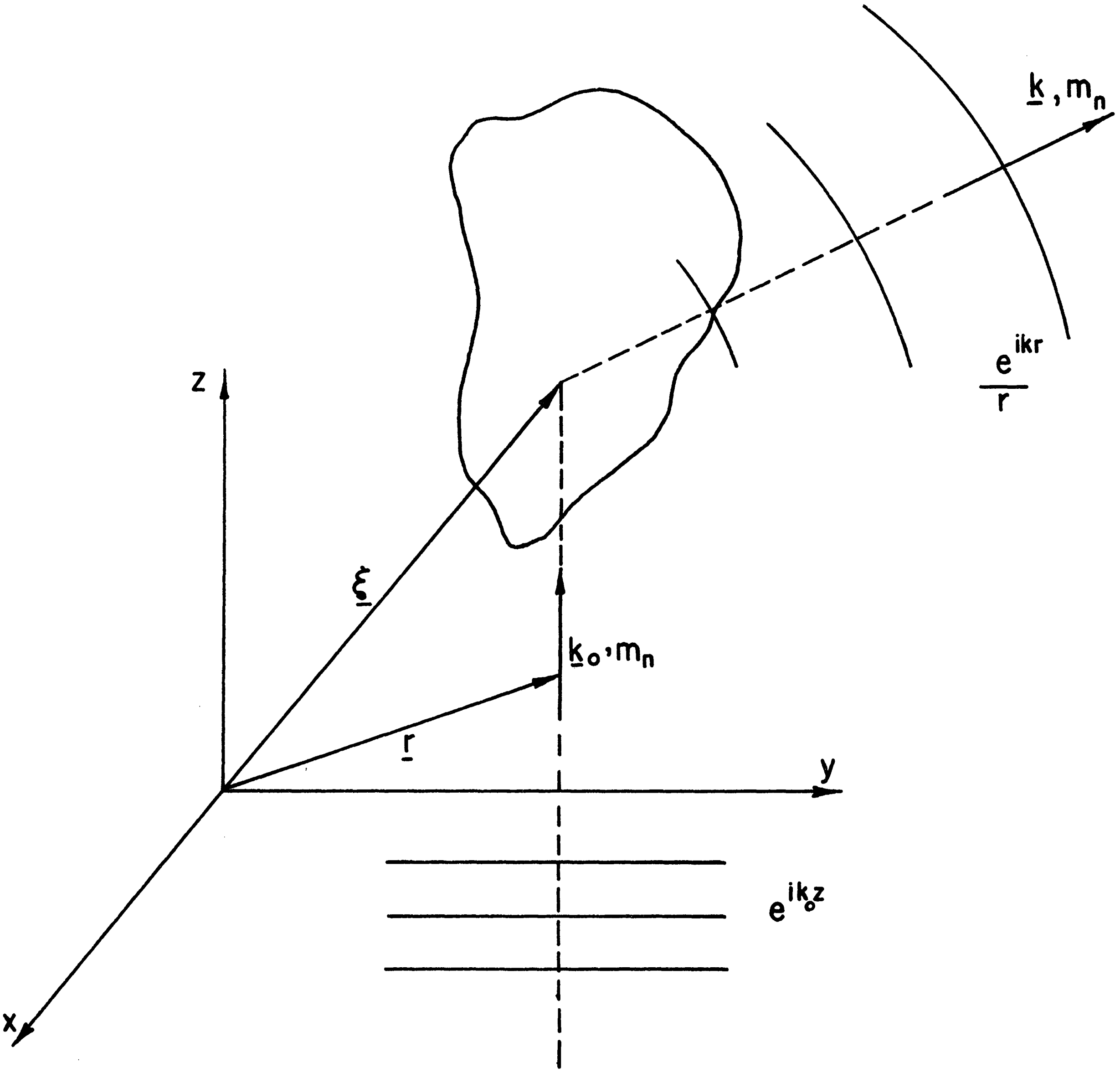

Figure 1. Scattering Collision Diagram.

Let Φ $(\underline{r})$ be the incident neutron wave function, (Figure 1), $G_{\epsilon_\eta}(r,r')$ the Green's function for the appropriate Schrödinger equation (Appendix A.2), and

$$\Gamma_{\eta\alpha} (\underline{r}) = (\eta|\Gamma (\underline{r}, \underline{\xi})|\alpha) = \int d^3 \xi \Lambda^*_\eta (\underline{\xi}) \Gamma (\underline{r}, \underline{\xi}) \Lambda_\alpha(\underline{\xi}),$$

then

$$\psi_\eta (\underline{r}) = \Phi(\underline{r}) + \sum_{\gamma=0}^{\infty} \int_{r'} d^3r' G_{\epsilon_\eta}(\underline{r}, \underline{r}') \Gamma_{\eta\gamma}(\underline{r}')\psi_\gamma(\underline{r}'), \qquad (1.3)$$

where $\Lambda_\eta(\underline{\xi})$ is an energy eigenfunction for the scattering system, will be an integral representation of the time independent Schrodinger equation

$$[H(\underline{\xi}) + H(\underline{r}) + \Gamma (\underline{r}, \underline{\xi}) - \epsilon_t] \Psi(\underline{r}, \underline{\xi}) = 0. \qquad (1.4)$$

In (1.4) $\underline{\xi} = \underline{\xi}_1, \underline{\xi}_2, \cdots, \underline{\xi}_N$ represent the position vectors of N bodies in the system, $H(\underline{\xi})$ the system Hamiltonian, $H(\underline{r})$ the neutron Hamiltonian, $\Gamma(\underline{r}, \underline{\xi})$ the neutron-system interaction potential, and ϵ_t the total neutron-system energy.

In order to solve Equation (1.3) we make use of the well known Born's approximation(7), which may be obtained by simply taking inside the integral sign in (1.3)

$$\psi_\gamma (\underline{r}') \cong \Phi (\underline{r}') \delta_{\gamma\alpha} \qquad (1.5)$$

which leaves us with

$$\psi_\eta(\underline{r}) \cong \Phi (\underline{r}) + \int_{r'} d^3r' G_{\epsilon_\eta}(\underline{r}, \underline{r}') \Gamma_{\eta\alpha}(\underline{r}') \Phi (\underline{r}') \qquad (1.6)$$

The boundary conditions that the solution of our problem must satisfy are that there is an incoming wave for the system initial state α, and asymptotically spherically outgoing waves in every state

$$\psi_\eta(\underline{r}) \overset{r\to\infty}{=} e^{ik_o z} + f_o^\alpha(\theta)e^{ik_o r}/r; \quad \eta = \alpha \tag{1.7}$$
$$\overset{r\to\infty}{=} f_\eta^\alpha(\theta)e^{ik_\eta r}/r; \text{ otherwise.}$$

Thus, if we introduce the asymptotic expression for $G_{\epsilon_\eta}(\underline{r},\underline{r}')$ (Appendix A.3) in (1.6), we get

$$\psi_\eta(\underline{r}) \overset{r\to\infty}{=} \Phi(\underline{r}) - \frac{m_n}{2\pi\hbar^2} \cdot \frac{e^{ik_\eta r}}{r} \int d^3r' e^{-i\underline{k}_\eta\cdot\underline{r}'}\Gamma_{\eta\alpha}(\underline{r}')\Phi(\underline{r}') \tag{1.8}$$

where m_n is the neutron's mass. Therefore,

$$f_\eta^\alpha(\theta) = -\frac{m_n}{2\pi\hbar^2} \int_{\underline{r}'} d^3r' \, e^{-i\underline{k}_\eta\cdot\underline{r}'} \, \Gamma_{\eta\alpha}(\underline{r}') \, \Phi(\underline{r}') \tag{1.9}$$

and since $\Phi(\underline{r}) = \exp(i\underline{k}_o \cdot \underline{r})$ (1.9) becomes

$$f_\eta^\alpha(\theta) = -\frac{m_n}{2\pi\hbar^2} \int_{r'} d^3r' e^{i\underline{r}'\cdot(\underline{k}_o-\underline{k}_\eta)} \Gamma_{\eta\alpha}(\underline{r}'). \tag{1.10}$$

Making use of this result and of Equation (1.2) we may write

$$\sigma(\theta) = \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \sum_\alpha p_\alpha \sum_\eta \frac{k_\eta}{k_o} \cdot \left| \int_{r'} d^3r' e^{i\underline{r}'\cdot\underline{K}_\eta}\Gamma_{\eta\alpha}(\underline{r}')\right|^2 \tag{1.11}$$

where $\underline{K}_\eta = \underline{k}_o - \underline{k}_\eta$ is the momentum transfer vector.

Thus far, we have said nothing with respect to $\Gamma(\underline{r},\underline{\xi})$. We will now assume it to be given by what is known as the Fermi pseudo-potential(7,8), and refer the reader elsewhere for justification of this assumption. Thus, let

$$\Gamma\,(\underline{r},\,\underline{\xi}) = \frac{2\pi\hbar^2}{m_n}\sum_{s=1}^{N} b_s\,\delta(\underline{r} - \underline{\xi}_s) \tag{1.12}$$

where b_s is the scattering length of the s-th atom and in general may be spin dependent, and $\delta(\underline{r})$ is the Dirac delta function.

Introducing in (1.11) the energy conservation relation$^{(2,9)}$, we get

$$\sigma(\epsilon,\theta)d\epsilon = \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \sum_{\alpha} p_\alpha \sum_{\eta} \frac{k}{k_o} \left|\int_{r'} d^3r' e^{i\underline{r}'\cdot\underline{K}}(\eta|\Gamma(\underline{r};\underline{\xi})|\alpha)\right|^2 \delta(\epsilon_\eta - \epsilon)d\epsilon \tag{1.13}$$

which with the help of Equation (1.12) and of the integral representation of Dirac's delta becomes (Appendix A.4)

$$\sigma(\epsilon,\theta) = \frac{k}{k_o}\cdot\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty} dt e^{itq} \sum p_\alpha (\alpha|\sum_{s=1}^{N}\sum_{j=1}^{N} b_s b_j e^{-i\underline{K}\cdot\underline{\xi}_s(t)} e^{i\underline{K}\cdot\underline{\xi}_j}|\alpha) \tag{1.14}$$

where

$$\hbar q = \epsilon_o - \epsilon \tag{1.15}$$

is the energy transfer, and

$$\underline{\xi}_s(t) = \exp\,(itH/\hbar)\;\underline{\xi}_s\;\exp\,(-itH/\hbar) \tag{1.16}$$

the Heisenberg's operator.

In order to proceed further we have to decide which system we are going to treat and, therefore, which Hamiltonian we are going to use. Having done this, we could formally calculate (1.16) and could go on with the operations indicated in (1.14).

CHAPTER II

NORMAL AND ASSOCIATED LIQUIDS

It has been customary to classify liquids into two categories, those that followed certain empirical rules, such as Trouton's Rule, and had similar physical properties like vapor pressure, surface tension, etc.; and that minority that did not show such correlations. As more data were accumulated and knowledge of the chemical structure of the molecules that formed these liquids increased, a better understanding of the empirical correlations was obtained.

These empirical correlations were only explainable if it was assumed that the internal degrees of freedom of the molecule were not seriously disturbed by the closely packed molecules in the liquid state; and that the molecule in the gaseous state was essentially spherically symmetric. It is thus implied that in the passage from the gas phase to the liquid phase the internal structure of the individual molecules was little modified. These liquids were called Normal. On the other hand, the liquids that deviated from these "normal" conditions were believed to form in the liquid phase links among molecules causing disturbances in the internal degrees of freedom (rotational, vibrational, and electronical). These liquids were called Associated.

Lennard-Jones and Devonshire Theory Review

Several attempts(10,11) have been made trying to explain the thermodynamic properties of liquids. Lennard-Jones and Devonshire(6) (LJD) made a significant contribution in this respect when they introduced a potential energy, already found empirically to fit the properties of slightly imperfect gases, in their liquid model. They found that this particular choice could predict with satisfactory accuracy the temperature dependence of the virial coefficient $B(PV/k_BT = 1 + B/V + C/V^2 + \cdots)$ of the slightly imperfect gas, the critical temperature, the boiling point, and the heat of evaporation.

In their work it is assumed that each molecule moves in its own cell and a calculation is performed in which the actual time varying field to which a molecule in the liquid is subjected is replaced by a suitable average. This average field for a molecule moving in its cell is then obtained by fixing the immediate neighbors to their respective equilibrium positions. All these "smeared" nearest neighbors are assumed to be arranged in a spherically symmetric fashion. That is, arranged with equal probability on the surface of the cell.

In Figure 2 the central molecule is at P, a distance r from the center of the cell. The center of the cells are separated a distance a. The probability of finding x "smeared" nearest neighbors in the area encircled by the rings is

$$x(2\pi a^2 \sin\theta \, d\theta \,/\, 4\pi a^2) = (x/2)\sin\theta \, d\theta; \tag{2.1}$$

the interaction potential between the particle at P and the particle at Q is given by $V(R)$. Therefore, the average potential energy within the cell $(r < a)$ will be given by

$$\overline{V}(r) = \int_0^{\pi/2} V\left(\sqrt{r^2 + a^2 - 2ar\cos\theta}\right) \frac{x}{2} \sin\theta \, d\theta \tag{2.2}$$

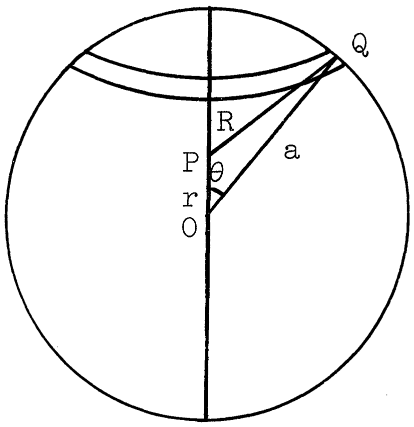

Figure 2. Lennard-Jones and Devonshire Cell

It was mentioned before that the interaction potential chosen will be that which predicts with reasonable accuracy the equilibrium properties of the slightly imperfect gases, namely

$$V(R) = -\frac{\mu}{R^6} + \frac{\nu}{R^{12}} \qquad (2.3)$$

the well-known Lennard-Jones six-twelve potential function.

Therefore, after trivial integration and rather lengthy algebraic manipulations, we obtain:

$$\overline{V}(r) = \overline{V}(o) + \Lambda^*(V^*/V)^2 \; [(V^*/V)^2 \cdot l(r^2/a^2) - 2m(r^2/a^2)] \qquad (2.4)$$

where

$$\overline{V}(o) = \Lambda^*(V^*/V)^2 \; [(V^*/V)^2 - 2] \qquad (2.5)$$

in which if ϵ^* denotes the minimum value of V(R), and r^* is the value of R at which this minimum occurs, then

$$\Lambda^* = -x\epsilon^* = x\mu^2/4\nu$$
$$V^*/V = (r^*/a)^3 = (2\nu/\mu)^{\frac{1}{2}}a^{-3} \qquad (2.6)$$

where V denotes the volume per molecule and l(y) and m(y) are functions defined by

$$l(y) = (1 + 12y + 25.2y^2 + 12y^3 + y^4)(1 - y)^{-10} - 1 \qquad (2.7)$$
$$m(y) = (1 + y)(1 - y)^{-4} - 1$$

Approximation for Potential

Equation (2.4) tells us how the potential energy of a given molecule changes as it moves in its cell, while (2.5) gives the value of this potential at the center of the cell. The zero of energy is, as usual, that of infinite separation. The right hand side (RHS) of (2.5) is a function of Λ^* and V^*/V only; that of (2.4) depends on these two quantities and also, through a, on the numerical constant γ ($a^3 = \gamma \cdot V$), which is determined by the geometrical arrangement of the molecules.

Some representative curves for $\bar{V}(r)$ for certain values of V^*/V are shown in Figure 3. Curves 1 and 2 have a potential hump at the center, while 3 does not. It is found that the field ceases to have this central hump when (Appendix A.5)

$$\frac{V^*}{V} = \left(\frac{2\nu}{\mu}\right)^{\frac{1}{2}} a^{-3} \gtrsim .67. \qquad (2.8)$$

For this range it is easy to see that if one expands $\bar{V}(r)$ in a series of even powers of r, the main contribution to $\bar{V}(r)$ comes from the r^2 term. The contribution from the rest of the terms being neglected.

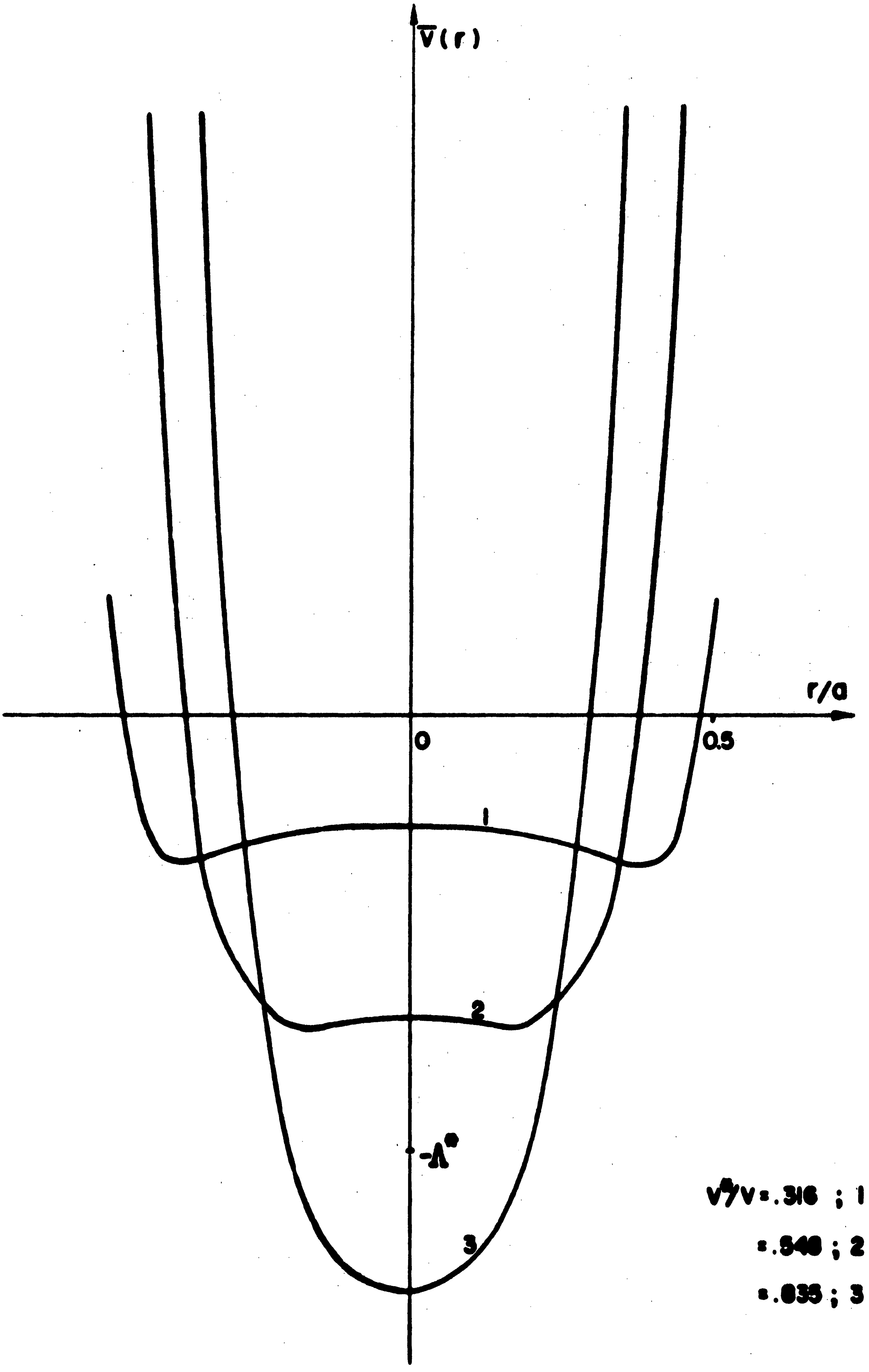

Figure 3. Lennard-Jones and Devonshire Potential.

Therefore, the potential can be written

$$\overline{V}(r) = \overline{V}(o) + sr^2 \tag{2.9}$$

where

$$s = \frac{M\omega^2}{2} = \frac{\Lambda^*}{a^2}\left(\frac{V^*}{V}\right)^2\left[22\left(\frac{V^*}{V}\right)^2 - 10\right] = \frac{x}{2a^2}\left(\frac{44\nu}{a^{12}} - \frac{10\mu}{a^6}\right) \tag{2.10}$$

Equation of State and Derived Thermodynamic Functions

It has been shown elsewhere(10) that the free energy of an assembly of N molecules in a volume V may be exhibited as the sum of three independent terms, the translational or kinetic motion, the potential, and the internal degrees of freedom contribution. This is possible if the partition functions of the system is given by the product of partition functions for the kinetic, potential, and internal degrees of freedom, respectively. This is satisfied by dilute gases and presumed to be a good approximation for highly compressed gases and for normal liquids. To these approximations the only distinctions among normal liquids, compressed gas, and a dilute gas are entirely due to differences in the potential part in the free energy.

Under this assumption one can show (Appendix A.6) that for our parabolic approximation the free energy per molecule is given by

$$f = \overline{V}(o) - 3k_BT \ln (k_BT/h\omega) - k_BT \ln j(T) \tag{2.11}$$

where j(T) stands for the internal degrees of freedom partition function.

From this relation one can derive related thermodynamic functions such as the partial potential Y, the molecular heat content H, and the equation of state (Appendix A.7).

Trouton's Rule

Trouton's rule can be formulated as follows: all normal liquids have the same entropy of evaporation at their boiling points.

It is shown in Appendix A.7 that the heat content H^L, for the harmonic oscillator model is given by

$$\begin{aligned} H^L &= \bar{V}(o) + 3k_BT[10 - 33\,(V^*/V)^2][5 - 11\,(V^*/V)^2]^{-1} + E^L_{int.} \\ &+ 4\Lambda^*(V^*/V)^2[1 - (V^*/V)^2] \end{aligned} \tag{2.12}$$

and for the gas-phase(10)

$$H^G = (5/2)k_BT + E^G_{int.} \tag{2.13}$$

Therefore, the molecular heat of evaporation Λ_e would be

$$\Lambda_e = H^G - H^L = (5/2)k_BT - \bar{V}(o) - G(V) + E^G_{int.} - E^L_{int.} \tag{2.14}$$

$$\begin{aligned} G(V) &= 3k_BT[10 - 33\,(V^*/V)^2][5 - 11\,(V^*/V)^2]^{-1} - 4\Lambda^*(V^*/V)^2 \cdot \\ &\cdot[1 - (V^*/V)^2] \end{aligned} \tag{2.15}$$

and the entropy at boiling is then

$$\frac{\Delta S}{k_B} = \frac{\Lambda e}{k_BT_B} = \frac{5}{2} - \frac{\bar{V}(o)}{k_BT_B} - \frac{G(V)}{k_BT_B} \tag{2.16}$$

where we have assumed

$$E^G_{int.} = E^L_{int.}$$

For Argon, for example,

$$(V^*/V) \cong 1, \ (\Lambda^*/k_BT) \cong 16.6 \ \therefore \ \Delta S/k_B \cong 7.65$$

The experimental value is approximately 8. (See Table 2 Chapter VI of reference 10).

