COLLISION THEORY

AS APPLIED TO

THE CALCULATION OF A RELAXATION TIME

by

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ABSTRACT

An expression for the spin-lattice relaxation time, T_1, of a dilute monatomic gas can be derived starting from the quantum-mechanical Boltzmann equation. The real difficulty in calculating the relaxation time for a particular system lies in the evaluation of the transition operator which appears in the expression for T_1^{-1}. In this thesis, the relevant part of the transition operator, t_1, is estimated by a distorted-wave Born approximation (DWBA).

The monatomic gas is approximated by a specific model. In this model the collisions described by $\mathfrak{t}_1$ are governed by two potentials: one, the isotropic rigid sphere potential, V_0, and the other, the anisotropic dipole-dipole nuclear spin interaction potential, V_1. The latter interaction describes the coupling between the degenerate nuclear spin states of the atoms and the translational degrees of freedom in the gas. The former (isotropic) potential governs the explicit form of the rigid sphere distorted wave.

After the DWBA transition operator is substituted into the equation for the relaxation time, the expression for T_1^{-1} breaks up into two terms, the "diagonal" and

"non-diagonal" contributions. At this stage the explicit expression for T_1^{-1} is sufficiently complicated that, in order to finish the calculation, analytical approximations to the diagonal and non-diagonal terms are made. These approximations may be succinctly described by stating that they result in two separate evaluations, a linear and a quadratic one, for the overall relaxation time. The magnitude of a small parameter c^2, which appears in the exponential term of T_1^{-1}, is used as the basis for neglecting certain contributions to the integrals which arise in estimating T_1^{-1}. The linear and quadratic approximations yield numerical factors of 3.50 and 2.56 respectively, in the expression for the relaxation time. These values are to be compared with the factor of 2 obtained elsewhere.

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CHAPTER I

INTRODUCTION

In the Boltzmann equation approach to the theory of nuclear magnetic relaxation in dilute monatomic gases, Chen and Snider[1] have derived a general expression for the spin-lattice relaxation time, T_1. Their expression for T_1^{-1} involves the transition operator, t, which arises naturally in the collision term of the modified quantum-mechanical Boltzmann equation of Waldmann[2] and Snider[3]. If a rigorous, analytical evaluation of t for the relevant interaction potential could be obtained, then it would be possible to evaluate T_1^{-1} completely and explicitly for a fluid relaxing because of this particular interaction potential.

The collisions in this thesis are governed by two potentials which affect the scattering to a different extent. Thus a "distorted-wave Born approximation" (DWBA)[4] can be used to estimate the anisotropic part, t_1, of the transition operator. Such an approximation leaves t_1 with rigorous distorted waves governed by the isotropic rigid sphere potential, V_0, and with a strictly linear dependence on the anisotropic dipole-dipole nuclear spin interaction potential, V_1. It is the purpose of this thesis to use the DWBA transition operator in order to obtain an approximate analytical expression for the relaxation time, T_1^{-1}, due to V_1.

A concise review of scattering theory for molecules with degenerate internal states is given in Chapter II. This is completed with a derivation of the DWBA to the anisotropic part of the transition operator. In the next chapter this transition operator is explicitly calculated for the rigid sphere potential and the dipole-dipole nuclear spin interaction potential. It is at this point that the work in this thesis differs from that of Chen and Snider. They performed essentially the same calculation; that is, they used the same two potentials as used here, but in their treatment they approximated the distorted waves by plane waves. The rigid sphere potential V_0 entered into the problem only as a lower limit on the radial integration in t_1, thus neglecting all scattering effects due to the isotropic potential. Such a plane wave approximation simplified the integrations in t_1 considerably.

The purpose of treating the wave functions more realistically is to see if there is a significant change in the value obtained for the relaxation time. Because the plane wave approach of Chen and Snider is so much simpler mathematically than, for example, this more extensive treatment, the improvement obtained by a more exact method would have to be considerable to outweigh the time and effort involved in evaluating t_1 more precisely. In fact, it was found that the simpler treatment gives 78% of the value for the relaxation time that is calculated by the more extensive treatment.

Because of the particular V_0 chosen in this thesis, the distorted waves could be expressed exactly in terms of a partial wave expansion. A neater solution to this particular scattering problem would be a Cartesian evaluation of the rigid sphere wavefunction. More generally, the most useful solution to any collision problem would be a good analytical Cartesian approximation to the distorted wave for a general isotropic potential.