Entropy of Melting

In reference 10 it is shown that using the harmonic oscillator liquid model, one can exhibit the entropy of melting as a function, although approximated, only of the frequency of vibration of the crystal and the liquid state.

The value obtained for the entropy of melting is

$$\Delta S_m/k_B = \Lambda_m/k_BT_m = 3 \ln(\omega^c/\omega^L) + 1 \qquad (2.17)$$

Formula (2.17) has been used in order to obtain ω^L for Lead. In order to do this, we have assumed that ω^c was determined by the characteristic Debye temperature $\Theta(\omega^c = (k_B\Theta/\hbar) = 12.371 \times 10^{12}$ sec^{-1} for $\Theta = 94.5°K$[12]) and that the entropy of melting $(\Lambda m/k_BT_m = .95$[10,13]. These values lead to $\omega^L = 12.57_3 \times 10^{12}$sec^{-1}. We will use this value of ω^L in Chapter V.

CHAPTER III

DIFFERENTIAL CROSS-SECTION ACCORDING TO THE APPROXIMATION TO THE LENNARD-JONES AND DEVONSHIRE LIQUID MODEL POTENTIAL

In Chapter I (1.14) we have established an expression for the differential cross-section, $\sigma(\epsilon, \theta)$, which we may write in the following form

$$\sigma(\epsilon, \theta) = \sigma_{\text{inner}}(\epsilon, \theta) + \sigma_{\text{outer}}(\epsilon, \theta) \qquad (3.1)$$

where

$$\sigma_{\text{inner}}(\epsilon,\theta) = \frac{k}{k_o} \cdot \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{itq} \sum_{\alpha} p_{\alpha} \cdot (\alpha | \sum_{s=1}^{N} b_s^2 e^{-i\underline{K} \cdot \underline{\xi}_s(t)} e^{i\underline{K} \cdot \underline{\xi}_s} | \alpha) \qquad (3.2)$$

and

$$\sigma_{\text{outer}}(\epsilon,\theta) = \frac{k}{k_o} \cdot \frac{1}{2\pi\hbar} \int_{-\infty}^{\infty} dt e^{itq} \sum_{\alpha} p_{\alpha} \cdot (\alpha | \sum_{\substack{s=1 \\ \neq j}}^{N} \sum_{j=1}^{N} b_s b_j \, e^{-i\underline{K} \cdot \underline{\xi}_s(t)} e^{i\underline{K} \cdot \underline{\xi}_j} | \alpha) \qquad (3.3)$$

The reason for this break-up of the cross-section is that for a monoatomic system $\sigma_{\text{inner}}(\epsilon, \theta)$ represents the non-interference cross-section, sometimes referred to as the direct-scattering part of the cross-section and gives the contribution to the cross-section from those waves scattered by each atom individually. The $\sigma_{\text{outer}}(\epsilon, \theta)$ represents the part due to the scattering by different atoms giving, thus, the interference part or outer effect.

Inner Effect

We will proceed first to calculate $\sigma_{\text{inner}}(\epsilon, \theta)$. In Chapter II we have established that when the range

$$(2\nu/\mu)^{\frac{1}{2}} a^{-3} \overset{\sim}{>} .67$$

is satisfied a suitable approximation to the LJD model potential was given by

$$\overline{V}(r) = \overline{V}(o) + s\, r^2;\; r < a$$

with $\overline{V}(o)$ and s given by (2.5) and (2.10), respectively.

With the help of Figures 1 and 2 we construct Figure 4, and we define

$$\underline{\xi}_s(t) = \underline{B}_s + \underline{r}_s(t). \tag{3.5}$$

The vector $\underline{\xi}_s(t)$ is then the position vector of the s-th nucleus at time t, and it is given by the vector addition of a fixed vector $\underline{B}_s$ to the center of the cell, and a vector $\underline{r}_s(t)$ which gives the actual position of the s-th nucleus with respect to its equilibrium position at time t.

We may write the true Hamiltonian

$$H' = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2M_i}\right)\nabla_i^2(\underline{R}) + \sum_{j=1}^{n}\left(-\frac{\hbar^2}{2m_e}\right)\nabla_j^2(\underline{r}) + V(\underline{r},\underline{R})$$

for n electrons, N nuclei, and V the sum of electrostatic interactions between all of them. In this section an approximate Hamiltonian has been used in which we have replaced the potential $V(\underline{r}, \underline{R})$ by our approximation to the LJD potential. Thus

$$H' \cong H = \sum_{s=1}^{N} H_s \tag{3.6}$$

and

$$H_s = (\underline{p}_s^2/2M_s) + (M_s\omega^2/2)r_s^2 + \overline{V}(o) \tag{3.7}$$

for monatomic systems $M_s = M$.

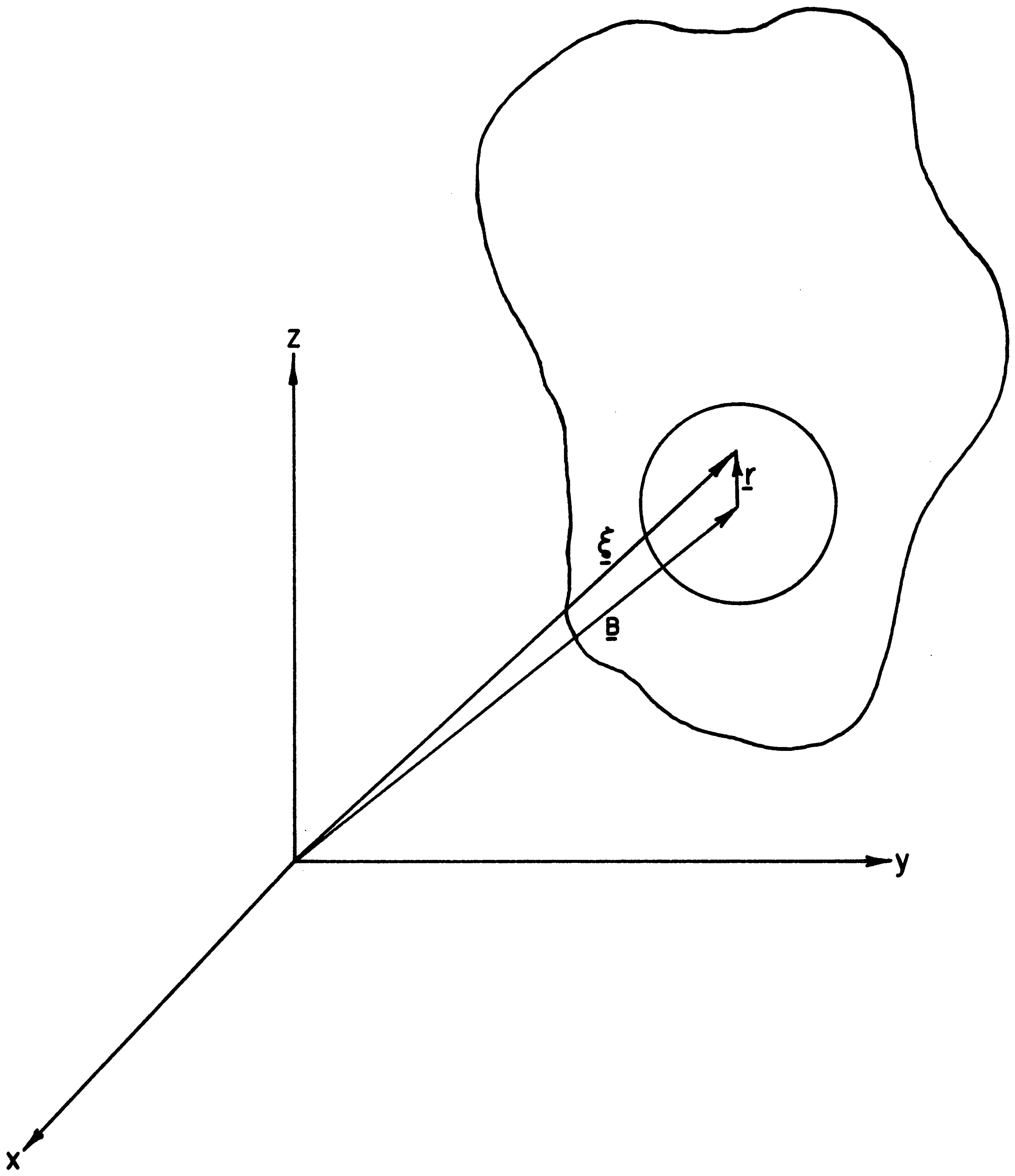

Figure 4. Nuclear Coordinates.

Let

$$\Omega_s(\underline{\xi},\ t) = \exp\ [-i\underline{K}\cdot\underline{\xi}_s(t)] \tag{3.8}$$

Then

$$\Omega_s(\underline{\xi},\ t)\Omega_s^+(\underline{\xi},0) = \Omega_s(\underline{r},t)\Omega_s^+(\underline{r},0) \tag{3.9}$$

where Ω^+ is the hermitean conjugate of Ω. Therefore,

$$\sigma_{inner}(\epsilon,\theta) = (k/2\pi\hbar k_o)\cdot\int_{-\infty}^{\infty} dt e^{itq} < \sum_{s=1}^{N} b_s^2 \Omega_s(\underline{r},t)\Omega_s^+(\underline{r},o)>_T \tag{3.10}$$

where the thermal average indicated by $< \ >_T$ is evaluated through the use of a corollary to Bloch's theorem[2, 14], and (Appendix A.9)

$$\begin{aligned} < \Omega_s(\underline{r},t)\Omega_s^+(\underline{r},0) >_T &\equiv \sum_\alpha p_\alpha(\alpha|b_s^2 e^{-i\underline{K}\cdot\underline{r}_s(t)} e^{i\underline{K}\cdot\underline{r}_s}|\alpha) \\ &= b_s^2 \sum_{n=-\infty}^{\infty} e^{nA_1 - int\omega - A_2' K^2} I_n(A'K^2). \end{aligned} \tag{3.11}$$

The Heisenberg's operator is given by (Appendix A.8)

$$\underline{r}_s(t) = \exp\ (iHt/\hbar)\underline{r}_s\ \exp(-iHt/\hbar) = \cos\ \omega t\underline{r}_s(o) + (\sin\ \omega t/M\omega)\underline{p}_s(o) \tag{3.12}$$

where

$$\begin{aligned} K^2 &= (2m_n/\hbar^2)(\epsilon + \epsilon_o - 2\sqrt{\epsilon\epsilon_o}\ \cos\ \theta) \\ A_1 &= (\hbar\omega/2k_BT) \\ A_2' &= (\hbar/2M\omega)\text{csch}\ A_1 \\ A_3' &= A_2'\ \cosh\ A_1 \end{aligned} \tag{3.13}$$

and $I_n(x)$ is the modified Bessel's function of order n, which can be written in terms of the ordinary Bessel's function, $J_n(x)$, of order n ($I_n(x) = i^{-n}J_n(ix)$).

Upon substitution of (3.11) into (3.10) we obtain

$$\sigma_{\text{inner}}(\epsilon, \theta) = b^2 N \sum_{n=-\infty}^{\infty} (k/k_o)\, e^{-A_3'K + nA_1} \cdot I_n(A_2'K^2)\, \delta(\epsilon_o - \epsilon - n\hbar\omega) \tag{3.14}$$

Outer Effect

As has been mentioned before, the interference between the amplitudes scattered by independent atoms of the system produces changes in the intensity which have been observed in X-ray diffraction and lately also in Neutron diffraction.

In order to calculate this intensity exactly, it is necessary to have a detailed knowledge of the interparticle interactions and of the position correlations to which they lead. In order to determine the inelastic part of the outer effect, a knowledge of the time dependence of these position correlations is necessary as well. The exact calculation of these effects is extremely difficult. This fact forces us to make some approximations as described below.

In what follows we will make use of the familiar Heisenberg's operator time expansion technique(2,15) to calculate the thermal average in σ_{outer}. We will then show, in the Appendices A.10 and A.11, that the zero-th order term of this expansion may be related to the well-known radial distribution function, g(r), through the use of the Irving Zwanzig theorem. The function $g(r)d^3r$ is defined to be the probability that, given an atom at the origin, a distinct one will be found simultaneously in d^3r about $\underline{r}$. The first order term is shown to be zero$^{(1)}$ if the Wigner distribution functions are assumed to be isotropic in the momenta, (Appendix A.10). In this way it is shown as has been pointed out elsewhere$^{(17)}$, that inelastic effects are much less prominent in the interference terms than in the direct scattering.

Therefore, we can write

$$\begin{aligned} \sigma_{\text{outer}}(\epsilon,\theta) &= (k/k_o)\delta(\epsilon_o-\epsilon) \left< \sum_{\substack{s=1 \\ \neq j}}^{N} \sum_{j=1}^{N} b_s b_j e^{i\underline{K}\cdot(\underline{\xi}_j-\underline{\xi}_s)} \right>_T \\ &= (Nb\ k/k_o)\delta(\epsilon_o-\epsilon)\ \rho \int d^3r e^{i\underline{K}\cdot\underline{r}}\, g(r) \end{aligned} \qquad (3.15)$$

where ρ is the number of atoms per unit volume. (See Spin Dependence Chapter VI).

Much theoretical and experimental work has been done with regard to the radial distribution function in liquids. On the theoretical side Kirkwood$^{(18)}$, Ivon$^{(19)}$, Green-Born$^{(20)}$ have derived integro-differential equations which through some approximations have been solved for certain choices of potentials. These cases have been reviewed in a book by T. L. Hill on Statistical Mechanics.$^{(11)}$

On the experimental side the determinations of the radial distribution function, using X-ray diffraction, for several elements have been reviewed to great extent by Gingrich$^{(21)}$; and for those cases in which neutron diffraction techniques have been used Henshaw, Pope, Hurst, and Brokhouse, to mention a few, have measured g(r) for Argon, Nitrogen molecule, Oxygen molecule, and Lead$^{(22,23)}$.

For our particular problem the choice of the theoretical radial distribution function, which we will use in our calculation of σ_{outer}, will be governed by the consistency in the interaction potential used to calculate on the one hand, the g(r) function and on the other our σ_{inner} calculation. Namely, we would have to calculate the g(r) function by using the six-twelve Lennard-Jones potential. But, since this calculation has been done elsewhere using a modified Lennard-Jones and Hard-sphere potential because the calculation of the Lennard-Jones potential alone turned out to be extremely difficult(11,24) there is no need to repeat it here. Instead we will use the hard-sphere potential.

$$
\begin{aligned}
U\,(r) &= 0;\ r > d \\
&= \infty;\ r \leq d
\end{aligned}
\qquad (3.16)
$$

and an expansion to first order in the density(11,29)

$$
\begin{aligned}
g(r) &= \begin{cases} 0; & r \geq d \\ 1; & r \leq 2d \end{cases} \\
&= 1 + (4\pi\rho d^3/3)[1 - (3r/4d) + (r/d)^3/16]\, d < r \leq 2d
\end{aligned}
\qquad (3.17)
$$

of the radial distribution function (Appendix A.12) for simplicity's sake, since the results may be exhibited in closed form.

Incident Spectrum

Although we have assumed in the theory that we had mono-energetic neutrons of incident energy ϵ_0, this is not achieved in practice, and therefore, in order to compare theoretical results with experiment, we have to introduce into the theory the fact that the incident beam has a finite energy width, about an average $\bar{\epsilon}_0$ rather than being of the ideal $\delta(\epsilon_0-\bar{\epsilon}_0)$ type. Assuming this energy spectrum is given by a Gaussian distribution (which is approximately the case for most crystal spectrometers) as

$$G(\epsilon_0,\bar{\epsilon}_0) = L \exp[-(\epsilon_0-\bar{\epsilon}_0)^2/\beta^2] \tag{3.18}$$

we may then calculate

$$\sigma(\epsilon,\theta;\bar{\epsilon}_0,\beta) = \int_0^\infty d\epsilon_0 G(\epsilon_0,\bar{\epsilon}_0)\,\sigma(\epsilon,\theta;\epsilon_0) \tag{3.19}$$

and obtain (Appendix A.13)

$$\begin{aligned}\sigma(\epsilon,\theta;\bar{\epsilon}_0,\beta)/Nb^2L = {} & \sigma_{outer}(\epsilon,\theta;\bar{\epsilon}_0,\beta) + \sigma_0(\epsilon,\theta;\bar{\epsilon}_0,\beta) + \sigma_+(\epsilon,\theta;\bar{\epsilon}_0,\beta) \\ & + \sigma_-(\epsilon,\theta;\bar{\epsilon}_0,\beta)\end{aligned} \tag{3.20}$$

where we have written

$$\sigma_{inner}(\epsilon,\theta;\bar{\epsilon}_0,\beta) = \sigma_0 + \sigma_+ + \sigma_-$$

and

$$Q_n^2 = \epsilon + n(\hbar\omega/2) - \sqrt{\epsilon(\epsilon+nh\omega)}\cos\theta \tag{3.21}$$

$$\sigma_0(\epsilon,\theta;\bar{\epsilon}_0,\beta) = \exp[-(\epsilon-\bar{\epsilon}_0)^2\beta^{-2}-2\epsilon A_3\sin^2\frac{\theta}{2}]\,I_0(2\epsilon A_2\sin^2\frac{\theta}{2}) \tag{3.22}$$

$$\sigma_+(\epsilon,\theta;\bar{\epsilon}_0,\beta) = \sum_{n=1}^{\infty}\sqrt{\epsilon(\epsilon+nh\omega)^{-1}}\,I_n(A_2Q_n^2)\exp[-A_3Q_n^2+nA_1-(\epsilon-\bar{\epsilon}_0+nh\omega)^2/\beta^2] \tag{3.23}$$

$$\sigma_-(\epsilon,\theta;\bar{\epsilon}_0,\beta) = \sum_{n=1}^{\infty}\sqrt{\epsilon(\epsilon-nh\omega)^{-1}}\,I_n(A_2Q^2-n)\cdot\exp[-A_3Q_{-n}^2-nA_1-(\epsilon-\bar{\epsilon}_0-nh\omega)^2/\beta^2] \tag{3.24}$$

and for σ_{outer} (Appendix A.14)

$$\sigma_{outer}(\epsilon,\theta;\bar{\epsilon}_0,\beta) = \exp[-(\epsilon-\bar{\epsilon}_0)^2\beta^{-2}]\{B\} \tag{3.25}$$

In expression (3.25) the bracket is given by

$$\begin{aligned}\{B\} = {} & -D\Lambda_{3/2}(y) + (3D^2/16)[24(y^2-1)\cdot\cos 2y - 48y\sin 2y \\ & + (5y^4+12y^2+24)\cdot\cos y + (4y^2+24y)\sin y]\end{aligned} \tag{3.26}$$

where

$$y = Kd = (4\pi d/\lambda) \sin (\theta/2) \tag{3.27}$$

and λ is the wavelength corresponding to the energy ϵ,

$$\begin{gathered} D = (4\pi d^3 \rho/3); \; A_2 = (4m_n/\hbar^2)A_2' \\ A_{3/2}(y) = 3(\sin y - y \cos y)y^{-3}; \; A_3 = A_2 \cosh A_1 \end{gathered} \tag{3.28}$$

In formula (3.26) we can immediately recognize the first term as the familiar Debye approximation to the outer effect, while the rest is closely related to a similar expression derived in the classical approximation (high temperature) by Mazo and Zemach(17) in connection with neutron diffraction by imperfect gases.

CHAPTER IV

CALCULATIONAL PROCEDURES AND DATA

Energy Transfers

In Chapter III, (3.20), we have expressed the cross-section as the sum of four terms, the second of which, $\sigma_0(\epsilon,\theta;\ \bar{\epsilon}_0,\beta\ )$, represents the elastic contribution to the direct scattering of the neutron final energy spectrum. This is seen to be the case because for a narrow width incident spectrum the main contribution to σ_0 comes from those values of ϵ close to $\bar{\epsilon}_0$, as given by the Gaussian centered at about $\bar{\epsilon}_0$. In the same way one can see that the Gaussians in the third and fourth terms (3.23) and (3.24) are centered about $\bar{\epsilon}_0 - n\hbar\omega$ and $\bar{\epsilon}_0 + n\hbar\omega$, respectively, which indicates that the neutron has lost or gained $n\hbar\omega$ units of energy in collision. Thus σ_+ and σ_- give the inelastic contribution to the cross-section resulting from the loss and gain of energy by the neutron. The first term, σ_{outer}, in the approximation considered is formed only of elastic scattering. Therefore, we can see that the summations in σ_+ and σ_- are limited, essentially by the amount of energy the neutron can lose to or gain from the system. We can then say that if in the average the system is in thermal equilibrium, and thus has k_BT units of energy the neutron can approximately gain this same amount. Then the upper limit in the summation in the σ_- expression would be given by

$$n_- = (k_BT\ /\ \hbar\omega) \tag{4.1}$$

On the other hand if the neutron has $\bar{\epsilon}_0$ units of energy with which it started out, it can only lose this much; and the upper limit in the summation in the σ_+ expression is

$$n_+ = (\bar{\epsilon}_0 / \hbar\omega) \tag{4.2}$$

Nearest Neighbor Distance and Hard Sphere Diameter

We have seen (Chapter II) that the average nearest neighbor distance or the distance between the center of the cells is given by "a", and that "a" enters into the expression for ω, the oscillator frequency. We have also seen (Chapter III) that in the calculation of $g(r)$ another parameter entered, d, the hard-sphere diameter. These two parameters are not equal. However, one may obtain an approximate relationship between them by noticing that if one would use the Lennard-Jones six-twelve potential to calculate the first peak in the $g(r)$ function, it would be given by the minimum of the Lennard-Jones potential.

The value at which the $g(r)$ function has its first maximum is then

$$r_{1\text{st max}} = r^* \qquad \text{for LJ potential} \tag{4.3}$$

For the hard-sphere potential this maximum appears at "d"

$$r_{1\text{st max}} = d \qquad \text{for hard-sphere potential} \tag{4.4}$$

Therefore, using (2.6) we get

$$d \cong r^* = a \left(\frac{V^*}{V}\right)^{1/3} \tag{4.5}$$

Calculational Procedure

We can summarize our results by writing for the differential cross-section of normal liquids

$$\sigma[\epsilon,\theta;\ \bar{\epsilon}_0,\beta,T;\ \omega(\mu,\nu,a),\rho] \tag{4.6}$$

which tells us that if the inequality

$$(2\nu/\mu)^{\frac{1}{2}} a^{-3} \gtrsim .67$$

is satisfied, and if we also know

- a) the experimental conditions
  - i. average incident neutron energy, $\bar{\epsilon}_0$,
  - ii. incident energy spectrum width, β, (which may easily be related to the half-height width), and
  - iii. the temperature, T, at which the liquid was kept during the experiment, and
- b) the liquid under investigation, defined by
  - i. the number of atoms per unit volume in the liquid, ρ, and
  - ii. the oscillator frequency, ω, which is related to the six-twelve Lennard-Jones gas-phase potential parameter μ and ν, and the nearest-neighbor's distance, a,

we can obtain the intensity of neutrons scattered through angle θ and into final energy ϵ.

Table I shows those elements for which there is gas-phase data[13] available and for which the cross-section has been calculated according to the parameters also shown.

In the Case of Lead the μ and ν parameters are not known. However, one can estimate the oscillator frequency for the liquid state by making use of an approximate expression for the entropy of melting (Chapter II, (2.17)). The value of ω thus obtained was used in our calculation.

The results for the angular cross-section are shown in Figures 5 through 9. Figures 5 and 6 show the angular cross-section

TABLE I

CALCULATIONAL PARAMETERS FOR MONATOMIC ELEMENTS

	$-\epsilon^*$	r^*	Λ^*	V^*	T	k_BT	Λ^*/kT	V^*/V	M	ρ	$\bar{\epsilon}_o$	ω
Elements	ergs/molecule ($x10^{-16}$)	(Å)	ev/molecule	($Å^3$)	(°K)	ev ($x10^{-3}$)			(grams) ($x10^{-24}$)	($Atoms/cm^3$) ($x10^{22}$)	ev ($x10^{-2}$)	sec^{-1} ($x10^{12}$)
Neon	48.2	3.12	.0361	21.2	24.57	2.13	16.9	.975	33.463	3.597	7.00	6.669
Argon	165.0	3.84	.1240	40.0	84.00	7.22	17.1	.970	66.370	2.130	7.57	8.198
Krypton	238.4	4.03	.1790	46.4	116.00	10.00	17.9	.990	138.940	1.765	7.00	5.855
Xenon	309.9	4.56	.2320	67.1	163.00	14.10	16.5	.960	217.695	1.400	7.00	4.500
Lead					609.00	5.25			344.864	3.067	6.85	12.600
Lead					620.00	5.34			344.864	3.060	4.42	12.600
Lead					823.00	7.09			344.864	2.995	6.85	12.600

for Argon and Lead, respectively. Experimental data (22,23) is available for these two elements, and we have shown it in the same graphs. The theoretical curves were obtained by integrating the final energy spectra at each angle, i.e.,

$$\sigma(\theta) = \int d\epsilon \sigma(\epsilon,\theta; \bar{\epsilon}_0,\beta) \qquad (4.7)$$

and the normalization of the experimental points is that which gives closest fit at large angles.

Notice, however, that in the last three figures 7, 8, and 9 (Neon, Krypton, and Xenon) we have only shown a few integrated points at large angles. The integrated points are properly indicated on the curves. The angular distribution shown is

$$\sigma(\theta) = \int d\epsilon \delta(\epsilon - \bar{\epsilon}_0) \; \sigma(\epsilon,\theta; \bar{\epsilon}_0,\beta) \qquad (4.8)$$

which is equivalent to counting particles with a counter that only detects those particles with final energy $\bar{\epsilon}_0$.

This was done due to the fact that there is not any experimental data available for these elements. Therefore, the nearest neighbor distance "a" is not known. We have guessed this parameter for Ne, Kr, and Xe from crystal data and calculated r*. Thus it was felt that the complete energy distributions were not necessary.

Notice, also that the asymptote (see diagram) about which the intensity fluctuates is a function of temperature. Although, not a very strong function of temperature, this feature may be detected experimentally.

The final energy spectra widths at half-maximum are given in Table II, Chapter V.

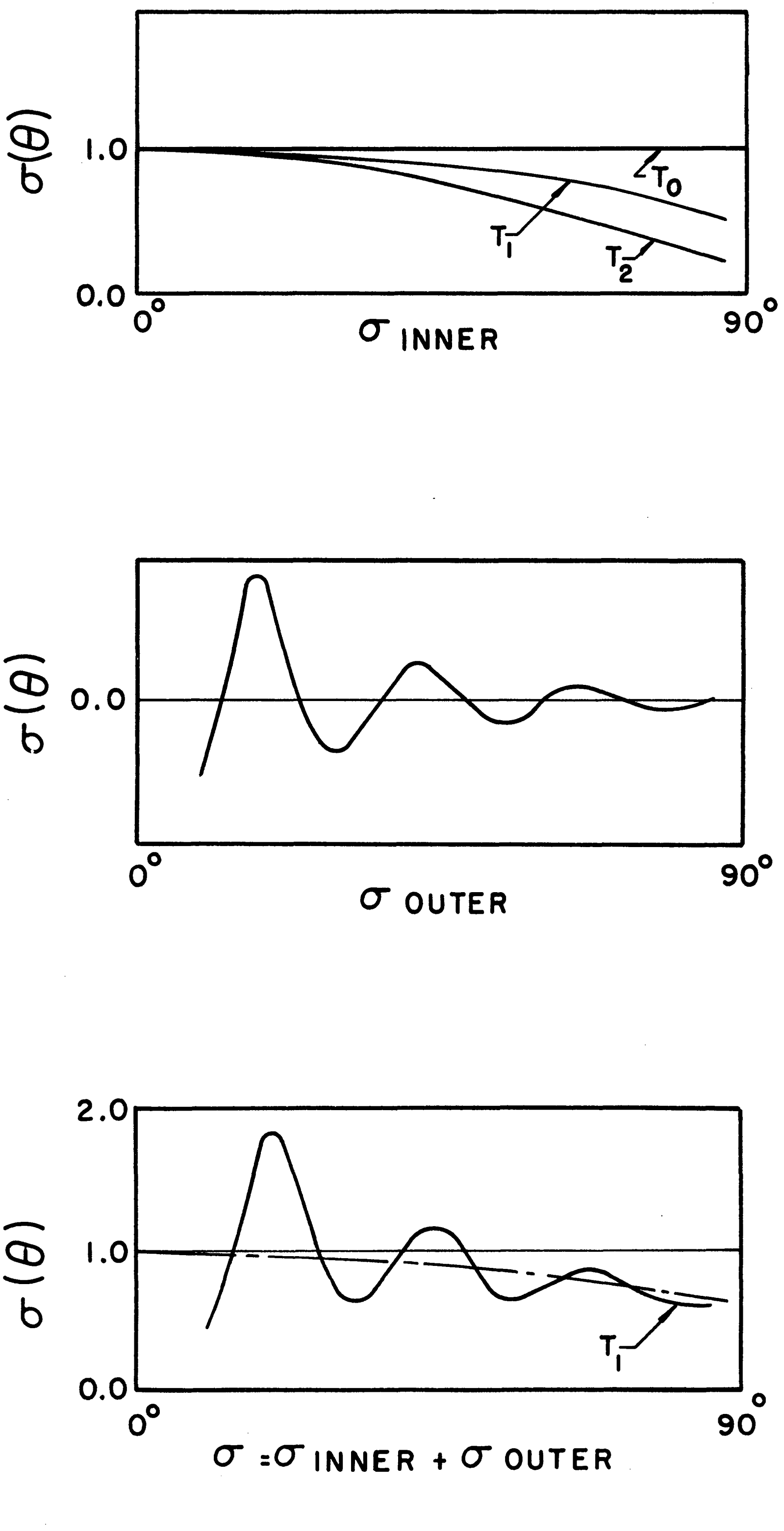

Diagram. Intensity versus Scattering Angle as a Function of Temperature.

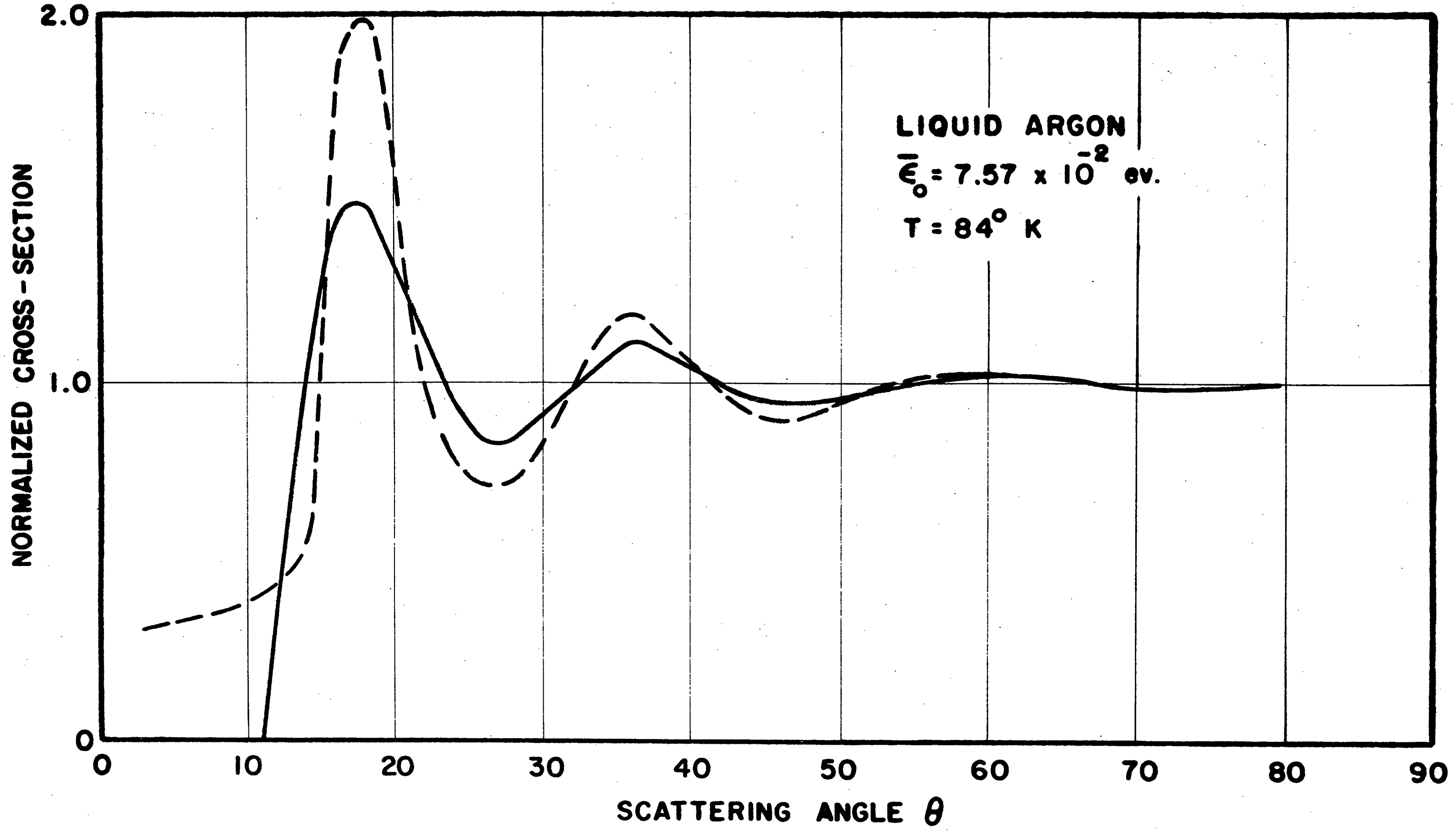

Figure 5. Normalized Cross-Section (4.7) for Liquid Argon at 84°K as a Function of Scattering Angle. Also shown is the experimental cross-section(22) (broken line).

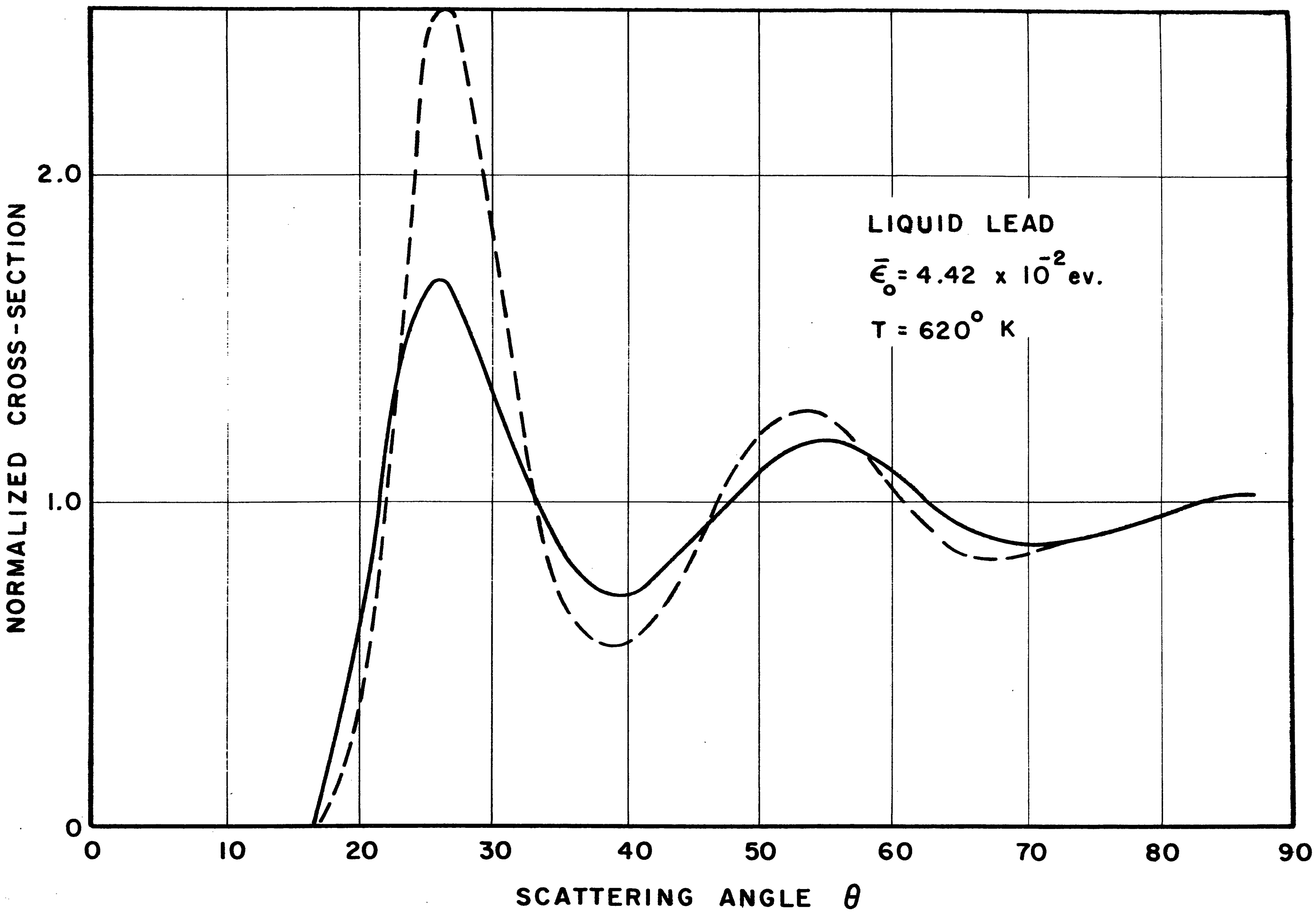

Figure 6. Normalized Cross-Section (4.7) for Liquid Lead at 620°K as a Function of Scattering Angle. Also shown is the experimental cross-section(23) (broken line).

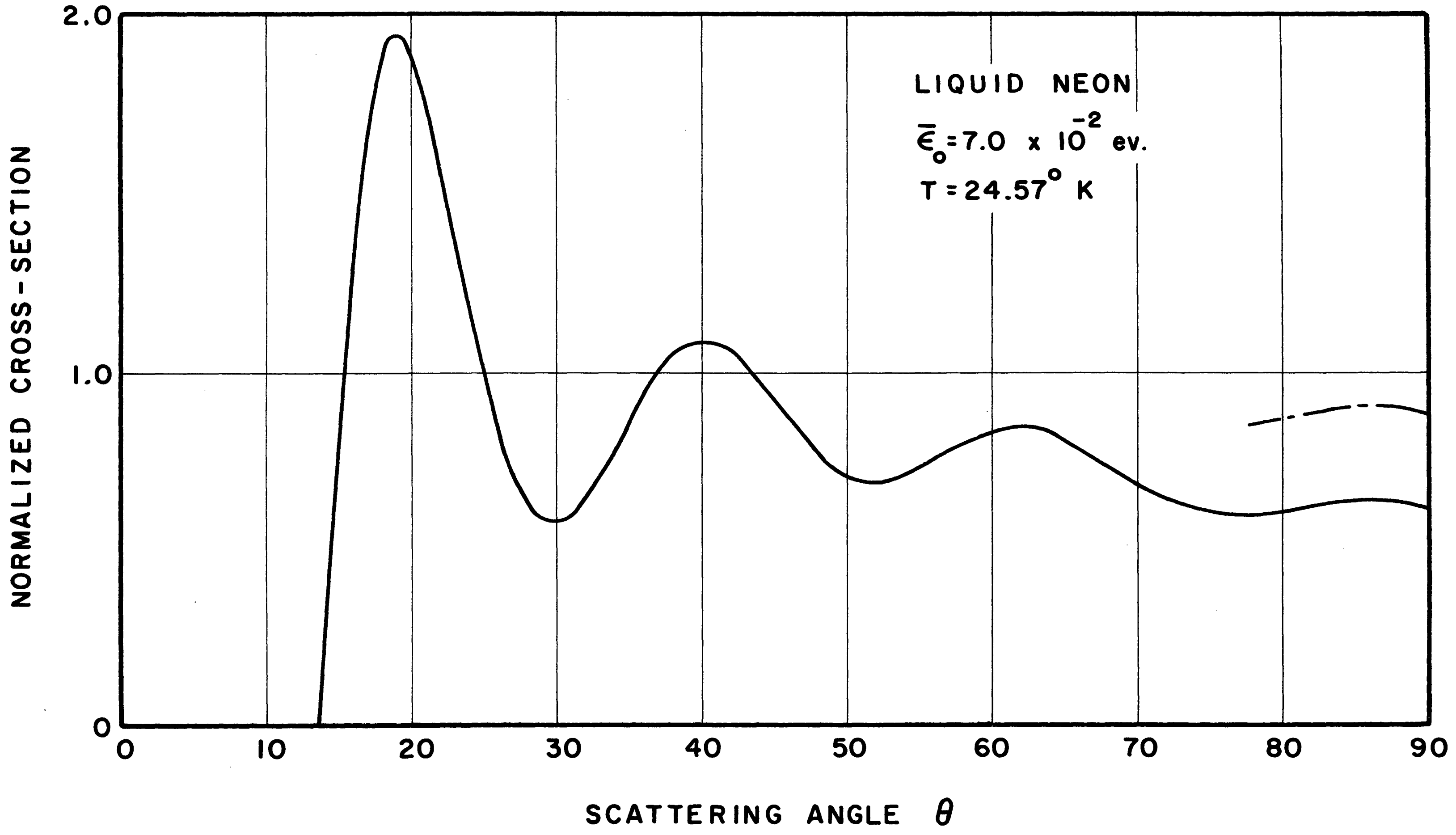

Figure 7. Normalized Cross-Section (4.8) for Liquid Neon at 24.57°K as a Function of Scattering Angle. Also shown are a few integrated points (4.7) (broken line).

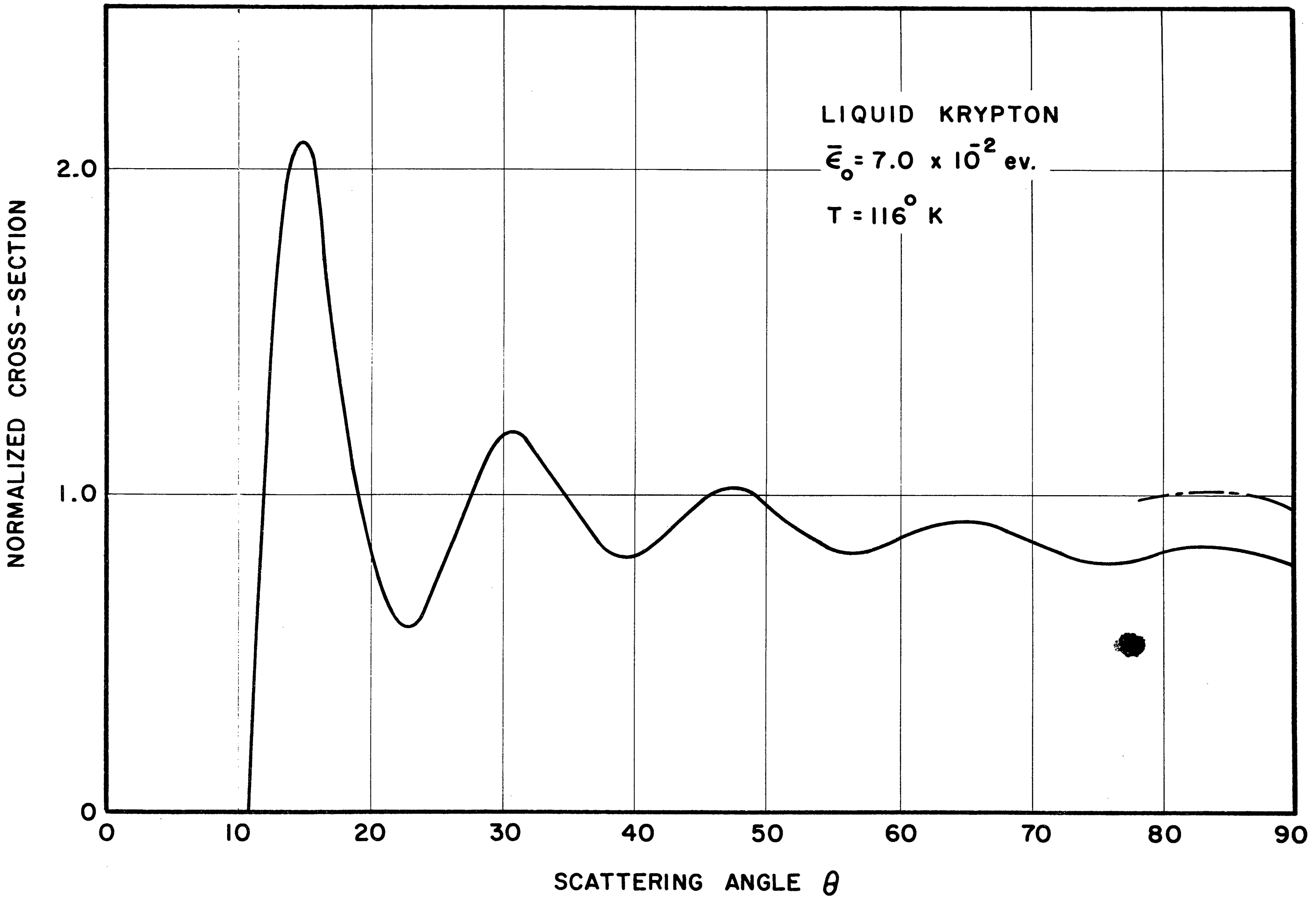

Figure 8. Normalized Cross-Section (4.8) for Liquid Krypton at 116°K as a Function of Scattering Angle. Also shown are a few integrated points (4.7) (broken line).