In Chapter IV the relaxation time is written down explicitly for the t_1 discussed above. Unfortunately, the expression which is thus obtained for T_1^{-1} is sufficiently complicated that an exact evaluation cannot be carried further. Consequently, in Chapters V and VI a "linear" and a "quadratic" approximation respectively, are carried out analytically in order to estimate the remaining sums and integration in T_1^{-1}. A certain small parameter, c^2, which appears in the expression for T_1^{-1} was used as a guide in performing the integrations in the "linear" and "quadratic" approximations. Because, for example, for ^{129}Xe, c^2 is of the order of 1.25×10^{-4} at 300° K., expansions are made in terms of this parameter and cut off at terms linear in c^2. In the last chapter a summary of the approximate evaluations to T_1^{-1} is given.

CHAPTER II

THEORY OF THE TRANSITION OPERATOR

A brief resumé of scattering theory[4] of molecules with degenerate internal states will be given in this chapter. The general purpose of this summary is to introduce and discuss the transition operator, but the ultimate aim is to exhibit the explicit operator equation for the anisotropic transition operator for a system interacting through an isotropic and an anisotropic potential. In fact, it is not the _whole_ anisotropic transition operator which is of interest here, but only a "linear in anisotropy" approximation, or, equivalently a "distorted-wave Born approximation" (DWBA) to the whole anisotropic transition operator.

A two body collision problem involving a central potential which is also an operator in internal state space, can always be reduced to a pseudo one-body scattering problem. Since the center of mass is not affected by the collision, the problem can be expressed exclusively in terms of the stationary state Schroedinger equation written in relative coordinates, namely

$$\left[\frac{-\hbar^2}{2\mu}\nabla^2_{\underset{\sim}{r}} + \mathcal{H}_{1_{int}} + \mathcal{H}_{2_{int}} + V_{int}(\underset{\sim}{r})\right]\Psi(\underset{\sim}{r}) = \mathcal{E}\,\Psi(\underset{\sim}{r})$$

(2-1)

where μ is the reduced mass of the two molecules, $\underline{r}$ is the relative coordinate $\underline{r}_1-\underline{r}_2$, and $\mathcal{E}$ is the total relative energy of the system plus the energy of the internal states. The Hamiltonians $\mathcal{H}_{1_{int}}$ and $\mathcal{H}_{2_{int}}$ are operators strictly in the internal state space of molecules 1 and 2 respectively, while $V_{int}(\underline{r})$ is an operator in both position space and internal state space.

The corresponding free particle Schroedinger equation for molecules with internal states is

$$\left[\frac{-\hbar^2}{2\mu}\nabla^2_{\underset{\sim}{r}} + \mathcal{H}_{1_{int}} + \mathcal{H}_{2_{int}}\right]\phi_{\underset{\sim}{k},i}(\underset{\sim}{r}) = \mathcal{E}\,\phi_{\underset{\sim}{k},i}(\underset{\sim}{r})$$

(2-2)

where

$$\phi_{\underset{\sim}{k},i}(\underset{\sim}{r}) = h^{-3/2}\, e^{\pm i\underset{\sim}{k}\cdot\underset{\sim}{r}}\,|i_1, i_2\rangle$$

$$\equiv h^{-3/2}\, e^{\pm i\underset{\sim}{k}\cdot\underset{\sim}{r}}\,|i\rangle$$

(2-3)

and

$$h^{-3/2} e^{i\underline{k}\cdot\underline{r}} |i\rangle = \langle \underline{r} | \underline{p}, i\rangle \tag{2-4}$$

$$h^{-3/2} e^{-i\underline{k}\cdot\underline{r}} |i\rangle = \langle \underline{p}, i | \underline{r}\rangle. \tag{2-5}$$

The label i_1 actually stands for the pair of quantum numbers i_1, d_{i_1} of molecule 1. The former quantum number labels states with different energies and the latter one labels the degeneracy. The solution to Eq. (2-2), $\phi_{\underline{k},i}(\underline{r})$, is a wave function in position space, but still an abstract vector in internal state space. Finally, the ket $|i_1,i_2\rangle$ is an eigenfunction of the internal state Hamiltonian for a pair of molecules, i.e.,

$$\left[\mathcal{H}_{1_{int}} + \mathcal{H}_{2_{int}}\right] |i_1, i_2\rangle = (\epsilon_{i_1} + \epsilon_{i_2}) |i_1, i_2\rangle$$

$$\equiv \epsilon_i |i\rangle.$$

(2-6)