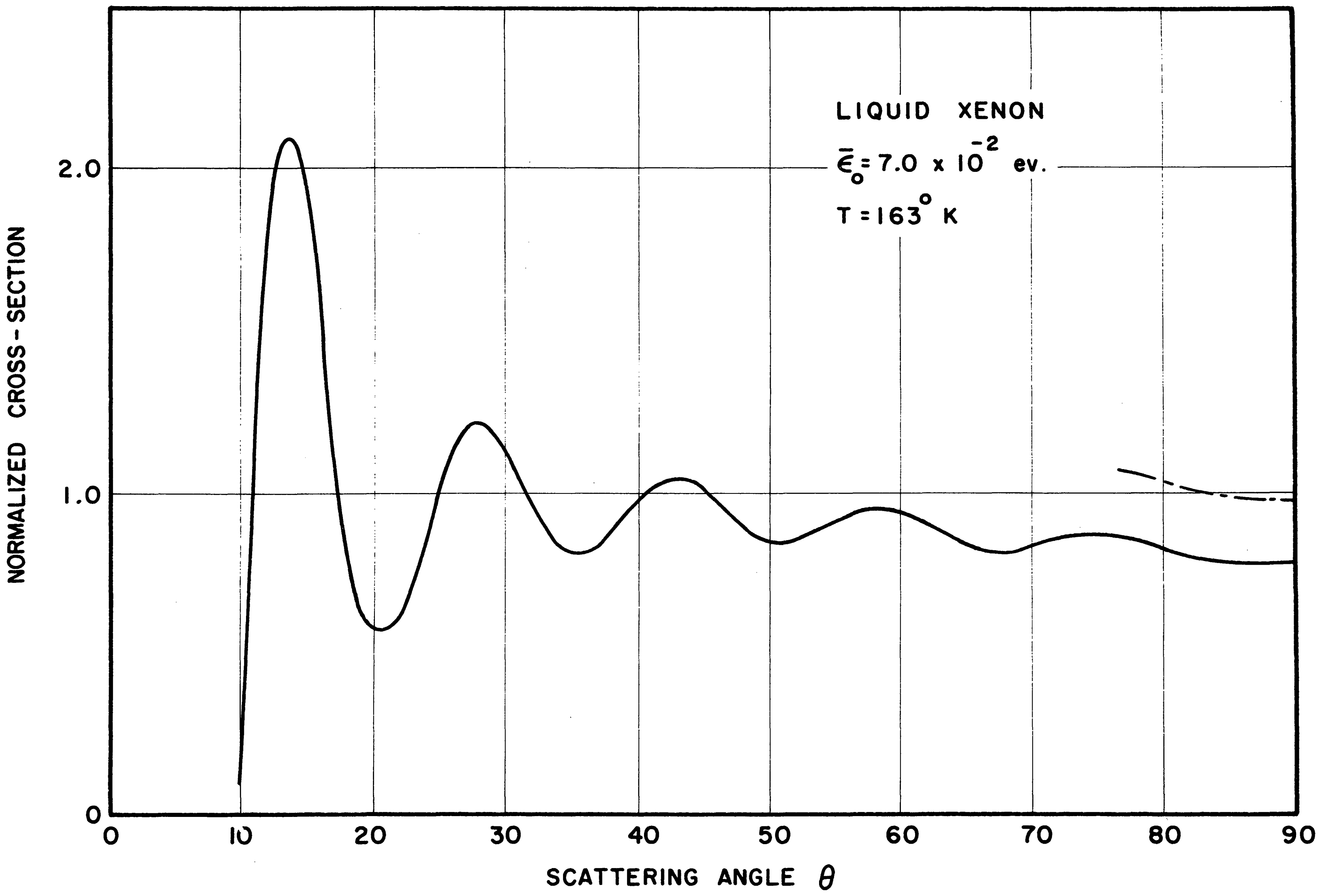

Figure 9. Normalized Cross-Section (4.8) for Liquid Xenon at 163°K as a Function of Scattering Angle. Also shown are a few integrated points (4.7) (broken line).

CHAPTER V

COMPARISON OF AVAILABLE THEORIES WITH "SMEARED" POTENTIAL MODEL

In what follows we will try to outline briefly some of the available theories and to compare the results obtained with these theories to those obtained with the model investigated in this work.

Zernike-Prins Static Approximation(4,25)

Although originally the Zernike-Prins formula (5.3) was not derived in the manner we will describe below, it is equivalent to assuming the time-dependent operator $\underline{\xi}_s(t)$ to be slowly varying in time. Thus, setting t = 0 (static approximation)

$$\Omega_s\,(\underline{\xi},t)\;\Omega_s^{+}\,(\underline{\xi},0) \cong \Omega_s(\underline{\xi},0)\;\Omega_s^{+}\,(\underline{\xi},0) = 1 \tag{5.1}$$

and as before (3.15)

$$<\sum_{\substack{s=1\\ \neq j}}^{N}\;\sum_{j=1}^{N}\;\Omega_s\,(\underline{\xi},t)\;\Omega_j\,(\underline{\xi},0)>_T = N\rho \int d^3r\; g(r)\;\exp\,(i\underline{K}\cdot\underline{r}) \tag{5.2}$$

Therefore

$$\sigma(\epsilon,\theta) = b^2N\delta(\epsilon_o-\epsilon)(k/k_o)(1+\rho \int d^3rg(r)\;\exp(i\underline{K}\cdot\underline{r})) \tag{5.3}$$

which with an incident spectrum of the form (3.18) gives

$$\sigma(\epsilon,\theta;\bar{\epsilon}_o,\beta)/Nb^2L = \exp[-(\epsilon-\bar{\epsilon}_o)^2/\beta^2](1+\rho\int d^3rg(r)\exp(i\underline{K}\cdot\underline{r})) \tag{5.4}$$

Convolution Approximation

This approximation due to George Vineyard(5) is essentially described in the following manner: define $g(r)d^3r$ = the radial distribution function = the probability that, if an atom is at the origin, a distinct atom will be found simultaneously in d^3r about $\underline{r}$, $G(\underline{r},t)d^3r$ the time-displaced pair distribution function, the probability that, if an atom is at the origin at time zero, an atom will be found in d^3r about $\underline{r}$, at time t. Therefore, we can write

$$G(\underline{r},t) = G_s(\underline{r},t) + G_d(\underline{r},t) \tag{5.5}$$

where $G_s(\underline{r},t)$ = the probability of finding at $\underline{r}$ and time t the atom that was at the origin at t = 0, and

$G_d(\underline{r},t)$ = the probability of finding at $\underline{r}$ and t an atom distinct from the one that was at the origin at t = 0.

These two functions are formally defined by

$$G_s(\underline{r},t) = (2\pi)^{-3}N^{-1} \int_{\underline{K}} d^3K e^{-i\underline{K}\cdot\underline{r}} < \sum_{\ell=1}^{N} \Omega_\ell(\underline{\xi},t)\Omega_\ell^*(\underline{\xi},0)>_T \tag{5.6}$$

and

$$G_d(\underline{r},t) = (2\pi)^{-3}N^{-1} \int_{\underline{K}} d^3K e^{-i\underline{K}\cdot\underline{r}} < \sum_{\substack{\ell=1\\ \neq j}} \sum_{j=1} \Omega_\ell(\underline{\xi},t)\Omega_j^*(\underline{\xi},0)>_T \tag{5.7}$$

If now in (5.7) we let (convolution approximation)

$$\begin{aligned} < \sum_{\substack{\ell=1\\ \neq j}}^{N} \sum_{j=1}^{N} \Omega_\ell(\underline{\xi},t)\Omega_j^+(\underline{\xi},0)>_T &= < \sum_{\substack{\ell=1\\ \neq j}}^{N} \sum_{j=1}^{N} \Omega_\ell(\underline{\xi},t)\Omega_\ell^+(\underline{\xi},0)\Omega_\ell(\underline{\xi},0)\Omega_j^+(\underline{\xi},0)>_T \\ &\cong \frac{1}{N} < \sum_{\ell=1} \Omega_\ell(\underline{\xi},t)\Omega_\ell^+(\underline{\xi},0)>_T < \sum_{\substack{\ell=1\\ \neq j}}^{N} \sum_{j=1} \Omega_\ell(\underline{\xi},0)\Omega_j^+(\underline{\xi},0)>_T \end{aligned} \tag{5.8}$$

(5.7) becomes

$$G_d(\underline{r},t) = (2\pi)^{-3}N^{-1}\int d^3Ke^{-i\underline{K}\cdot\underline{r}}\cdot[N^{-1}<\sum_{\ell=1}\Omega_\ell(\underline{\xi},t)\Omega_\ell^{+}(\underline{\xi},0)>_T$$

$$\cdot<\sum_{\substack{\ell=1\\ \neq j}}^{N}\sum_{j=1}^{N}\Omega_\ell(\underline{\xi},0)\Omega_j^{+}(\underline{\xi},0)>_T = \int d^3r'[\int d^3Ke^{-i\underline{K}\cdot\underline{r}'}<\sum_{\substack{\ell=1\\ \neq j}}^{N}\sum_{j=1}^{N}\Omega_\ell(\underline{\xi},0)\Omega_j(\underline{\xi},0)>_T] \tag{5.9}$$

$$\cdot[\int_{\underline{K}'}d^3K'e^{-i\underline{K}'\cdot(\underline{r}-\underline{r}')}<\sum_{\ell=1}^{N}\Omega_\ell'(\underline{\xi},t)\Omega_\ell'^{+}(\underline{\xi},0)>_T$$

$$G_d(\underline{r},t) = \int_{\underline{r}'}d^3r'\ g(\underline{r}')\ G_s\ (\underline{r}-\underline{r}';\ t)$$

where $g(\underline{r})$ is formally defined by

$$g(\underline{r}) = (2\pi)^{-3}N^{-1}\int_{\underline{K}}d^3Ke^{i\underline{K}\cdot\underline{r}}<\sum_{\substack{\ell=1\\ \neq 1}}^{N}\sum_{j=1}^{N}\Omega_\ell(\underline{\xi},0)\Omega_j^{+}(\underline{\xi},0)>_T \tag{5.10}$$

Finally, by applying the convolution theorem, Vineyard showed that

$$\sigma(\epsilon,\theta) = \frac{k}{k_o}\frac{b^2}{2\pi\hbar}\int_{\infty}^{\infty}dte^{itq}<\sum_{\ell=1}^{N}\sum_{j=1}^{N}\Omega_\ell(\underline{\xi},t)\Omega_j^{+}(\underline{\xi},0)>_T \cong Nb^2\frac{k}{k_o}\Gamma_s(\underline{K},q)[1+\gamma(\underline{K})] \tag{5.11}$$

where

$$\Gamma_s(\underline{K},q) = \int_{-\infty}^{\infty}dt\ \int_{\underline{r}'}d^3r\ G_s(\underline{r},t)e^{i(\underline{K}\cdot\underline{r}-qt)} \tag{5.12}$$

and

$$\gamma(\underline{K}) = \int_{\underline{r}} g(\underline{r})\ e^{i\underline{K}\cdot\underline{r}}d^3r \tag{5.13}$$

By definition the $G_s(\underline{r},t)$ function is interpreted to give the wandering away of an atom from the origin. In one of the models Vineyard used, he assumed that this distribution was governed by the diffusion equation

$$(D\nabla^2 + \frac{\partial}{\partial t})\ G_s(\underline{r},t) = 0 \tag{5.14}$$

which when solved for a point source at the origin gives

$$G_s(\underline{r},t) = (4\pi Dt)^{-3/2}\exp(-r^2/4Dt) \tag{5.15}$$

This result leads to

$$\Gamma_s(\underline{K},q) = 2DK^2[(DK^2)^2 + q^2]^{-1} \tag{5.16}$$

and thus to

$$\sigma(\epsilon,\theta) = (Nb^2k/k_o)2DK^2[(DK^2)^2 + q^2]^{-1}(1 + \rho\int e^{i\underline{K}\cdot\underline{r}}g(r)d^3r) \tag{5.17}$$

Summary

Let $\sigma_1(\epsilon,\theta)$, $\sigma_2(\epsilon,\theta)$, and $\sigma_3(\epsilon,\theta)$, represent the Zernike-prins formula, the Vineyard diffusion model, and the "smeared" potential liquid model cross-sections, respectively as given below

$$\sigma_1(\epsilon,\theta)/b^2N = \frac{k}{k_o}\,\delta(\epsilon-\epsilon_o)(1 + \rho\int e^{i\underline{K}\cdot\underline{r}}\,g(r)d^3r) \tag{5.18}$$

$$\sigma_2(\epsilon,\theta)/b^2N = \frac{k}{k_o}\,\frac{2DK^2}{(DK^2)^2 + q^2}\,(1 + \rho\int e^{i\underline{K}\cdot\underline{r}}\,g(r)d^3r) \tag{5.19}$$

$$\begin{aligned}\sigma_3(\epsilon,\theta)/b^2N = \frac{k}{k_o}\sum_{n=-\infty}^{\infty}\delta(\epsilon_o-\epsilon-n\hbar\omega)[e^{-A_3Q_n^2+nA_1}\cdot I_n(A_2Q_n^2)\\ + \rho\delta_{no}\int e^{i\underline{K}\cdot\underline{r}}\,g(r)d^3r].\end{aligned} \tag{5.20}$$

We, therefore, have that

(a) the static approximation, $\sigma_1(\epsilon,\theta)$, gives no final energy spectrum broadening,

(b) the diffusion model, $\sigma_2(\epsilon,\theta)$, gives an energy broadening given by the half-height width equal to $\Delta\epsilon_3 \cong 2\hbar DK^2$, and

(c) the "smeared" potential, $\sigma_3(\epsilon,\theta)$, although difficult to write in closed form, gives an energy broadening, calculated by a 704 IBM machine, usually smaller than that predicted by (b).

The half-height widths for liquid Lead, at two different temperatures, have been measured and reported in the literature(26) in an attempt to check the diffusion model.

We have calculated these widths using the "smeared" potential model. The results of the experiment, the diffusion model and the "smeared" potential model are shown in Table II. The incident half-height width is given by $\Delta\epsilon_0$, the "smeared" potential half-height width by $\Delta\epsilon_1$, the experimental half-height widths by $\Delta\epsilon_2$, and the diffusion model by $\Delta\epsilon_3$.

It is observed that the width at half-maximum increases with temperature. This effect is also observed in the other elements studied. It is also observed that the energy spectra are more sensitive to these changes in temperature than the angular distributions (See end of Chap. IV).

TABLE II

LIQUID LEAD FINAL ENERGY SPECTRUM WIDTHS

	T	$\Delta\epsilon_0$	$\Delta\epsilon_1$	$\Delta\epsilon_2$	$\Delta\epsilon_3$
Element	°K	$(\times 10^{-2})$ ev	$(\times 10^{-2})$ ev	$(\times 10^{-2})$ ev	$(\times 10^{-2})$ ev
Lead	609	1.06	1.78	1.86 ± .11	2.30
Lead	823	1.06	2.07	1.98 ± .11	4.60

NOTE: Comparison for Liquid Lead of Experimental Widths at Half-Maximum, $\Delta\epsilon_2$(26), with the Widths at Half Maximum for the "Smeared" Potential, $\Delta\epsilon_1$, Calculated for an Oscillator Frequency, $\omega = 12.6 \times 10^{12}\ \mathrm{sec}^{-1}$ (See Chapter II, p. 15) and the Diffusion Model $\Delta\epsilon_3$(5,26).

CHAPTER VI

NORMAL DIATOMIC LIQUIDS

Diatomic Molecule

The time independent Schrödinger equation for a molecule may be written as

$$\left(- \frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \nabla_i^2 - \sum_{j=1}^{N} \frac{\hbar^2}{2M_j} \nabla_j^2 + V\right)\Psi = E\Psi \tag{6.1}$$

There are n electrons and N nuclei and V is the sum of electrostatic interactions between all pairs of them.

It can be shown(27) that the above equation may be separated into two equations. One of them describing the electrons motion and the other an approximate equation for the nuclear motion. Born and Oppenheimer(28) have shown formally that this approximation is justified so long as not too high vibrational and rotational modes are excited.

In Figure 10 we show a diatomic molecule, the center of mass position vector $\underline{R}$, and the relative position vector $\underline{r}$. We will use the following notation. The actual position vector of the νth atom in the s-th molecule will be denoted by $\underline{\xi}_s^{\nu}$. In terms of the center of mass position vector and the relative vector it is given by

$$\underline{\xi}_s^{\nu} = \underline{R}_s + f^{\nu}\, \underline{r}_s \tag{6.2}$$

where

$$\begin{aligned} f^{\nu} &= - \frac{M_2}{M} \ ; \ \nu = 1 \\ &= \frac{M_1}{M} \ ; \ \nu = 2 \end{aligned} \tag{6.3}$$

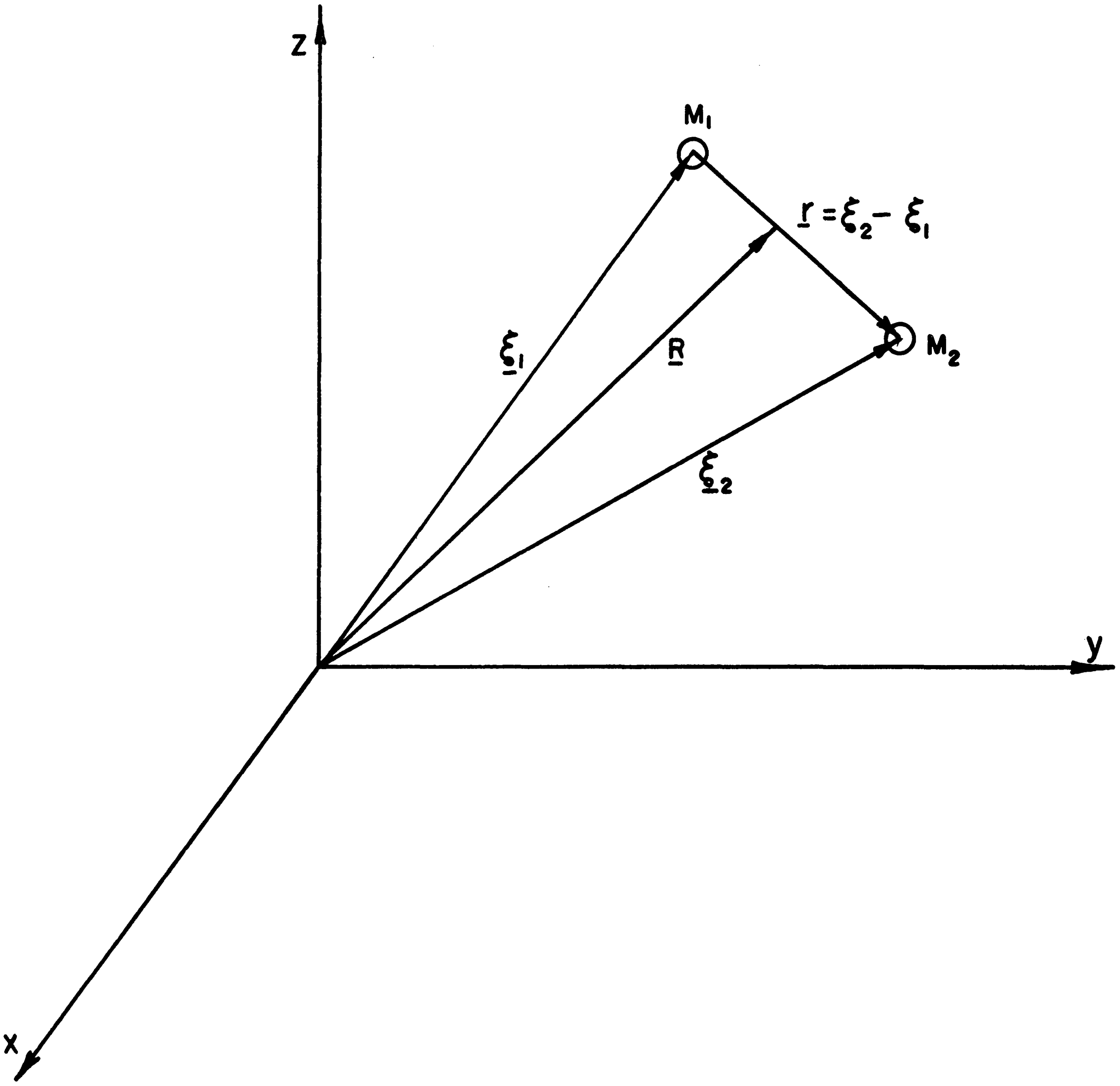

Figure 10. Diatomic Molecule Coordinates.

Turning our attention to the diatomic molecule Hamiltonian, we can show that the approximate nuclear motion Hamiltonian, H_{DM}, may be written as the sum of the relative, H_r, and the center of mass Hamiltonian, H_{CM}, as follows

$$H_{DM} = H_{CM} + H_r \tag{6.4}$$

where

$$H_{CM} = -\frac{\hbar^2}{2M} \nabla^2(\underline{R}) \; ; \quad M = M_1 + M_2 \tag{6.5}$$

and

$$H_r = -\frac{\hbar^2}{2\mu} \cdot \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{\hbar^2 \underline{L}^2}{2\mu r^2} + U(r) \quad , \tag{6.6}$$

where μ is the reduced mass ($= M_1 M_2/M$), $\underline{L}^2$ the angular momentum operator and $U(r)$ the potential energy.

In order to describe the motion of the diatomic molecule in the liquid phase, we introduce our approximation to the LJD liquid model potential as an additional potential to which the center of mass is subjected. For normal liquids this is believed to be a good assumption (see discussion in Chapter II). We may thus write as an approximation for the diatomic liquid Hamiltonian,

$$H_{DL} = H_{CM} + \bar{V}(0) + \frac{M\bar{\omega}^2}{2} R^2 + H_r \tag{6.7}$$

Spin Dependence

Spin dependence may be introduced through the neutron-system interaction potential (1.12) if one writes for the scattering length

$$b_\ell^\nu = \alpha_\ell^\nu + \beta_\ell^\nu \underline{\sigma} \cdot \underline{S}_\ell^\nu \tag{6.8}$$

where b_ℓ^ν is the scattering length associated with the νth atom in the ℓ-th molecule, $\underline{\sigma}$ is the neutron spin operator (Pauli spin matrices), $\underline{S}_\ell^\nu$ and S_ℓ^ν are the nuclear spin operator and the nuclear spin of the νth atom in the ℓth molecule, respectively; α_ℓ^ν and β_ℓ^ν are given by

$$\alpha_\ell^\nu = [(S_\ell^\nu + 1)A_\ell^{\nu+} + S_\ell^\nu\, A^{\nu-}](2S_\ell^\nu + 1)^{-1} \tag{6.9}$$

$$\beta_\ell^\nu = 2(A_\ell^{\nu+} - A_\ell^{\nu-})(2S_\ell^\nu + 1)^{-1}$$

These are the customary definitions of coherent and incoherent scattering amplitudes, respectively. The scattering amplitudes for the two values of the total angular momentum $S_\ell^\nu \pm 1/2$ are given by $A_\ell^{\nu\pm}$.

For unpolarized neutron beams and nuclear spins we want to calculate the average over neutron and nuclear spin direction of the thermal average. We will indicate these averages by $\{\ \}_\sigma^S$. Therefore, we want

$$\{ < \sum_{\ell=1}^{N} \sum_{j=1}^{N} \sum_{\nu=1}^{2} \sum_{\mu=1}^{2} b_\ell^\nu\, b_j\, \Omega_\ell^\nu\, (\underline{\xi},t)\, \Omega_j^{\mu+}(\underline{\xi},0) >_T\}_\sigma^S \tag{6.10}$$

where

$$\Omega_\ell^\nu\, (\underline{\xi},t) = \exp\,[-i\underline{k} \cdot \underline{\xi}_\ell^\nu(t)]$$

which in Appendix A.15 is shown to be equal to

$$\{ < \sum_{\ell j \nu\mu} b_\ell^\nu b_j^\mu\, \Omega_\ell^\nu\, (\underline{\xi},t)\, \Omega_j^{\mu+}\, (\xi,0) >_T\}_\sigma^S \tag{6.11}$$

$$= \sum_{\ell j \nu\mu} [\alpha_\ell^\nu \alpha_j^\mu + \frac{1}{4}\, \beta_\ell^\nu \beta_j^\mu\, S_\ell^\nu (S_\ell^\nu + 1)\, \delta_{\ell j} \delta_{\nu\mu}]$$

$$\cdot < \Omega^\nu\, (\xi,t)\, \Omega^{\mu+}(\xi,0) >_T + \frac{1}{4} \sum_{\ell j \nu\mu} \beta_\ell^\nu \beta_j^\mu\, \delta_{\ell j} \delta_{L_\mu L_\nu}$$

$$\{ < \underline{s}_\ell^\nu \cdot \underline{s}_j^\mu\, \Omega_\ell^\nu(\xi,t)\, \Omega_j^{\mu+}\, (\xi,0) >_T\}^S$$

where $\delta_{L_\mu L_\nu}$ = 1, if atoms ν and μ in molecule ℓ are alike,

= 0, otherwise.

For spinless systems this reduces to

$$\left\{ < \sum_{\ell j \nu \mu} b_\ell^\nu b_j^\mu \Omega_\ell^\nu(\underline{\xi},t)\Omega_j^{\mu+}(\underline{\xi},0)>_T \right\}_\sigma^S = \sum_{\ell j \nu \mu} \alpha_\ell^\nu \alpha_j^\mu < \Omega_\ell^\nu(\underline{\xi},t)\Omega_j^{\mu+}(\underline{\xi},0)>_T \tag{6.12}$$

For monatomic systems we have

$$\begin{aligned} \left\{ < \sum_{\ell j \mu \nu} b_\ell b_j \Omega_\ell(\underline{\xi},t)\Omega_j^+(\underline{\xi},0)>_T \right\}_\sigma^S &= \sum_{\ell=1}^{N} [\alpha_\ell^2 + \tfrac{1}{4}\beta_\ell^2 S_\ell(S_\ell+1)] < \Omega_\ell(\underline{\xi},t)\Omega_\ell^+(\underline{\xi},0)>_T \\ &+ \sum_{\substack{\ell=1 \\ \neq j}}^{N} \sum_{j=1}^{N} \alpha_j \alpha_\ell < \Omega_\ell(\underline{\xi},t)\Omega_j^+(\underline{\xi},0)>_T . \end{aligned} \tag{6.13}$$

<u>Thermal</u> <u>Average</u>

We can write for the Thermal average with the help of (6.2),

$$\begin{aligned} < \Omega_\ell^\nu(\underline{\xi},t)\Omega_j^{\mu+}(\underline{\xi},0)>_T &= < e^{-i\underline{K}\cdot[\underline{R}_\ell(t)+f^\nu \underline{r}_\ell(t)]} e^{i\underline{K}\cdot(\underline{R}_j+f^\mu \underline{r}_j)}>_T \\ &= < \psi_c | e^{-i\underline{K}\cdot\underline{R}_\ell(t)} e^{i\underline{K}\cdot\underline{R}_j} | \psi_c>_T < \psi_r | e^{-if^\nu \underline{K}\cdot\underline{r}_\ell(t)} e^{if^\mu \underline{K}\cdot\underline{r}_j} | \psi_r>_T \end{aligned} \tag{6.14}$$

The last step is easy to obtain once one notices that the diatomic liquid Hamiltonian is separated in two, the center of mass hamiltonian, $H_c = H_{cM} + \overline{V}(o) + M\omega^2 R^2/2$, and the relative motion hamiltonian, H_r, and that they commute. Also because of this fact, the total wave function may be written as a product

$$\psi(\underline{\xi}_1,\underline{\xi}_2) = \psi_c(\underline{R})\psi_r(\underline{r}). \tag{6.15}$$

In (6.14) we recognize the thermal average of the center of mass motion as the one we encountered in the monatomic liquid treatment, and, of course, the same remarks apply. That is, when $\ell = j$ we use (6.19) for the Hamiltonian, and for $\ell \neq j$ we use the Heisenberg's operator time expansion method, which we have seen lead to the radial distribution function.

Static Approximation

The relative motion thermal average will be treated in this section in the static approximation (See Appendix A.16 for discussion of further correction terms). Therefore, setting $t = 0$ we have

$$< \psi_r | e^{-if^\nu \underline{K}\cdot\underline{r}_\ell(t)} e^{if^\mu \underline{K}\cdot\underline{r}_j} | \psi_r >_T \cong < \psi_r | \exp[i\underline{K}\cdot(f^\mu \underline{r}_j - f^\nu \underline{r}_\ell)] | \psi_r >_T \tag{6.16}$$

At this point it is necessary to make an approximation in the relative motion Hamiltonian. As it is standard practice in treating diatomic molecules, we will expand the potential $U(r)$ about its minimum r_M. Thus

$$H_r \cong H_{rot} + H_{vib} \tag{6.17}$$

where

$$H_{rot} = \hbar^2 \underline{L}^2 / 2\mu r_M^2 \tag{6.18}$$

and

$$H_{vib} = -\frac{\hbar^2}{2\mu}\frac{1}{r^2}\frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + U(r_M) + \frac{\mu\omega_M^2}{2}(r-r_M)^2 \tag{6.19}$$

The relative motion wave function ψ_r separates into a product of the rigid rotator wave function, ψ_{rot}, and the vibrational wave function ψ_{vib}. Averaging over directions of the molecule axis, we obtain

$$\begin{aligned} &< \psi_r \,|\exp[i\underline{K}\cdot(f^{\mu}\underline{r}_j - f^{\nu}\underline{r}_{\ell})]\,|\psi_r> \cong < \psi_{vib}\,|j_o[Kr_j(f^{\mu}-f^{\nu})]|\,\psi_{vib}> \quad ; \ \ell = j \\ &= \langle \psi_{vib}\,|j_o(Kr_j f^{\mu})\,j_o(Kr_{\ell} f^{\nu})\,|\psi_{vib}>_T \quad ; \ \ell \neq j. \end{aligned} \tag{6.20}$$

Expanding r_j about the minimum r_M of the potential U(r) we finally obtain

$$\begin{aligned} &< \psi_r \,|\exp[i\underline{K}\cdot(f^{\mu}r_j - f^{\nu}r_{\ell})]\,|\psi_r > \cong j_o[Kr_{Mj}(f^{\mu}-f^{\nu})] \quad ; \ \ell = j \\ &= j_o(Kr_{Mj}f^{\mu})\,j_o(Kr_{M\ell}f^{\nu}) \quad ; \ell \neq j. \end{aligned} \tag{6.21}$$

The cross-section may then be written, after integrating over incident energy spectrum

$$\begin{aligned} \sigma(\epsilon,\theta;\bar{\epsilon},\beta)\Big/2A_o^2NL &= \sum_{-\infty}^{\infty} \sqrt{\frac{\epsilon}{\epsilon+nh\omega}}\, e^{-A_3Q_n^2+nA_1-(\epsilon-\bar{\epsilon}_o+nh\omega)^2/\beta^2} \\ &\cdot I_n(A_2Q_n^2)\,[j_o(a_1r_MQ_n)+B_o^2/A_o^2]+2j_o^2(a_1r_MQ_o/2)\rho\int_r drg(r)4\pi r^2[\sin(a_1Q_or)/a_1Q_or] \end{aligned} \tag{6.22}$$

where $a_1 = \sqrt{8m_n/\hbar^2}$

A_o = coherent scattering amplitude,

$4\ B_o^2$ = the bound-scattering cross-section $= \alpha^2 + \frac{1}{4}\beta^2 S(S+1)$

and Q_n is given by (3.21).

In the aforementioned we have assumed equal mass atoms in the molecule and neglected the spin correlation term that appears when the atoms are alike (last term (6.11)). In Reference 2 the spin correlation term is discussed, and it was found to be negligible except for very low mass number atoms.

Equation (6.22) has been computed in a 704 IBM machine for the Nitrogen molecule. The results are shown in Figure 11 together with the experimental data$^{(22)}$. In Table 3 we have given the numerical constants that entered in this calculation.

Results

In Figures 5 through 9 we have shown the calculated and the experimental angular cross-sections (when available) for the monatomic elements studied. In Figure 11 we have shown the nitrogen diatomic molecule angular cross-section. The agreement observed is believed to be satisfactory. However, a radial distribution function more accurate than the one employed in this paper for the outer effect would probably improve the agreement.

In Table II we have shown the broadening of the neutron final energy spectrum as calculated with the "smeared potential" liquid model and compared it with the experimental data as well as with the diffusion model. It is seen that the "smeared potential" model is in better agreement with experiment than the diffusion model. It is felt, however, that more experiments on the broadening of the energy spectrum should be performed, using monatomic elements as well as polyatomic elements, in order to further test the accuracy of the model introduced in this dissertation. No experiments on the energy distribution of normal polyatomic liquids have been reported in the literature.

TABLE III

NITROGEN MOLECULE CALCULATIONAL PARAMETERS

	$-\epsilon^*$	r^*	Λ^*	V^*	T	Λ^*/kT	V^*/V
Element	(ergs/molec.) (x 10^{-16})	(Å)	(ev/molec.)	(Å^3)	(°K)		
Nitrogen	132.40	4.15	.0994	51.3	77.40	14.9	.99

	M	ρ	$\bar{\epsilon}_o$	ω	Bound	Coh.	r_M
Element	(grams) (x 10^{-24})	(atoms/cm^3) (x 10^{22})	(ev) (x 10^{-2})	(sec^{-1}) (x 10^{12})	barns	barns	(Å)
Nitrogen	46.48	3.480	7.0	7.857	11.4	11.0	1.094

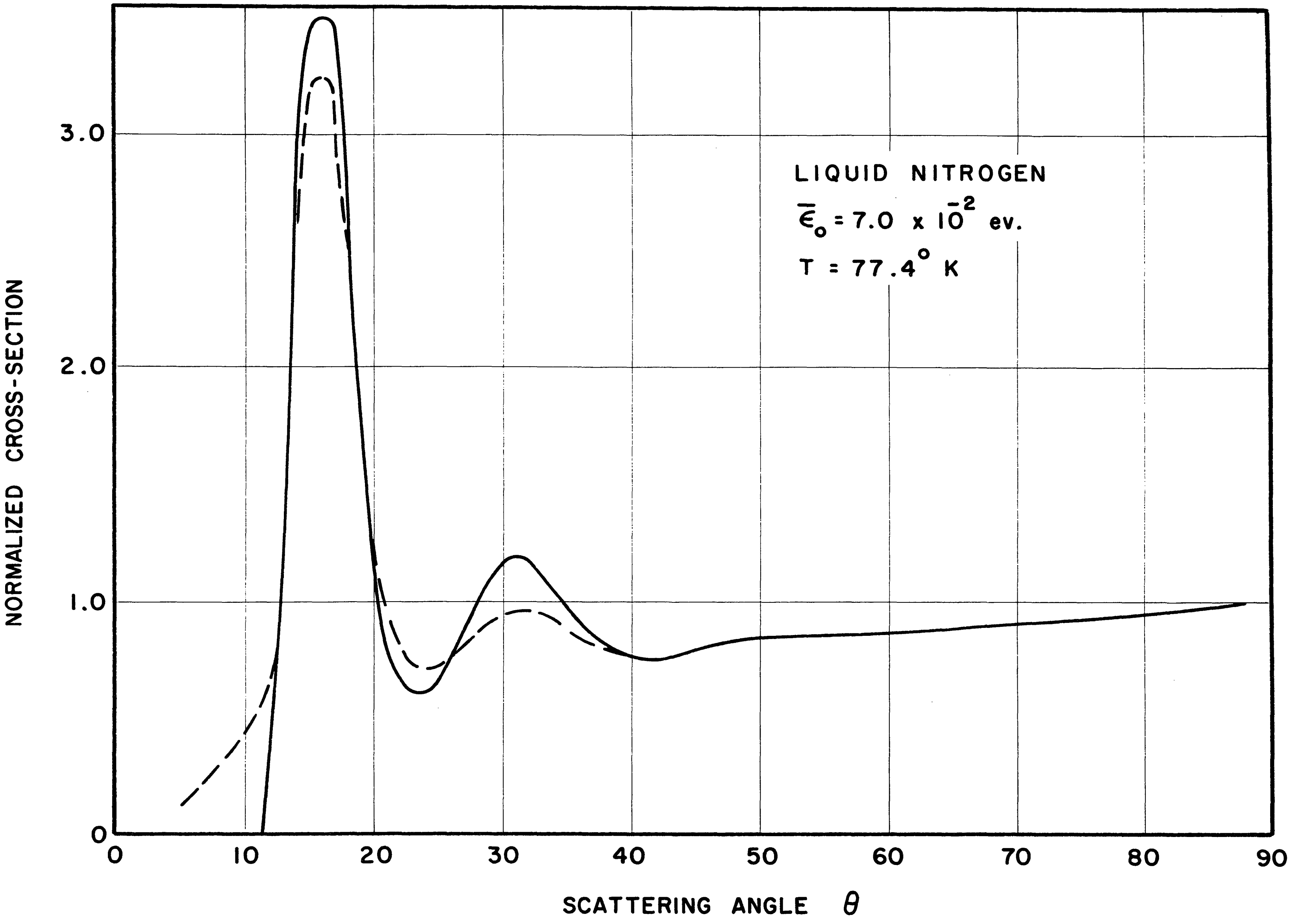

Figure 11. Normalized Cross-Section for Liquid Nitrogen at 77.4°K as a Function of Scattering Angle. Also shown is the experimental cross-section(22) (broken line).

APPENDICES

APPENDIX A.1

TRANSITION CROSS-SECTION(31,32)

Let $\psi_{\eta s}^{\alpha}(\underline{r})$ represent the scattered wave function from initial state α to final state η. We determine the number $P_{\eta s}^{\alpha}(\theta)d\Omega$ of particles scattered per second into $d\Omega$ by equating it to the flux through a surface element of the sphere of radius R,

$$P_{\eta s}^{\alpha}(\theta)\,d\Omega = \frac{\hbar}{2mi}\left(\psi_{\eta s}^{\alpha^*}\frac{\partial\psi_{\eta s}^{\alpha}}{\partial r} - \frac{\partial\psi_{\eta s}^{\alpha^*}}{\partial r}\psi_{\eta s}^{\alpha}\right)R^2\,d\Omega \tag{A.1.1}$$

and since $\psi_{\eta s}^{\alpha}(\underline{r})$ has the form

$$\psi_{\eta s}^{\alpha}(\underline{r}) = f_{\eta}^{\alpha}(\theta)\ \exp(ik_{\eta}r)\ /\ r \tag{A.1.2}$$

we obtain for the transition cross-section per unit incident flux in the z direction, j_{0z},

$$\sigma_{\eta}^{\alpha}(\theta) = P_{\eta s}^{\alpha}(\theta)d\Omega\ /\ j_{oz} \tag{A.1.3}$$

$$= \left[\hbar k_{\eta}\left|f_{\eta}^{\alpha}(\theta)\right|^2 R^2/mR^2\right](\hbar k_o/m)^{-1}$$

$$= (k_{\eta}/k_o)\left|f_{\eta}^{\alpha}(\theta)\right|^2 \tag{A.1.4}$$

APPENDIX A.2

INTEGRAL EQUATION

The time independent Schrodinger equation is given by

$$\left[H(\underline{r}) + H(\underline{\xi}) + \Gamma(\underline{r},\underline{\xi}) - \epsilon_t \right] \Psi(\underline{r},\underline{\xi}) = 0 \tag{A.2.1}$$

Expand $\Psi(\underline{r},\underline{\xi})$ in terms of the complete set of stationary state wave function of the system

$$\Psi(\underline{r},\underline{\xi}) = \sum_\beta \psi_\beta(\underline{r}) \Lambda_\beta(\underline{\xi}) \tag{A.2.2}$$

where

$$H(\underline{\xi}) \Lambda_\beta(\underline{\xi}) = E_\beta \Lambda_\beta(\underline{\xi}) \tag{A.2.3}$$

Then (A.2.1) becomes after substitution of (A.2.2) and (A.2.3)

$$\sum_\beta \left[E_\beta - \epsilon_t + H(\underline{r}) + \Gamma(\underline{r},\underline{\xi}) \right] \psi_\beta(\underline{r}) \Lambda_\beta(\underline{\xi}) = 0 \tag{A.2.4}$$

Define

$$\epsilon_\beta = \epsilon_t - E_\beta \tag{A.2.5}$$

and multiply Equation (A.2.4) on the left by $\Lambda^*_\gamma(\underline{\xi})$ and integrate over $\underline{\xi}$ space, then we obtain

$$[H(\underline{r}) - \epsilon_\gamma]\,\psi_\gamma(\underline{r}) = -\sum_\beta \psi_\beta \Gamma_{\gamma\beta}(\underline{r}) \tag{A.2.6}$$

where

$$\begin{aligned} \Gamma_{\gamma\beta}(\underline{r}) &= (\gamma|\,\Gamma(\underline{r},\underline{\xi})\,|\beta) \\ &= \int_{\underline{\xi}} d^3\xi\, \Lambda^*_\gamma(\underline{\xi})\, \Gamma(\underline{r},\underline{\xi})\, \Lambda_\beta(\underline{\xi}) \end{aligned} \tag{A.2.7}$$

Introducing the Green's Function, $G_{\epsilon_\gamma}(\underline{r},\underline{r}')$ defined in Appendix A.3 we can write Equation (A.2.6) in the form

$$\psi_\gamma(\underline{r}) = \Phi(\underline{r}) + \sum_\beta \int_{\underline{r}'} d^3r'\, G_{\epsilon_\gamma}(\underline{r},\underline{r}')\, \Gamma_{\gamma\beta}(\underline{r}')\, \psi_\beta(\underline{r}') \tag{A.2.8}$$

where $\Phi(\underline{r})$ is an incident plane wave.

APPENDIX A.3

GREEN'S FUNCTION

Define $G_k(\underline{r},\underline{r}')$ by the following equation

$$(\nabla^2 + k^2)\, G_k(\underline{r},\underline{r}') = -\delta(\underline{r}-\underline{r}') \qquad (A.3.1)$$

and take the Fourier transform of both sides of this equation

$$(2\pi)^{-\frac{3}{2}} \Big\{ \int_{\underline{r}} d^3r\, e^{-i\underline{k}'\cdot\underline{r}}\, \nabla^2 G_k(\underline{r},\underline{r}') \; + $$

$$+ \, k^2 \int_{\underline{r}} d^3r\, e^{-i\underline{k}'\cdot\underline{r}}\, G_k(\underline{r},\underline{r}') + e^{-i\underline{k}'\cdot\underline{r}'} \Big\} = 0 \qquad (A.3.2)$$

and since

$$\int_{\underline{r}} d^3r\, e^{-i\underline{k}'\cdot\underline{r}}\, \nabla^2 G_k(\underline{r},\underline{r}') =$$

$$= -k'^2 \int_{\underline{r}} d^3r\, e^{-i\underline{k}'\cdot\underline{r}}\, G_k(\underline{r},\underline{r}') \qquad (A.3.3)$$

we obtain

$$F(\underline{r}',\underline{k}') = (2\pi)^{-3/2} \int_{\underline{r}} d^3r\, e^{-i\underline{k}'\cdot\underline{r}}\, G(\underline{r},\underline{r}')$$

$$= -(2\pi)^{-3/2}\, e^{-i\underline{k}'\cdot\underline{r}'} / (k^2 - k'^2) \qquad (A.3.4)$$

Therefore, by inverse transformation, we obtain that

$$\begin{aligned} G_k(\underline{r},\underline{r}') &= (2\pi)^{-3/2} \int_{\underline{k}'} d^3k' \, e^{i\underline{k}'\cdot\underline{r}} \, F(\underline{r}',\underline{k}') \\ &= -(2\pi)^{-3} \int_{\underline{k}'} d^3k' \, \frac{e^{i\underline{k}'\cdot(\underline{r}-\underline{r}')}}{k^2 - k'^2} \end{aligned} \tag{A.3.5}$$

This integral has been evaluated elsewhere(27), and the result is

$$G_k(\underline{r},\underline{r}') = \frac{e^{ik|\underline{r}-\underline{r}'|}}{4\pi|\underline{r}-\underline{r}'|} \tag{A.3.6}$$

That takes the asymptotic form

$$G_k(\underline{r},\underline{r}') \overset{r\to\infty}{=} \exp(ikr - i\underline{k}\cdot\underline{r}')/r \tag{A.3.7}$$

since

$$\begin{aligned} |\underline{r}-\underline{r}'| &\overset{r\to\infty}{=} r - \omega r' \\ |\underline{r}-\underline{r}'|^{-1} &\overset{r\to\infty}{=} [1 + (\omega r'/r)]\, r^{-1} \\ \omega &= (\underline{r}\cdot\underline{r}')(r r')^{-1} \end{aligned} \tag{A.3.8}$$

APPENDIX A.4

ENERGY CONSERVATION(2)

In Chapter I we obtained (1.11)

$$\sigma(\theta) = (m_n/2\pi\hbar^2)^2 \sum_\alpha p_\alpha \sum_\eta (k_\eta/k_0) \cdot \left| \int_{\underline{r}'} d^3r' \, e^{i\underline{r}'\cdot\underline{K}_\eta} \, \Gamma_{\eta\alpha}(\underline{r}') \right|^2 \tag{A.4.1}$$

which may be written

$$\sigma(\theta) = (m_n/2\pi\hbar^2)^2 \sum_\alpha p_\alpha \sum_\eta \cdot \int_k \frac{k}{k_0} \left| \int_{\underline{r}'} d^3r' \, e^{i\underline{r}'\cdot\underline{K}} \, \Gamma_{\eta\alpha}(\underline{r}') \right|^2 \delta(k_\eta - k)\, dk \tag{A.4.2}$$

$$= \left(\frac{m_n}{2\pi\hbar^2}\right)^2 \sum_{\alpha\eta} p_\alpha \int_\epsilon \frac{k}{k_0} \left| \int_{\underline{r}'} d^3r' \, e^{i\underline{r}'\cdot\underline{K}} \, \Gamma_{\eta\alpha} \right|^2 \delta(\epsilon_\eta - \epsilon)\, d\epsilon$$

in which

$$\sigma(\epsilon,\theta) = (m_n/2\pi\hbar^2)^2 \sum_\alpha \sum_\eta p_\alpha (k/k_0) \left| \int_{\underline{r}'} d^3r' \, e^{i\underline{r}'\cdot\underline{K}} \, \Gamma_{\eta\alpha}(\underline{r}') \right|^2 \delta(\epsilon_\eta - \epsilon) \tag{A.4.3}$$

represents the differential cross-section (in angle and energy), and where $\delta(\epsilon_\eta - \epsilon)$ takes care of energy conservation.