With the substitution of Eq. (2-6) into Eq. (2-2), the latter equation can be written as

$$\left[\frac{-\hbar^2}{2\mu}\nabla_{\underset{\sim}{r}}^2 + \epsilon_i\right]\phi_{\underset{\sim}{k},i}(\underset{\sim}{r}) = \xi\,\phi_{\underset{\sim}{k},i}(\underset{\sim}{r}) \,. \tag{2-7}$$

Because the set of states $\{|i\rangle\}$ form a complete orthonormal set of vectors in internal state space, $\Psi(\underline{r})$, the solution to Eq. (2-1), can be expanded in terms of them in the manner

$$\Psi(\underset{\sim}{r}) = \sum_{i_1,i_2} \Psi_{i_1,i_2}(\underset{\sim}{r})\, |i_1,i_2\rangle. \tag{2-8}$$

When the pair of operators $\mathcal{H}_{1_{int}}$, $\mathcal{H}_{2_{int}}$ act upon $\Psi(\underline{r})$ as given in Eq. (2-6), the result is

$$\left[\mathcal{H}_{1_{int}} + \mathcal{H}_{2_{int}}\right]\Psi(\underset{\sim}{r}) = \sum_{i_1,i_2} \Psi_{i_1,i_2}(\underset{\sim}{r})\,\epsilon_i\, |i_1,i_2\rangle. \tag{2-9}$$

It can be seen from the last equation that $\Psi(\underline{r})$ is not necessarily an eigenfunction of $\mathcal{H}_{1_{int}} + \mathcal{H}_{2_{int}}$.

Since the total energy of the system is conserved, $\mathcal{E}$ can be expressed as

$$\mathcal{E} = \frac{p^2}{2\mu} + \epsilon_i = \frac{(p')^2}{2\mu} + \epsilon_{i'} \qquad (2\text{-}10)$$

where the left hand side of the equation refers to the total energy of the system before collision, and the right hand side, to the total energy after collision. Only elastic scattering will be discussed in this thesis; that is, none of the translational energy of the system is transferred to the internal states (and vice versa). Consequently, the kinetic and internal state energies are separately conserved and, in fact, ϵ_i becomes independent of the internal state labelling. Since the internal states are degenerate, they can still change within the internal state energy shell. Now the right hand side of Eq. (2-9) is a multiple of $\Psi(\underset{\sim}{r})$, and for elastic scattering, Eq. (2-1) becomes

$$\left[\frac{\hbar^2}{2\mu}\nabla^2_{\underset{\sim}{r}} + \frac{\hbar^2 k^2}{2\mu}\right]\Psi_{\underset{\sim}{k}}(\underset{\sim}{r}) = V_{int}(\underset{\sim}{r})\,\Psi_{\underset{\sim}{k}}(\underset{\sim}{r}) \,. \qquad (2\text{-}11)$$

The wavenumber k is related to the total energy $\mathcal{E}$ and the internal energy ϵ by

$$\mathcal{E} - \epsilon \equiv \frac{\hbar^2}{2\mu} k^2$$

$$\equiv E. \qquad (2\text{-}12)$$

The wave vector $\underline{k}$ is defined in terms of the relative linear momentum $\underline{p}$ by means of the equation

$$\hbar \underset{\sim}{k} \equiv \underset{\sim}{p}$$

$$\equiv \mu \underset{\sim}{g} \qquad (2\text{-}13)$$

where $\underline{g}$ is the relative velocity of the two molecules. For elastic scattering the wavenumber must be the same before and after the collision, i.e.,

$$|\underset{\sim}{k}| = |\underset{\sim}{k}'| = k. \qquad (2\text{-}14)$$

If Eq. (2-11) is rewritten to look like an inhomogeneous differential equation,

$$\left[\frac{\hbar^2}{2\mu}\nabla_{\underset{\sim}{r}}^2+E\right]\Psi_{\underset{\sim}{k}}(\underset{\sim}{r}) = V_{int}(\underset{\sim}{r})\,\Psi_{\underset{\sim}{k}}(\underset{\sim}{r})$$

$$\equiv \eta(\underset{\sim}{r}), \tag{2-15}$$

then by standard Green's function techniques[5], Eq. (2-15) can be expressed as the integral equation

$$\Psi_{\underset{\sim}{k}}(\underset{\sim}{r}) = \int G(\underset{\sim}{r},\underset{\sim}{r}')\,V_{int}(\underset{\sim}{r}')\,\Psi_{\underset{\sim}{k}}(\underset{\sim}{r}')\,d\underset{\sim}{r}'. \tag{2-16}$$