Consider

$$\sum_\eta \left| \int_{\underline{r}'} d^3r' \, e^{i\underline{r}'\cdot\underline{k}} (\eta|\Gamma(\underline{r}',\underline{\xi})|\alpha) \right| \delta(\epsilon_\eta - \epsilon)$$

$$= \sum_\eta (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt \, e^{\frac{it}{\hbar}(\epsilon_0-\epsilon)} \Big[\int_{\underline{r}'} d^3r' \, e^{-i\underline{r}'\cdot\underline{k}} \int_{\underline{\xi}} d^3\xi \; e^{iE_\alpha t/\hbar} \Lambda^*_\alpha(\underline{\xi}) \, \Gamma^*(\underline{r}',\underline{\xi}) \, e^{-iE_\eta t/\hbar} \Lambda_\eta(\underline{\xi}) \Big] \cdot \tag{A.4.4}$$

$$\cdot \Big[\int_{\underline{r}'} d^3r' \, e^{i\underline{r}'\cdot\underline{k}} (\eta| \Gamma(\underline{r}',\underline{\xi})|\alpha) \Big]$$

$$= (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt \, e^{it(\epsilon_0-\epsilon)/\hbar} \iint_{\underline{r}'\underline{r}''} d^3r \, d^3r' \, e^{-i\underline{r}'\cdot\underline{k}} \, e^{i\underline{r}''\cdot\underline{k}} \sum_\eta (\alpha| e^{iH(\underline{\xi})t/\hbar} \, \Gamma^*(\underline{r}',\underline{\xi}) \, e^{-iH(\underline{\xi})t/\hbar} |\eta) \, \Gamma_{\eta\alpha}(\underline{r}'')$$

$$\sum_\eta \left| \int_{\underline{r}'} d^3r' \, e^{i\underline{K}\cdot\underline{r}'} \Gamma_{\eta\alpha}(\underline{r}') \right|^2 \delta(\epsilon_\eta - \epsilon) \tag{A.4.5}$$

$$= (2\pi\hbar)^{-1} \int_{-\infty}^{\infty} dt \, e^{itq} \iint_{\underline{r}'\underline{r}''} d^3r' \, d^3r'' \, e^{-i\underline{r}'\cdot\underline{k}} \, e^{i\underline{r}''\cdot\underline{k}} \cdot (\alpha| \Gamma^*(\underline{r}',\underline{\xi},t) \, \Gamma(\underline{r}'',\underline{\xi}) |\alpha)$$

where we have used the hermiticity property of $H(\underline{\xi})$ and the relation

$$e^{iE_\alpha t/\hbar}\,\Lambda_\alpha(\underline{\xi}) = e^{iH(\underline{\xi})t/\hbar}\,\Lambda_\alpha(\underline{\xi}) \tag{A.4.6}$$

easily proved by expansion, and

$$\hbar q = \epsilon_0 - \epsilon$$

According to (1.12) we have that

$$\Gamma(\underline{r}', \underline{\xi}) = \frac{2\pi\hbar^2}{m_n}\sum_{s=1}^{N} b_s\,\delta(\underline{r}' - \underline{\xi}_s)$$

therefore

$$\begin{aligned}&(\alpha|\,\Gamma^*(\underline{r}', \underline{\xi}, t)\,\Gamma(\underline{r}'', \underline{\xi})\,|\alpha) \\ &= \left(\frac{2\pi\hbar^2}{m_n}\right)^2 \sum_{s=1}^{N}\sum_{j=1}^{N}(\alpha|\,b_s b_j\,\delta[\underline{r}' - \underline{\xi}_s(t)]\,\delta(\underline{r}'' - \underline{\xi}_j)\,|\alpha)\end{aligned} \tag{A.4.7}$$

which when substituted back into (A.4.5) gives

$$\begin{aligned}&\sum_{\eta}\left|\int_{\underline{r}'} d^3r'\, e^{i\underline{k}\cdot\underline{r}'}(\eta|\,\Gamma(\underline{r}', \underline{\xi})\,|\alpha)\right|^2 \delta(\epsilon_\eta - \epsilon) \\ &= (2\pi\hbar)^{-1}\left(\frac{2\pi\hbar^2}{m_n}\right)^2 \sum_{s,j=1}^{N}\int_{-\infty}^{\infty} dt\, e^{itq}(\alpha|\,e^{-i\underline{k}\cdot\underline{\xi}_s(t)}\,e^{i\underline{k}\cdot\underline{\xi}_j}\,|\alpha)\end{aligned} \tag{A.4.8}$$

APPENDIX A.5

PARABOLIC RANGE[10]

In order to show that in the range $V^*/V \geq .67$ the LJD potential $\bar{V}(r)$ has a minimum at $r = 0$ and no other, one would have to take the derivative with respect to r of $\bar{V}(r)$, equate it to zero, and then show that $r = 0$ is a root; and that there are no other real roots for the above indicated range. Also the second derivative at $r = 0$ must be positive.

Thus, using (2.4) and $y = r^2/a^2$

$$\frac{\partial}{\partial r}\bar{V}(\underline{r}) = \underline{\Lambda}^{*}\left(V^{*}/V\right)^{2}\Big[\left(V^{*}/V\right)^{2}\frac{d}{dy}\,l(y) + \qquad \text{(A.5.1)}$$

$$-\,2\frac{d}{dy}\,m(y)\Big]\frac{2r}{a^{2}} = 0$$

Therefore, $r = 0$, and

$$b\,l'(y) = m'(y) \quad ; \quad b = \left(V^{*}/V\right)^{2}/2 \qquad \text{(A.5.2)}$$

which leads to

$$(22b-5) + (158.4b+33)y + (237.6b-93)y^{2} + \qquad \text{(A.5.3)}$$

$$+ (88b+145)y^{3} + (6b-135)y^{4} + 75y^{5} - 23y^{6} + 3y^{7} = 0$$

For the range 2b = 5/11 and for $y \leq 1$ there are no positive roots.

The second derivative evaluated at r = 0 is

$$b\,l''(0) - m''(0) = 400.4\,b - 28 > 0 \qquad (A.5.4)$$

for 2b = 5/11.

APPENDIX A.6

HARMONIC OSCILLATOR FREE ENERGY

It is shown in Reference 10 that the free energy of an imperfect gas or normal liquid is given by

$$F = -k_B T \Big[N \ln (2\pi k_B T / h^3) + + N \ln j(T) + \ln \Omega(T) \Big] \tag{A.6.1}$$

where the first term represents the contribution from the translational motion, the second the internal degrees of freedom, j(T) the partition function for the internal degrees of freedom, and $\Omega(T)$ the potential energy W contribution,

$$\Omega(T) = \frac{1}{N!} \int \cdots \int d\omega_1 \cdots d\omega_N \, e^{-W/k_B T} \tag{A.6.2}$$

$d\omega_i$ the volume element, to which the center of the i-th molecule in the liquid belongs. For a harmonic oscillator $W = \overline{V}(o) + sr^2$

$$\Omega(T) = (N!)^{-1} \exp[-N \overline{V}(o) / k_B T] \cdot \int_0^\infty \exp\left[-\frac{s}{k_B T} r^2\right] 4\pi r^2 \, dr \tag{A.6.3}$$

$$\Omega(T) = -3Nk_BT\ln(k_BT/\hbar\omega) + \\ -Nk_BT - N\bar{V}(0) - Nk_BT\ln j(T) \tag{A.6.4}$$

APPENDIX A.7

THERMODYNAMICAL FUNCTIONS[10]

By definition we have that

$$P = \text{Pressure} = -\left[\frac{\partial}{\partial V}\left(\frac{F}{N}\right)\right]_{T,N} = \frac{(-1)}{N}\left(\frac{\partial F}{\partial V}\right)_T \tag{A.7.1}$$

$$E = \text{Molecular energy} = -T^2\frac{\partial}{\partial T}\left(F/NT\right) \tag{A.7.2}$$

$$Y = \text{Partial potential} = \frac{F}{N} + PV \tag{A.7.3}$$

and

$$H = \text{Heat content} = E + PV \tag{A.7.4}$$

which for the harmonic oscillator potential, and with the help of (A.6.4) become

$$\begin{aligned} P = V^{-1}\Big\{&4\Lambda^*(V^*/V)^2\left[(V^*/V)^2 - 1\right] + \\ &+ 3k_BT\left[5-22(V^*/V)^2\right]\left[5-11(V^*/V)^2\right]^{-1}\Big\} \end{aligned} \tag{A.7.5}$$

$$\begin{aligned} E &= \bar{V}(0) + 3k_BT + E^L_{int} \\ E^L_{int} &= k_BT^2\frac{\partial}{\partial T}\ln j(T) \end{aligned} \tag{A.7.6}$$

$$
\begin{aligned}
H = \bar{V}(0) + 3 k_B T \left[10 - 33 \left(V^{*}/V \right)^{2} \right] \\
\cdot \left[5 - 11 \left(V^{*}/V \right)^{2} \right]^{-1} + 4 \Lambda^{*} \left(V^{*}/V \right)^{2} \cdot \\
\left[\left(V^{*}/V \right)^{2} - 1 \right] + E_{int}^{L} \quad .
\end{aligned}
\qquad \text{(A.7.7)}
$$

APPENDIX A.8

HEISENBERG'S OPERATOR[32]

Making use of the expansion

$$\theta(t) = \exp(iHt/\hbar)\,\theta\,\exp(-iHt/\hbar) \qquad \text{(A.8.1)}$$

$$= \sum_{n=0}^{\infty} (it/\hbar)^{n}\,[H,\theta]^{n}\,/\,n!$$

where

$$[H,\theta]^{0} = \theta\ ;\ [H,\theta] = H\theta - \theta H\ ;\ [H,\theta]^{2} = [H,[H,\theta]]\ ; \qquad \text{(A.8.2)}$$

$$\cdots$$

and with

$$H = p^{2}/2m + s r^{2} + \text{const.} \qquad \text{(A.8.3)}$$

we can show that

$$[H,\underline{r}]^{2n} = (-1)^{n}\,(i\hbar)^{2n}\,2^{2n}\,(s/2m)^{n}\,\underline{r}(0) \qquad \text{(A.8.4)}$$

and

$$[H,\underline{r}]^{2n+1} = (-1)^{n+1}\,(i\hbar)^{2n+1}\,(s/2m)^{n}\,\underline{p}(0)/2m \qquad \text{(A.8.5)}$$

where

$$[r_s, p_k] = i\hbar\,\delta_{sk}$$

which when substituted back into (A.8.1) gives

$$\underline{r}(t) = \underline{r}(0) \sum_{n=0}^{\infty} (-1)^n \left(\sqrt{2s/m}\, t\right)^{2n} / (2n)!$$

$$+ \left[\underline{p}(0) / \sqrt{2sm}\right] \sum_{n=0}^{\infty} (-1)^n \left(\sqrt{2s/m}\, t\right)^{2n+1} / (2n+1)! \qquad (A.8.6)$$

which for $s = \frac{m\omega^2}{2}$ gives

$$\underline{r}(t) = \underline{r}(0) \cos \omega t + \underline{p}(0) (\sin \omega t / m\omega) . \qquad (A.8.7)$$

It is interesting to notice that this result is just what one would get by solving

$$m \ddot{\underline{r}}(t) = - k\, \underline{r}(t) \qquad (A.8.8)$$

APPENDIX A.9

THERMAL AVERAGE

We will show that, making use of Bloch's theorem[14]

$$< e^{Q} >_T = e^{\frac{1}{2} < Q^2 >_T} \tag{A.9.1}$$

where Q is an oscillator coordinate, and of the Baker-Hausdorff theorem

$$e^{A} e^{B} = e^{C} \tag{A.9.2}$$

where

$$\begin{aligned} C = A + B + \frac{1}{2}[A, B] + \frac{1}{12}[A-B, [A, B]] + \\ - \frac{1}{24}[B, [A, [A, B]]] + \cdots \end{aligned} \tag{A.9.3}$$

the thermal average, operationally defined by (A.9.4) is equal to

$$\begin{aligned} &< e^{-i\underline{k}\cdot\underline{r}_s(t)} e^{i\underline{k}\cdot\underline{r}_s} >_T \equiv \\ &\equiv \left(\sum_\alpha p_\alpha\right)^{-1} \sum_\alpha p_\alpha (\alpha | e^{-i\underline{k}\cdot\underline{r}_s(t)} e^{i\underline{k}\cdot\underline{r}_s} | \alpha) \\ &= \sum_{n=-\infty}^{\infty} e^{-A'_3 k^2} e^{nA_1} e^{-in\omega t} I_n(A'_2 k^2) \end{aligned} \tag{A.9.4}$$

where

$$K^2 = (2m_n/\hbar^2)(\epsilon + \epsilon_0 - 2\sqrt{\epsilon\epsilon_0}\cos\theta)$$

$$A_1 = \hbar\omega / k_B T \qquad \text{(A.9.5)}$$

$$A'_2 = (\hbar/2M\omega)\,\mathrm{csch}\,A_1 \;;\; A'_3 = A'_2 \cosh A_1$$

From (A.9.2) we get

$$< e^{-i\underline{k}\cdot\underline{r}_s(t)}\, e^{i\underline{k}\cdot\underline{r}_s} >_T =$$

$$= < e^{-i\underline{k}\cdot[\underline{r}_s(t) - \underline{r}_s]} >_T \; e^{\frac{1}{2}k_\alpha k_\beta [r_{s\alpha}(t), r_{s\beta}]} \qquad \text{(A.9.6)}$$

The last term may be factored out of the thermal average because the commutator is a constant. Using (A.9.1)

$$< e^{-i\underline{k}\cdot\underline{r}_s(t)}\, e^{i\underline{k}\cdot\underline{r}_s} >_T =$$

$$= e^{-\frac{1}{2}<\{\underline{k}\cdot[\underline{r}_s(t) - \underline{r}_s]\}^2>_T + \frac{1}{2}k_\alpha k_\beta [r_{s\alpha}(t), r_{s\beta}]} \qquad \text{(A.9.7)}$$

((A.9.7) cont'd)

$$= \exp\Big\{-\tfrac{1}{2} < [\underline{k}\cdot\underline{r}_s(t)]^2 + [\underline{k}\cdot\underline{r}_s]^2 - [\underline{k}\cdot\underline{r}_s(t)][\underline{k}\cdot\underline{r}_s]$$

$$- [\underline{k}\cdot\underline{r}_s][\underline{k}\cdot\underline{r}_s(t)] >_T + \tfrac{1}{2} k_\alpha k_\beta [r_{s\alpha}(t), r_{s\beta}]$$

$$= \exp\Big\{- < [\underline{k}\cdot\underline{r}_s]^2 - [\underline{k}\cdot\underline{r}_s(t)][\underline{k}\cdot\underline{r}_s] >_T\Big\}$$

$$= \exp\Big\{-k_\alpha k_\beta \Big[< r_{s\alpha} r_{s\beta} >_T (1-\cos\omega t) - \frac{\sin\omega t}{M\omega} < p_{s\alpha} r_{s\beta} >\Big\}$$

and since we will show, at the end of this appendix, that

$$< r_{s\alpha}(t)\, r_{s\beta}(t) >_T = < r_{s\alpha} r_{s\beta} >_T \qquad \text{(iii. A.9.1)}$$

and that for $z = \exp(\hbar\omega/k_BT)$

$$< r_{s\alpha} r_{s\beta} >_T = \frac{\hbar}{2M\omega} \cdot \frac{z+1}{z-1} \cdot \delta_{\alpha\beta} \qquad \text{(i. A.9.7)}$$

$$< p_{s\alpha} r_{s\beta} >_T = -\frac{i\hbar}{2}\, \delta_{\alpha\beta} \qquad \text{(ii. A.9.3)}$$

$$\langle e^{-i\underline{K}\cdot\underline{r}_s(t)} \; e^{i\underline{K}\cdot\underline{r}_s} \rangle_T$$

$$= \exp\Big[-K^2 \hbar (z+1)/2M\omega(z-1) + $$

$$+ K^2 \hbar z^{1/2} (z^{1/2} e^{-i\omega t} + z^{-\frac{1}{2}} e^{i\omega t})/2M\omega(z-1) \Big] \quad \text{(A.9.8)}$$

$$= \sum_{n=-\infty}^{\infty} e^{-A_3' K^2} \; e^{nA_1} \; e^{-in\omega t} \; I_n(A_2' K^2)$$

where we have used the expansion $e^{\frac{x}{2}(y+\frac{1}{y})} = \sum_{n=-\infty}^{\infty} y^n \, I_n(x)$

$$\langle q_\alpha q_\beta \rangle_T = [\hbar(z+1)/2M\omega(z-1)] \, \delta_{\alpha\beta} \quad \text{(i.)}$$

We can show that for the harmonic oscillator the following relations hold

$$p_\alpha \psi_{n\alpha} = \sqrt{\hbar M\omega} \Big[\sqrt{(n_\alpha+1)/2} \; \psi_{n\alpha+1} + \quad \text{(i. A.9.1)}$$

$$+ \sqrt{n_\alpha/2} \; \psi_{n\alpha-1} \Big]$$

$$i\,q_\alpha \psi_{n\alpha} = \sqrt{\hbar/M\omega}\left[\sqrt{(n_\alpha+1)/2}\;\psi_{n\alpha+1} + \right. \qquad \text{(i. A.9.2)}$$
$$\left. - \sqrt{n_\alpha/2}\;\psi_{n\alpha-1}\right]$$

Therefore,

$$(n_x n_y n_z \,|\, q_\alpha q_\beta \,|\, n_x n_y n_z)$$

$$= (n_x|x^2|n_x) = (n_y|y^2|n_y) =$$
$$= (n_z|z^2|n_z) \qquad ; \ \alpha = \beta . \qquad \text{(i. A.9.3)}$$

$$= (n_x|x|n_x)(n_y|y|n_y) = (n_x|x|n_x)$$
$$(n_z|z|n_z) = (n_y|y|n_y)(n_z|z|n_z) = 0 \quad ; \ \alpha \neq \beta$$

since

$$(n_x|x|n_x) = (n_y|y|n_y) = (n_z|z|n_z) = 0 \ .$$

Consider

$$(n_x | x^2 | n_x) = \int \psi^*_{nx} \, x^2 \, \psi_{nx} \, dx$$

$$= -i\sqrt{\hbar/M\omega} \int \psi^*_{nx} \, x \left[\sqrt{(n_x+1)/2} \, \psi_{nx+1} + \right.$$

$$\left. -\sqrt{n_x/2} \, \psi_{nx-1} \right]$$

$$= -(\hbar/M\omega)\left[\sqrt{(n_x+1)/2} \int \psi^*_{nx} \left(\sqrt{(n_x+2)/2} \right.\right. \tag{i. A.9.4}$$

$$\left. \psi_{nx+2} - \sqrt{(n_x+1)/2} \, \psi_{nx} \right) - \sqrt{n_x/2} \int \psi^*_{nx}$$

$$\left.\left(\sqrt{n_x/2} \, \psi_{nx} - \sqrt{(n_x-2)/2} \, \psi_{nx-2} \right)\right]$$

$$= (\hbar/M\omega)(n_x + \tfrac{1}{2})$$

The thermal average thus becomes

$$< q_\alpha q_\beta >_T =$$

$$= \left(\sum_{n_x n_y n_z} e^{-\frac{\hbar\omega}{k_B T}(n_x+n_y+n_z+\frac{3}{2})} \right)^{-1} \tag{i. A.9.5}$$

$$\cdot \sum_{n_x n_y n_z} e^{-\frac{\hbar\omega}{k_B T}(n_x+n_y+n_z+\frac{3}{2})} (n_x | x^2 | n_x)$$

(i. A.9.5 con't)

$$= (\hbar / M\omega) \left(\sum_{n_x} e^{f n_x} \right)^{-1} \cdot \sum_{n_x} e^{f n_x} (n_x + \tfrac{1}{2}) = (\hbar / M\omega) \left[\left(\sum_{n_x} e^{f n_x} \right)^{-1} \cdot \frac{\partial}{\partial f} \sum_{n_x} e^{f n_x} + \tfrac{1}{2} \right]$$

$$= (\hbar / M\omega) \left[e^{f} / (1 - e^{f}) + \tfrac{1}{2} \right]$$

$$f = -(\hbar\omega / k_B T) \qquad \text{(i. A.9.6)}$$

$$\langle q_\alpha q_\beta \rangle_T = [\hbar (z+1) / 2M\omega (z-1)] \delta_{\alpha\beta} \qquad \text{(i. A.9.7)}$$

where

$$z = \exp(\hbar\omega / k_B T) \qquad \text{(i. A.9.8)}$$

$$< p_\alpha p_\beta >_T = [\hbar M\omega (z+1)/2(z-1)]\, \delta_{\alpha\beta} \qquad \text{(ii.)}$$

$$(n_x n_y n_z | p_\alpha p_\beta | n_x n_y n_z)$$

$$= (n_x | p_x^2 | n_x) = (n_y | p_y^2 | n_y) = (n_z | p_z^2 | n_z) \quad ; \alpha = \beta$$

(ii. A.9.1)

$$= (n_x | p_x | n_x)(M_y | p_y | n_y) = (n_x | p_x | n_x)$$

$$(n_z | p_z | n_z) = (n_y | p_y | n_y)(n_z | p_z | n_z) = 0 \quad ; \quad \alpha \neq \beta$$

since $(n_x | p_x | n_x) = (n_y | p_y | n_y) = (n_z | p_z | n_z) = 0$.

Consider

$$(n_x | p_x^2 | n_x) = \int dx \; \psi_{nx}^* \; p_x^2 \; \psi_{nx}$$

(ii. A.9.2)

$$= \sqrt{\hbar M\omega} \int \psi_{nx}^* \, p_x \Big(\sqrt{(n_x+1)/2} \; \psi_{nx+1} +$$

$$+ \sqrt{n_x/2} \; \psi_{nx-1} \Big)$$

(ii. A.9.2 cont'd)

$$(n_x | p_x^2 | n_x) = \hbar M \omega (n_x + \tfrac{1}{2}).$$

Therefore, the thermal average

$$< p_\alpha p_\beta >_T = [\hbar M \omega (z+1)/2(z-1)] \delta_{\alpha\beta} \qquad \text{(ii. A.9.3)}$$

Similarly,

$$< r_\alpha p_\beta >_T = \frac{i\hbar}{2} \delta_{\alpha\beta} \qquad \text{(ii. A.9.4)}$$

$$< p_\beta r_\alpha >_T = -\frac{i\hbar}{2} \delta_{\alpha\beta} \qquad \text{(ii. A.9.5)}$$

$$\langle r_\alpha(t)\, r_\beta(t) \rangle_T = \langle r_\alpha r_\beta \rangle_T \qquad \text{(iii.)}$$

We had in Appendix 8 (A.8.7)

$$\langle r_\alpha(t)\, r_\beta(t) \rangle_T$$

$$= \langle [\, r_\alpha(0) \cos\omega t + p_\alpha(0) (\sin\omega t / M\omega)]$$

$$[\, r_\beta(0) \cos\omega t + p_\beta(0) (\sin\omega t / M\omega)] \rangle_T$$

$$= \cos^2\omega t \, \langle r_\alpha r_\beta \rangle_T + (\sin^2\omega t / M^2\omega^2) \langle p_\alpha p_\beta \rangle_T \qquad \text{(iii. A.9.1)}$$

$$+ (\sin\omega t \cos\omega t / M\omega) [\, \langle r_\alpha p_\beta \rangle_T + \langle p_\alpha r_\beta \rangle_T]$$

$$= \cos^2\omega t \, [\hbar(z+1)/2M\omega(z-1)]\, \delta_{\alpha\beta} +$$

$$+ (\sin^2\omega t / M^2\omega^2) [\hbar M\omega(z+1)/2(z-1)]\, \delta_{\alpha\beta}$$

$$= [\hbar(z+1)/2M\omega(z-1)]\, \delta_{\alpha\beta} = \langle r_\alpha r_\beta \rangle_T$$

APPENDIX A.10

IRVING-ZWANZIG THEOREM AND RADIAL DISTRIBUTION FUNCTION

The Irving-Zwanzig theorem(16) states that the expectation value over a state ψ, of an operator depending on the position and momentum operators of N bodies, is identical with the integral of the corresponding classical function of position and momentum, over the so-called Wigner distribution function of the state ψ. The Wigner distribution function is the quantum mechanical analogue of the classical phase distribution function, and depends on the position and momenta of the N bodies. It is defined as

$$W(\underline{r},\underline{p})=(2\pi\hbar)^{-3N}\int\cdots\int d\underline{R}\, e^{-\frac{i}{\hbar}\underline{p}\cdot\underline{R}}\, \psi^{*}(\underline{r}-\frac{\underline{R}}{2})\,\psi(\underline{r}+\frac{\underline{R}}{2}) \qquad (A.10.1)$$

in which

$$\underline{r}=(\underline{r}_1,\underline{r}_2,\cdots,\underline{r}_N) \quad ; \quad \underline{p}=(\underline{p}_1,\underline{p}_2,\cdots,\underline{p}_N)$$

and has the following properties

$$W(\underline{r},\underline{p})=(2\pi\hbar)^{-3N}\int\cdots\int d\underline{P}\, e^{\frac{i}{\hbar}\underline{P}\cdot\underline{r}}\, \Phi^{*}(\underline{p}-\frac{\underline{P}}{2})\,\Phi(\underline{p}+\frac{\underline{P}}{2}) \qquad (A.10.2)$$

$$\int \cdots \int d\underline{p}\, W(\underline{r}, \underline{p}) = \psi^{*}(\underline{r})\, \psi(\underline{r}) \tag{A.10.3}$$

$$\int \cdots \int d\underline{r}\, W(\underline{r}, \underline{p}) = \Phi^{*}(\underline{p})\, \Phi(\underline{p}) \tag{A.10.4}$$

We will also define the reduced Wigner distribution functions

$$f_h(\underline{r}_1, \cdots, \underline{r}_h; \underline{p}_1, \cdots, \underline{p}_h)$$

$$= \frac{N!}{(N-h)!} \int \cdots \int d^3r_{h+1} \cdots d^3r_N\, d^3p_{h+1} \cdots d^3p_N\, W(\underline{r}, \underline{p}) \tag{A.10.5}$$

and the reduced spatial distribution functions

$$n_h(\underline{r}_1, \cdots, \underline{r}_h) = \int \cdots \int d^3p_1 \cdots d^3p_h\, f_h(\underline{r}_1, \cdots, \underline{r}_h; \underline{p}_1, \cdots, \underline{p}_h) \tag{A.10.6}$$

$$= \frac{N!}{(N-h)!} \int \cdots \int d^3r_{h+1} \cdots d^3r_N\, \psi^{*}(\underline{r})\, \psi(\underline{r})$$

The theorem states that

$$(\psi|G(\underline{R},\underline{P})|\psi) = \int\cdots\int d\underline{r}\,d\underline{p}\; g(\underline{r},\underline{p})\, W(\underline{r},\underline{p}) \qquad \text{(A.10.7)}$$

where the classical function $g(\underline{r}, \underline{p})$ may be obtained[30] from the function of operators by substituting the operators $\underline{R}$ and $\underline{P}$ in $G(\underline{R}, \underline{P})$ by the variables $\underline{r}$, $\underline{p}$, and by applying the operator $\exp [\frac{1}{2}\, ih\, \underline{\nabla}_p\cdot\underline{\nabla}_r]$ on the left. Therefore,

$$g(\underline{r},\underline{p}) = \exp\left(\tfrac{1}{2}\, i\hbar\, \underline{\nabla}_p\cdot\nabla_r\right) G(\underline{r},\underline{p}) \qquad \text{(A.10.8)}$$

NOTE. The sign in the exponential is negative if in the function $G(\underline{R}, \underline{P})$ the operator $\underline{R}$ appears on the right. Consider

$$\begin{aligned} a^{\alpha\alpha}_{js} &= (\alpha|\exp[i\underline{k}\cdot(\underline{r}_j-\underline{r}_s)]|\alpha) \\ &= \int\cdots\int d\underline{r}\,d\underline{p}\; \exp[i\underline{k}\cdot(\underline{r}_j-\underline{r}_s)]\; W^{\alpha\alpha}(\underline{r},\underline{p}) \qquad \text{(A.10.9)} \end{aligned}$$

Look at

$$a^{\alpha\alpha}_{12} = \int\cdots\int d\underline{r}\,d\underline{p}\; e^{i\underline{k}\cdot\underline{r}_{12}}\; W^{\alpha\alpha}(\underline{r},\underline{p})$$

$$a_{12}^{\alpha\alpha} = [N(N-1)]^{-1} \int_{\underline{r}_1}\int_{\underline{r}_2}\int_{\underline{p}_1}\int_{\underline{p}_2} f_2^{\alpha\alpha}(\underline{r}_1, \underline{r}_2; \underline{p}_1, \underline{p}_2)\, e^{i\underline{k}\cdot\underline{r}_{12}}$$

$$= [N(N-1)]^{-1} \int_{\underline{r}_1}\int_{\underline{r}_2} d^3r_1\, d^3r_2\, n_2^{\alpha\alpha}(\underline{r}_1, \underline{r}_2)\, e^{i\underline{k}\cdot\underline{r}_{12}} \qquad (A.10.10)$$

Let $\underline{r}_1 = \underline{r}_2'$ and $\underline{r}_2 = \underline{r}_1'$

$$a_{12}^{\alpha\alpha} = [N(N-1)]^{-1} \int_{\underline{r}_1}\int_{\underline{r}_2} d^3r_1'\, d^3r_2'\, e^{i\underline{k}\cdot(\underline{r}_2' - \underline{r}_1')}\, n_2^{\alpha\alpha}(\underline{r}_2', \underline{r}_1') \qquad (A.10.11)$$

If

$$n_2^{\alpha\alpha}(\underline{r}_1, \underline{r}_2) = n_2^{\alpha\alpha}(\underline{r}_2, \underline{r}_1)$$

and dropping the primes in (A.10.11) we get

$$a_{12}^{\alpha\alpha} = a_{21}^{\alpha\alpha} \qquad (A.10.12)$$

The thermal average of $n_2^{\alpha\alpha}$ is equal to

$$\langle n_2^{\alpha\alpha} \rangle_T = \Big(\sum_\alpha e^{-E_\alpha / k_B T} \Big)^{-1}$$

$$\cdot \sum_\alpha e^{-E_\alpha / k_B T} \int \cdots \int d^3r_3 \cdots d^3r_N \, \Lambda_\alpha^+ (\underline{r}_1, \ldots, \underline{r}_N)$$

$$\cdot \Lambda_\alpha (\underline{r}_1, \ldots, \underline{r}_N) = \int \cdots \int d^3r_3 \cdots d^3r_N \Big(\sum_\alpha e^{-E_\alpha / k_B T} \Big)^{-1}$$

$$\cdot \sum_\alpha \Lambda_\alpha^+ e^{-H / k_B T} \Lambda_\alpha = \rho_2 (\underline{r}_1, \underline{r}_2)$$

The function ρ_2 $(\underline{r}_1, \underline{r}_2)$ is just the quantum mechanical analogue of the one defined in Chapter VI of Hill's book(11). This is seen to be the case after recognizing Slater's sum inside the integral sign.

It is shown in Reference 11, p. 185, that for a fluid this function is related to the experimental radial distribution function g (r) by

$$\rho_2 (\underline{r}_1, \underline{r}_2) = \rho^2 g (r_{12}) = \rho_2 (\underline{r}_2, \underline{r}_1) \qquad \text{(A.10.14)}$$

where ρ = number of atoms per unit volume = N/V.

Therefore, our thermal average becomes

$$\left\langle \sum_{\substack{s=1 \\ \neq j}}^{N} \sum_{j=1}^{N} \exp[-i\underline{k}\cdot(\underline{\xi}_s - \underline{\xi}_j)] \right\rangle_T$$

$$= \rho N \int_{\underline{r}} d^3r \, e^{i\underline{k}\cdot\underline{r}} \, g(r) \tag{A.10.15}$$

since there are N(N - 1) terms in the summation.

APPENDIX A.11

TIME EXPANSION

In Chapter III we encountered the σ_{outer} thermal average, and we established the fact that in order to calculate it one was forced into using the Heisenberg's operator time expansion.(2) It was also mentioned that in order to calculate g(r) there was no need to go to the averaged LJD potential, since calculations for g(r) have been performed using the Lennard-Jones six-twelve potential.

The thermal average was of the form

$$\langle e^{-i\underline{k}\cdot\underline{\xi}_s(t)}\, e^{i\underline{k}\cdot\underline{\xi}_j} \rangle_T$$

$$= \langle e^{-i\underline{k}\cdot(\underline{\xi}_s-\underline{\xi}_j)} \rangle_T + \frac{it}{\hbar} \langle [H, e^{-i\underline{k}\cdot\underline{\xi}_s}]\, e^{i\underline{k}\cdot\underline{\xi}_j} \rangle_T + \frac{1}{2}\left(\frac{it}{\hbar}\right)^2 \langle [H,[H, e^{-i\underline{k}\cdot\underline{\xi}_s}]]\, e^{i\underline{k}\cdot\underline{\xi}_j} \rangle_T + \cdots \qquad \text{(A.11.1)}$$

in which we have only shown a few term of the expansion (A.8.1).

In Appendix 10 we have shown that the zero-th order term is related to the g(r) function.

For the first and second order terms, we have that for a Hamiltonian of the form

$$H = \sum_{\alpha=1}^{N} \underline{p}_{\alpha}^{2} / 2M_{\alpha} + V(\underline{\xi}_1, \dots, \underline{\xi}_N) \qquad (A.11.2)$$

the commutators take the following form

$$[H, e^{-i\underline{k}\cdot\underline{\xi}_s}] = [(\hbar\underline{k})^2 / 2M_s]\, e^{-i\underline{k}\cdot\underline{\xi}_s} + - (\hbar/M_s)\, e^{-i\underline{k}\cdot\underline{\xi}_s}\, \underline{k}\cdot\underline{p}_s \qquad (A.11.3)$$

and

$$[H, [H, e^{-i\underline{k}\cdot\underline{\xi}_s}]] = (\hbar/M_s)\, e^{-i\underline{k}\cdot\underline{\xi}_s} \cdot \left\{ -i\hbar\, \underline{k}\cdot\underline{\nabla}_s V + (\hbar/M_s) \cdot [\hbar\underline{k}\cdot(\frac{\underline{k}}{2} - \frac{\underline{p}_s}{\hbar})]^2 \right\} \qquad (A.11.4)$$

Consider

$$\langle [H, e^{-i\underline{k}\cdot\underline{\xi}_s}]\, e^{i\underline{k}\cdot\underline{\xi}_j} \rangle_T$$

$$= [(\hbar \underline{k})^2/2M_s] \langle \exp[-i\underline{k}\cdot(\underline{\xi}_s - \underline{\xi}_j)] \rangle_T + \qquad \text{(A.11.5)}$$

$$-(\hbar/M_s)\, \underline{k} \cdot \langle \exp[-i\underline{k}\cdot(\underline{\xi}_s - \underline{\xi}_j)\, \underline{p}_s \rangle_T \,.$$

In order to evaluate the second term in the RHS of (A.11.5) we made use of the Irving-Zwanzig theorem and of the Weyl correspondence rule to evaluate the classical function that enters in the theorem (see Appendix 10).

$$g(\underline{r}, \underline{p}) = \exp(\tfrac{1}{2} i\hbar \underline{\nabla}_p \cdot \underline{\nabla}_r)\, G(\underline{r}, \underline{p}) \qquad \text{(A.11.6)}$$

which applies when the operators R appear on the left in the function G ($\underline{p}$, $\underline{r}$). Therefore,

$$g(\underline{r}, \underline{p}) = (1 + \tfrac{1}{2} i\hbar\, \underline{\nabla}_{p_s} \cdot \underline{\nabla}_{r_s})\, e^{-i\underline{k}\cdot\underline{r}_s}\, \underline{p}_s \qquad \text{(A.11.7)}$$

Since there are only terms linear in $\underline{p}_s$. We obtain

$$g(\underline{r},\underline{p}) = e^{-i\underline{k}\cdot\underline{r}_s}\left(\underline{p}_s + \frac{\hbar\underline{k}}{2}\right) \qquad \text{(A.11.8)}$$

Therefore, the thermal average may be written as follows:

$$\begin{aligned}
&\sum_\alpha p_\alpha (\alpha|\exp[-i\underline{k}\cdot(\underline{\xi}_s - \underline{\xi}_j)]\,\underline{p}_s|\alpha) \\
&= \sum_\alpha p_\alpha \iint_{\underline{p}\,\underline{\xi}} d^3\xi\, d^3p\, e^{-i\underline{k}\cdot(\underline{\xi}_s-\underline{\xi}_j)}\left(\underline{p}_s + \frac{\hbar\underline{k}}{2}\right) W(\underline{\xi},\underline{p}) \\
&= (\hbar\underline{k}/2)\int_{\underline{\xi}_1}\int_{\underline{\xi}_2} d^3\xi_1\, d^3\xi_2\, e^{-i\underline{k}\cdot(\underline{\xi}_1-\underline{\xi}_2)}\,\rho_2(\underline{\xi}_1,\underline{\xi}_2) \\
&\quad + \int_{\underline{p}_1}\cdots\int_{\underline{p}_2\,\underline{\xi}_1\,\underline{\xi}_2} f_2(\underline{\xi}_1,\underline{\xi}_2;\underline{p}_1,\underline{p}_2)\,\underline{p}_1\, e^{-i\underline{k}\cdot(\underline{\xi}_1-\underline{\xi}_2)} \qquad \text{(A.11.9)}
\end{aligned}$$

$$= \frac{1}{2}\hbar\underline{k}\,\left\langle \exp[-i\underline{k}\cdot(\underline{\xi}_s - \underline{\xi}_j)]\right\rangle_T$$

The last term vanishes on the assumption that the f_2 distribution is isotropic in the momenta.

Substituting this result in (A.11.5) we see that the first order term in the expansion is zero.

$$\langle [H, e^{-i\underline{k}\cdot\underline{\xi}_s}]\, e^{i\underline{k}\cdot\underline{\xi}_j} \rangle_T = 0 \tag{A.11.10}$$

Proceeding in the same fashion, we obtain

$$\begin{aligned} g(\underline{r},\underline{p}) &= \left[1 + \tfrac{1}{2} i\hbar \underline{\nabla}_p \cdot \underline{\nabla}_r - \tfrac{1}{8}\hbar^2 (\underline{\nabla}_p \cdot \underline{\nabla}_r)^2 \right] \cdot \\ &\quad \cdot e^{-i\underline{k}\cdot\underline{r}}\, \underline{p}_s^2 \\ &= e^{-i\underline{k}\cdot\underline{r}} \left[\underline{p}_s^2 + \hbar \underline{k}\cdot\underline{p}_s + \tfrac{1}{4}\hbar^2 \underline{k}^2 \right] \end{aligned} \tag{A.11.11}$$

and

$$\begin{aligned} &\langle [H,[H, e^{-i\underline{k}\cdot\underline{\xi}_1}]]\, e^{i\underline{k}\cdot\underline{\xi}_2} \rangle_T \\ &= [(\hbar \underline{k})^2/M_1^2] \int\!\!\cdots\!\!\int_{\underline{\xi}_1 \underline{\xi}_2 \underline{p}_1 \underline{p}_2} \langle f_2(\underline{\xi}_1, \underline{\xi}_2; \underline{p}_1, \underline{p}_2) \cdot \\ &\quad e^{-i\underline{k}\cdot\underline{\xi}_{12}}\, \underline{p}_1^2 \rangle_T + (\hbar^2 \underline{k} \cdot / iM_1) \cdot \\ &\quad \int_{\underline{\xi}_1}\!\int_{\underline{\xi}_2} d^3\xi_1\, d^3\xi_2\, \rho_2(\underline{\xi}_1, \underline{\xi}_2)\, e^{-i\underline{k}\cdot\underline{\xi}_{12}}\, \underline{\nabla}_1 V \quad . \end{aligned} \tag{A.11.12}$$

APPENDIX A.12

HARD SPHERE RADIAL DISTRIBUTION AND DENSITY EXPANSION

All thermodynamical functions of a system of N bodies can be expressed in term of two very simple distribution functions(11), the $\rho_1(\underline{r}_1)$ and the $\rho_2(\underline{r}_1, \underline{r}_2)$. This fact alone makes distribution functions very useful tools. However, things get complicated because in order to calculate the $\rho_2(\underline{r}_1, \underline{r}_2)$ one has to know the $\rho_3(\underline{r}_1, \underline{r}_2, \underline{r}_3)$ etc. To this effect several approaches have been tried. Most outstanding are those of Kirkwood(18) and Ivon(19)-Green-Born(20) who have obtained integro-differential equations linking these distribution functions.

In this appendix we will limit ourselves to briefly outlining the Kirkwood method, since it is the one we have used in order to obtain the radial distribution function. In order to do this we define a potential energy

$$U(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N ; \underline{a}) = \sum_{1 \le i < j \le N} a_i a_j \, u(r_{ij})$$

$$\underline{a} = a_1, a_2, \ldots, a_N \qquad \text{(A.12.1)}$$

where the a's represent the intermolecular couplings. They range from zero to unity. Full coupling (real fluid) $a_j = 1$, for all j's, and

$$\rho_n(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_n)\, d^3r_1 \, d^3r_2 \cdots d^3r_n \qquad \text{(A.12.2)}$$

the probability that a molecule (not necessarily molecule 1) will be found in the element of volume d^3r_1 at $\underline{r}_1$, a second in d^3r_2 at r_2, ..., another in d^3r_n at $\underline{r}_n$ =

$$= [\,N!\,/\,(N-n)!\,Z\,]\cdot$$

$$\int\cdots\int d^3r_{n+1}\cdots d^3r_N\; e^{-V(\underline{r},\underline{a})/k_BT}$$

where

$$Z = \int\cdots\int d^3r_1\cdots d^3r_N\; e^{-V(\underline{r},\underline{a})/k_BT} \qquad \text{(A.12.3)}$$

By taking the derivative with respect to one of the a's of Equation (A.12.2) the Kirkwood integro-differential equation is obtained (Ivon-Green-Born take derivative with respect to one of the r's). The result may be written as(11)

$$k_BT\,\frac{\partial}{\partial a}\ln\rho_2(\underline{r}_1,\underline{r}_2;a) = -u(r_{12}) +$$

$$+ (1/N)\int_{\underline{r}_1}\int_{\underline{r}_3} d^3r_1\,d^3r_3\; u(r_{13})\,\rho_2(\underline{r}_1,\underline{r}_3;a) + \qquad \text{(A.12.4)}$$

(A.12.4 cont'd)

$$-\left[\rho_2(\underline{r}_1, \underline{r}_2; a)\right]^{-1} \int_{\underline{r}_3} d^3r_3\, u(r_{13})\, \rho_3(\underline{r}_1, \underline{r}_2, \underline{r}_3; a)$$

which in terms of the correlation function, g_2 ($\underline{r}_1$, $\underline{r}_2$; $\underline{a}$),

$$\rho_2(\underline{r}_1, \underline{r}_2; \underline{a}) = \rho_1(\underline{r}_1; \underline{a})\, \rho_1(\underline{r}_2; a) \cdot \cdot g_2(\underline{r}_1, \underline{r}_2; \underline{a}) \qquad \text{(A.12.5)}$$

can be written in the following form after integration over a

$$-k_B T \ln g_2(\underline{r}_1, \underline{r}_2; a) = a\, u(r_{12}) + + \rho \int_0^a \int_{\underline{r}_3} d^3r_3\, da\, u(r_{13}) \left[g_3(\underline{r}_1, \underline{r}_2, \underline{r}_3; a) - g_2(\underline{r}_1, \underline{r}_2, a)\right] \qquad \text{(A.12.6)}$$

It can be shown that(11) for $\rho \to 0$ the g_n ($\underline{r}_1$, ••• , $\underline{r}_n$; a) equation (neglecting terms of order 1/N) is

$$-k_B T \ln g_n(\underline{r}_1, \ldots, \underline{r}_n; a)$$

$$= \sum_{2 \leq i < j \leq n} u(r_{ij}) + a \sum_{i=2}^{n} u(r_{1i}) \tag{A.12.7}$$

that, when substituted in Equation (A.12.6), as a first approximation for g_3 and g_2 inside the integral sign, gives(11, 29)

$$g_2(\underline{r}_1, \underline{r}_2; a) = \exp\Big\{[-u(r_{12}) / k_B T] +$$

$$+ \rho \int_{\underline{r}_3} d^3 r_3 \,[e^{-au(r_{13})/k_B T} - 1][e^{-u(r_{23})/k_B T} - 1] \tag{A.12.8}$$

For a fluid (a = 1)

$$g_2(\underline{r}_1, \underline{r}_2; a) = g_2(r_{12}) \tag{A.12.9}$$

$$= \exp\Big\{-u(r_{12}) / k_B T + \rho \int_{\underline{r}_3} d^3 r_3 \,[e^{-u(r_{13})/k_B T} - 1] \cdot$$

$$\cdot [e^{-u(r_{23})/k_B T} - 1]$$

(A.12.9 cont'd)

$$\cong e^{-u(r_{12})/k_B T}\left\{1+\rho\int_{\underline{r}_3} d^3 r_3\left[e^{-u(r_{13})/k_B T}-1\right]\left[e^{-u(r_{23})/k_B T}-1\right]\right.$$

Hard Sphere Potential

$$\begin{aligned} u(r) &= 0 & &; r > d \\ &= \infty & &; r \leq d \end{aligned} \qquad \text{(A.12.10)}$$

Using cylindrical coordinates it is easy to show that for the above potential

$$\begin{aligned} &\int_{\underline{r}_3} d^3 r_3\left[e^{-u(r_{13})/k_B T}-1\right]\left[e^{-u(r_{23})/k_B T}-1\right] \\ &\quad = 0 \quad ; r \leq d \\ &\quad = (4\pi d^3/3)\left[1-(3r/4d)+(r/2d)^3/2\right] \quad ; d < r \leq 2d \\ &\quad = 0 \quad ; r \geq 2d \end{aligned} \qquad \text{(A.12.11)}$$

Therefore, (A.12.9) becomes(11, 29)

$$\begin{aligned} g(r) &= 0 & &; r \leq d \\ &= 1+\frac{4\pi}{3}(\rho d^3)\left[1-\frac{3}{4}\left(\frac{r}{d}\right)+\frac{1}{16}\left(\frac{r}{d}\right)^3\right] & &; d < r \leq 2d \\ &= 1 & &; r \geq 2d \end{aligned} \qquad \text{(A.12.12)}$$

APPENDIX A.13

INCIDENT SPECTRUM CALCULATION

We have shown that (3.14 and 3.15)

$$\sigma_{inner}(\epsilon,\theta)/b^2N = \sum_{n=-\infty}^{\infty}(k/k_0)\cdot \exp[-A'_3K^2+nA_1]\, I_n(A'_2K^2)\,\delta(\epsilon_0-\epsilon-n\hbar\omega) \tag{A.13.1}$$

$$\sigma_{outer}(\epsilon,\theta)/b^2N = (k/k_0)\,\delta(\epsilon_0-\epsilon)\cdot \cdot\rho\int_{\underline{r}} d^3r\, e^{i\underline{k}\cdot\underline{r}}\, g(r) \tag{A.13.2}$$

These are the results one would get for the theoretical cross-sections when a monochromatic beam of neutrons of energy ϵ_0 hits the target. However, this is not accomplished in practice. The true energy distribution out of a crystal spectrometer is of the Gaussian type rather than of the ideal Delta type. We will here assume that the incident energy spectrum distribution is given by (3.18)

$$G(\epsilon_0;\bar{\epsilon}_0,\beta) = L\exp[-(\epsilon_0-\bar{\epsilon}_0)^2/\beta^2] \tag{A.13.3}$$

Therefore the theoretical cross-section would become

$$\sigma(\epsilon,\theta;\bar{\epsilon}_0,\beta) = \int_0^\infty G(\epsilon_0;\bar{\epsilon}_0,\beta)\,\sigma(\epsilon,\theta;\epsilon_0)\,d\epsilon$$

$$= \int_0^\infty L \exp[-(\epsilon_0-\bar{\epsilon}_0)^2/\beta^2]\, b^2 N \sum_{n=-\infty}^{\infty} \sqrt{\epsilon/\epsilon_0}\,\cdot$$

$$\exp[-A_3' K^2 + nA_1]\, I_n(A_2' K^2)\, \delta(\epsilon_0-\epsilon-n\hbar\omega) +$$

$$+ L b^2 N \rho \int_0^\infty d\epsilon_0 \exp[-(\epsilon_0-\bar{\epsilon}_0)^2/\beta^2]\, \delta(\epsilon_0-\epsilon)\cdot$$

$$\cdot \int_{\underline{r}} d^3r \exp(i\,\underline{k}\cdot\underline{r})\, g(r) \qquad \text{(A.13.4)}$$

$$= L b^2 N \Big\{ \sum_{n=-\infty}^{\infty} \sqrt{\epsilon/(\epsilon+n\hbar\omega)}\; e^{-(\epsilon-\bar{\epsilon}_0-n\hbar\omega)^2/\beta^2}$$

$$e^{nA_1}\; e^{-A_3' \frac{2m_n}{\hbar^2}(2\epsilon+n\hbar\omega-2\sqrt{\epsilon(\epsilon+n\hbar\omega)}\cos\theta)}$$

$$I_n[A_2'(2m_n/\hbar^2)(2\epsilon+n\hbar\omega-2\sqrt{\epsilon(\epsilon+n\hbar\omega)}\cos\theta)]$$

$$+ L b^2 N \rho \int_0^\infty 4\pi r^2 dr\, g(r) \sin[\sqrt{4m_n/\hbar^2}\, Q_0 r]\cdot$$

$$\cdot[\sqrt{4m_n/\hbar^2}\, Q_0 r]^{-1}$$

therefore

$$\Gamma(\epsilon,\theta;\bar{\epsilon}_0,\beta)/Lb^2N$$

$$= \sum_{n=-\infty}^{\infty} \sqrt{\epsilon/(\epsilon+n\hbar\omega)}\ \exp\Big[-(\epsilon-\bar{\epsilon}_0+n\hbar\omega)^2/\beta^2 + \tag{A.13.5}$$

$$+ nA_1 - A_3 Q_n^2\Big]\ I_n(A_2 Q_n^2) +$$

$$+ \rho\int_0^{\infty} 4\pi r^2 dr\, g(r)\, \sin\Big[\sqrt{4m_n/\hbar^2}\, Q_0 r\Big]\Big[\sqrt{4m_n/\hbar^2}\, Q_0 r\Big]^{-1}$$

where

$$Q_n^2 = \epsilon + n\frac{\hbar\omega}{2} - \sqrt{\epsilon(\epsilon+n\hbar\omega)}\cos\theta$$

$$A_2 = A_2'(4m_n/\hbar^2) \tag{A.13.6}$$

$$A_3 = A_3'(4m_n/\hbar^2)$$

The summation over n may be divided into three parts as follows

$$\sigma_0(\epsilon,\theta;\bar{\epsilon}_0,\beta) = \exp[-(\epsilon-\bar{\epsilon}_0)^2/\beta^2 - A_3 Q_0^2] \cdot \cdot I_0(A_3 Q_0^2) \tag{A.13.7}$$

$$\sigma_+(\epsilon,\theta;\bar{\epsilon}_0,\beta) = \sum_{n=1}^{\infty} \sqrt{\epsilon/(\epsilon+n\hbar\omega)}\; I_n(A_2 Q_n^2) \cdot \cdot \exp[-(\epsilon-\bar{\epsilon}_0+n\hbar\omega)^2/\beta^2 + nA_1 - A_3 Q_n^2] \tag{A.13.8}$$

$$\sigma_-(\epsilon,\theta;\bar{\epsilon}_0,\beta) = \sum_{n=1}^{\infty} \sqrt{\epsilon/(\epsilon-n\hbar\omega)}\; I_n(A_2 Q_{-n}^2) \cdot \cdot \exp[-(\epsilon-\bar{\epsilon}_0-n\hbar\omega)^2/\beta^2 - nA_1 - A_3 Q_{-n}^2] \tag{A.13.9}$$

APPENDIX A.14

OUTER EFFECT CALCULATION

We have shown with the help of Appendices A.10 and A.11 that the outer effect may be exhibited as follows.

$$\Gamma_{outer}(t,\theta) = Nb^2(k/k_0)\,\delta(t_0-t)\,\rho\int d^3r\, e^{i\underline{K}\cdot\underline{r}}\, g(r) \qquad (A.14.1)$$

Also in Appendix A.12 we have shown that

$$\begin{aligned} g(r) &= 0 && ; r \le d \\ &= 1 + \frac{4\pi}{3}\rho d^3\left[1 - \frac{3}{4}\left(\frac{r}{d}\right) + \frac{1}{16}\left(\frac{r}{d}\right)^3\right] && ; d < r \le 2d \qquad (A.14.2) \\ &= 1 && ; r > 2d \end{aligned}$$

Therefore

$$\rho\int_0^\infty\int_0^{2\pi}\int_0^\pi r^2\,dr\,\sin\theta\,d\theta\; e^{i\underline{K}\cdot\underline{r}}\, g(r)$$

$$= \rho\,\frac{4\pi}{K}\left\{\int_0^d g(r)\sin Kr\; r\,dr + \int_0^{2d} g(r)\sin Kr\; r\,dr + \qquad (A.14.3)\right.$$

$$\left. + \int_{2d}^\infty g(r)\sin Kr\; r\,dr\right\}$$

leads after trivial integration and somewhat lengthy manipulation to

$$\sigma_{outer}(\epsilon,\theta) = N b^2 (k/k_0)\, \delta(\epsilon_0 - \epsilon) \left\{ B \right\} \tag{A.14.4}$$

where

$$\begin{aligned} \left\{ B \right\} = & -D\, \Lambda_{3/2}(x) + (3D^2/16x^6) \cdot \\ & \cdot \left[24(x^2-1)\cos 2x - 48x \sin 2x + \right. \\ & \left. + (5x^4+12x^2+24)\cos x + 4(x^3+6x)\sin x \right] \end{aligned} \tag{A.14.5}$$

in which

$$\begin{aligned} D &= (4\pi d^3 \rho / 3) \\ x &= K d \\ \Lambda_{3/2} &= (3/x^3)(\sin x - x\cos x). \end{aligned} \tag{A.14.6}$$

Integrating (A.14.4) over incident energies, after introducing the incident energy spectrum we get (3.25).

APPENDIX A.15

SPIN DEPENDENCE(31)

We want to calculate the average over neutron and nucleus spin directions $\{\ \}_\sigma^S$ of the thermal average $<\ >_T$ given by

$$\left\{ \left\langle \sum_{lj\lambda\mu} b_l^\lambda b_j^\mu \, \Omega_l^\lambda(\underline{\xi},t)\, \Omega_j^{\mu *}(\underline{\xi},0) \right\rangle_T \right\}_\sigma^S \tag{A.15.1}$$

The molecular wave functions may be written as a product of a spatial function ψ and a spin function χ provided the molecule does not have like nuclei. In this section we will assume this to be the case and refer the reader elsewhere(2) for the opposite case.

We will assume

$$\Lambda_\alpha = \psi_\alpha \chi \tag{A.15.2}$$

This allows us to write the average (A.15.1) as a product. The neutron and nuclear spin average times the usual thermal average. Consider the former

$$\begin{aligned} &\left\{ b_l^\lambda b_j^\mu \right\}_\sigma^S \\ &= \left\{ \left(\alpha_l^\lambda + \beta_l^\lambda \, \underline{\sigma} \cdot \underline{S}_l^\lambda \right) \left(\alpha_j^\mu + \beta_j^\mu \, \underline{\sigma} \cdot \underline{S}_j^\mu \right) \right\}_\sigma^S \end{aligned} \tag{A.15.3}$$

(A.15.3 cont'd)

$$= \left\{ \alpha_\ell^\lambda \alpha_j^\mu + \alpha_\ell^\lambda \beta_j^\mu \, \underline{\sigma} \cdot \underline{S}_j^\mu + \alpha_j^\mu \beta_\ell^\lambda \, \underline{\sigma} \cdot \underline{S}_\ell^\lambda + \right.$$

$$\left. + \beta_\ell^\lambda \beta_j^\mu \, (\underline{\sigma} \cdot \underline{S}_\ell^\lambda) (\underline{\sigma} \cdot \underline{S}_j^\mu) \right\}_\sigma^S$$

Making use of the well-known relation between the Pauli matrices and any vector $\underline{A}$ and $\underline{B}$,

$$(\underline{\sigma} \cdot \underline{A}) (\underline{\sigma} \cdot \underline{B}) = \frac{1}{4} \underline{A} \cdot \underline{B} + \frac{1}{2} i \, \underline{\sigma} \cdot (\underline{A} \times \underline{B}) \qquad \text{(A.15.4)}$$

we obtain for (A.15.3)

$$\left\{ b_\ell^\lambda b_j^\mu \right\}_\sigma^S = \left\{ \alpha_\ell^\lambda \alpha_j^\mu + \alpha_\ell^\lambda \beta_j^\mu \, \underline{\sigma} \cdot \underline{S}_j^\mu + \right.$$

$$+ \alpha_j^\mu \beta_\ell^\lambda \, \underline{\sigma} \cdot \underline{S}_\ell^\lambda + \frac{1}{4} \beta_\ell^\lambda \beta_j^\mu \, \underline{S}_\ell^\lambda \cdot \underline{S}_j^\mu + \qquad \text{(A.15.5)}$$

$$\left. + \frac{1}{2} i \, \beta_\ell^\lambda \beta_j^\mu \, \underline{\sigma} \cdot (\underline{S}_\ell^\lambda \times \underline{S}_j^\mu) \right\}_\sigma^S$$

For unpolarized neutrons the average over neutron spin directions of the operator $\underline{\sigma}$ vanishes. The average of $\underline{S}_\ell^\gamma \cdot \underline{S}_j^\mu$ over nuclear spin directions is just

$$\left\{ \underline{S}_\ell^\lambda \cdot \underline{S}_j^\mu \right\}^S = S_\ell^\lambda \left(S_\ell^\lambda + 1 \right) \delta_{\ell j} \delta_{\lambda\mu} \qquad \text{(A.15.6)}$$

These two results simplify expression (A.15.5) considerably

$$\left\{ b_\ell^\lambda b_j^\mu \right\}_\sigma^S = \alpha_\ell^\lambda \alpha_j^\mu + \qquad \text{(A.15.7)}$$
$$+ \frac{1}{4} \beta_\ell^\lambda \beta_j^\mu S_\ell^\lambda \left(S_\ell^\lambda + 1 \right) \delta_{\ell j} \delta_{\lambda\mu} .$$

APPENDIX A.16

TIME EXPANSION FOR INTERNAL DEGREES OF FREEDOM

In Chapter VI we made use of the static approximation in order to calculate the internal degrees of freedom thermal average. Here we will outline the time expansion technique used in order to obtain further correction terms. However, due to the fact that the thermal average under discussion reduces to that discussed in great length in reference 2, we will limit ourselves to illustrate the calculation for the direct non-interference scattering contribution.

The thermal average was given by (6.16)

$$\langle \psi_r | e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s(t)} \, e^{if^{\mu}\underline{k}\cdot\underline{r}_j} | \psi_r \rangle_T \qquad \text{(A.16.1)}$$

Expanding the time operator in the usual form (A.8.1)

$$e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s(t)} = \sum_{n=0}^{\infty} (it/\hbar)^n (1/n!) [H, e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s}]^n$$

$$= e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s} + (it/\hbar)[H, e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s}] + \qquad \text{(A.16.2)}$$

$$+ (it/\sqrt{2}\,\hbar)^2 [H, [H, e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s}]] + \cdots .$$

It is observed that for diatomic molecules(13) the rotational energy level separation is in general very much smaller than the corresponding vibrational level. The vibrational energy separation is usually greater than the neutron energy used in neutron diffraction experiments. On the other hand, the rotational energy level separation is smaller than the incident neutron energy. In particular for the Nitrogen molecule the rotational level separation is approximately .3 ev. and the vibrational level separation is approximately 4.9×10^{-4} ev. The incident neutron energy used in diffraction experiments is of the order 7×10^{-2} ev. This implies that the neutron will excite very many rotational levels but none of the vibrational levels.

In order to go further in the calculation of the thermal average, we are forced to make the following approximations

i) the Hamiltonian H_c is written in the approximation used in Chapter VI (6.17 to 6.19), i.e.,

$$H_r \cong H_{rot} + H_{vib}$$

In lieu of the aforementioned discussion we will take as the second approximation

ii) the static approximation for the vibrational degrees of freedom.

These approximations enable us to write for (A.16.2)

$$e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s(t)}$$

$$= e^{iH_{rot}t/\hbar}\, e^{iH_{vib}t/\hbar}\, e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s}\, e^{-iH_{rot}t/\hbar}\, e^{-iH_{vib}t/\hbar}$$

$$\cong e^{iH_{rot}t/\hbar}\, e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s}\, e^{-iH_{rot}t/\hbar} \qquad \text{(A.16.3)}$$

$$= e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s} + (it/\hbar)\left[H_{rot}, e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s}\right] +$$

$$+ (it/\sqrt{2}\hbar)^2 \left[H_{rot}, \left[H_{rot}, e^{-if^{\lambda}\underline{k}\cdot\underline{r}_s}\right]\right] + \cdots$$

Let

$$x = \underline{k}\cdot\underline{r}_s / k r_s \qquad \text{(A.16.4)}$$

and write the angular momentum operator in the form

$$\underline{L}^2 = -\left\{ -\frac{\partial}{\partial x}(1-x^2)\frac{\partial}{\partial x} - \frac{m^2}{1-x^2} \right\} \tag{A.16.5}$$

After substitution of (A.16.3) and (A.16.5) into (A.16.1) we obtain

$$< \psi_{vib} | \chi^{\lambda\mu}_{sj} | \psi_{vib} >_T \tag{A.16.6}$$

where

$$\chi^{\lambda\mu}_{sj} = \left(\sum_{lm} \exp[-\hbar^2 l(l+1)/2Ik_BT] \right)^{-1} \cdot$$

$$\sum_{lm} \exp[-\hbar^2 l(l+1)/2Ik_BT] \left(Y_l^m \,|\, e^{-i\underline{k}\cdot(\underline{r}_s f^\lambda - \underline{r}_j f^\mu)} + \right. \tag{A.16.7}$$

$$\left. +(it/\hbar)[H_{rot}, e^{-i\underline{k}\cdot\underline{r}_s f^\lambda}]\, e^{i\underline{k}\cdot\underline{r}_j f^\mu} + \ldots \,|\, Y_l^m \right).$$

Consider the coefficient of the term linear in the time for $s = j$ and $\mu = \nu$

$$I_{s\ell}^{\lambda m} = \left[\frac{\hbar^2 L^2}{2\mu r_M^2}, e^{-if^\lambda \underline{k}\cdot\underline{r}_s} \right] e^{i\underline{k}\cdot\underline{r}_s f^\lambda} P_\ell^m$$

$$= (i\hbar^2 k r_s f^\lambda / 2\mu r_M^2)\left\{ 2\left[(1-x^2)\frac{d}{dx} P_\ell^m + - x P_\ell^m\right] + i k r_s f^\lambda (1-x^2) P_\ell^m \right\} \qquad (A.16.8)$$

and using the recursion relations for the associated Legendre functions, we get

$$I_{s\ell}^{\lambda m} = (i\hbar^2 k r_s f^\lambda / 2\mu r_M^2)\left\{ 2\left[\ell x P_\ell^m - (\ell-m+1) P_{\ell+1}^m\right] + + i k r_s f^\lambda (1-x^2) P_\ell^m \right\}. \qquad (A.16.9)$$

The matrix element becomes

$$\int_{-1}^{1} dx\, P_\ell^m\, I_{s\ell}^{\lambda m}$$

$$= (i\hbar^2 k r_s f^{\lambda} / 2\mu r_M^2)\Big\{2\ell \int_{-1}^{1} x P_\ell^m P_\ell^m\, dx \; +$$

$$- 2(\ell - m + 1)\int_{-1}^{1} dx\, P_\ell^m P_{\ell+1}^m \; +$$

$$+ i k r_s f^{\lambda} \int_{-1}^{1} dx\, (1-x^2)\, P_\ell^m P_\ell^m \Big\} \qquad \text{(A.16.10)}$$

$$= -(\hbar^2 k^2 r_s^2 f^{\lambda 2} / 3\mu r_M^2)$$

This term reduces to the equivalent one in reference 2 when we expand r_s about the minimum r_M of the potential $U(r)$. That is

$$\chi_{ss}^{\lambda\lambda} = 1 - \frac{it}{\hbar}\,\frac{\hbar^2 K^2}{3\mu}\,f^{\lambda\,2} + \dots \tag{A.16.11}$$

The contribution of the term linear in time to the cross-section is

$$\sigma'_\lambda(\epsilon,\theta) = \frac{k}{k_0}\,\frac{N}{2\pi\hbar}\int_{-\infty}^{\infty} dt\; e^{itq}\left[-\frac{it}{\hbar}\,\frac{\hbar^2 K^2}{3\mu}\,f^{\lambda\,2}\right] \tag{A.16.12}$$

$$= -\frac{Nk}{k_0}\,\frac{\hbar^2 K^2}{3\mu}\,f^{\lambda\,2}\,\frac{\partial}{\partial\epsilon_0}\,\delta(\epsilon_0-\epsilon) \quad .$$

For purposes of comparing the order of magnitude of this term with respect to the static approximation term, we will assume that the center of mass thermal average is unity. We will then integrate (A.16.12) over incident energies after multiplying by the usual Gaussian. The result obtained is

$$\int_0^{\infty} d\epsilon_0 \, e^{-(\epsilon_0-\bar{\epsilon}_0)^2/\beta^2} \, \sigma'_{\gamma}(\epsilon,\theta;\epsilon_0)$$

$$= N\,\frac{4}{3}\,\frac{m_n}{\mu}\,f^{\gamma 2}\,\frac{\epsilon(\epsilon-\bar{\epsilon}_0)}{\beta^2}\,\sin^2\frac{\theta}{2}\,\exp\left[-(\epsilon-\bar{\epsilon}_0)^2/\beta^2\right]. \tag{A.16.13}$$

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