The Green's function $G(\underline{r},\underline{r}')$ is a solution of the equation

$$\left[\frac{\hbar^2}{2\mu}\nabla_{\underset{\sim}{r}}^2+E\right]G(\underset{\sim}{r},\underset{\sim}{r}') = \delta(\underset{\sim}{r}-\underset{\sim}{r}'), \tag{2-17}$$

where $\delta(\underline{r}-\underline{r}')$ is the three-dimensional Dirac delta function.

The solution $\Psi_{\underline{k}}(\underline{r})$ to Eq. (2-15) is completely defined by asymptotic boundary conditions imposed on it by the collision process. $\Psi_{\underline{k}}(\underline{r})$ must essentially be the sum of an incoming plane wave plus an outgoing spherical scattered wave. The explicit boundary condition is thus

$$\Psi^{(+)}_{\underset{\sim}{k},i}(\underset{\sim}{r}) \xrightarrow[r\to\infty]{} h^{-3/2}\left[e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}|i\rangle + f_i(\theta,\phi)\frac{e^{ikr}}{r}\right]. \tag{2-18}$$

$\Psi^{(+)}_{\underline{k},i}(\underline{r})$ designates that $\Psi_{\underline{k}}(\underline{r})$ consists of a free particle incident wave plus an outgoing spherical scattered wave. The subscript i is a reminder that the incoming plane wave has a particular internal state $|i\rangle$ associated with it. Analogously, $\Psi^{(-)}_{\underline{k},i}(\underline{r})$ designates the sum of a free particle outgoing wave in internal state i, plus an incoming spherical wave.

The particular solution

$$G^{(+)}(\underset{\sim}{r},\underset{\sim}{r}') = \left(\frac{-2\mu}{4\pi\hbar^2}\right)\cdot\frac{\exp(ik|\underset{\sim}{r}-\underset{\sim}{r}'|)}{|\underset{\sim}{r}-\underset{\sim}{r}'|} \tag{2-19}$$

to Eq. (2-17) is chosen because it represents an outgoing spherical wave (originating at $\underline{r}'$). Since $G^{(+)}(\underline{r},\underline{r}')$ only partially satisfies the asymptotic boundary conditions on

$\Psi_{\underline{k}}(\underline{r})$, Eq. (2-16) cannot represent the entire solution of the inhomogeneous differential equation. Consequently, if another term were added to the right hand side of Eq. (2-16) in such a way as to fulfill the plane wave portion of the boundary condition, Eq. (2-18), then the expression for $\Psi^{(+)}_{\underline{k},i}(\underline{r})$ as a solution to Eq. (2-15) would be complete. The appropriate term is the particular free particle wave function $\phi_{\underline{k},i}(\underline{r})$ which satisfies the equation.

$$\left[\frac{\hbar^2}{2\mu}\nabla_{\underset{\sim}{r}}^2 + E\right]\phi_{\underset{\sim}{k},i}(\underset{\sim}{r}) = 0. \qquad (2\text{-}20)$$

Eq. (2-20) is, of course, just Eq. (2-7) for an elastic scattering process. Now the complete formal solution to Eq. (2-15) is

$$\Psi^{(+)}_{\underset{\sim}{k},i}(\underset{\sim}{r}) = \phi_{\underset{\sim}{k},i}(\underset{\sim}{r}) + \int G^{(+)}(\underset{\sim}{r},\underset{\sim}{r}')V(\underset{\sim}{r}')\Psi^{(+)}_{\underset{\sim}{k},i}(\underset{\sim}{r}')d\underset{\sim}{r}'. \qquad (2\text{-}21)$$

The manipulations in the preceding paragraphs become more transparent when Eqs. (2-15), (2-16), (2-20), and (2-21) are cast into operator form:

$$(E - H_0)\, \Psi_{\underset{\sim}{k}} = V \Psi_{\underset{\sim}{k}} \quad , \tag{2-22}$$

$$\Psi_{\underset{\sim}{k}} = G V \Psi_{\underset{\sim}{k}} \quad , \tag{2-23}$$

$$(E - H_0)\, \phi_{\underset{\sim}{k}, i} = 0 \quad , \tag{2-24}$$

and

$$\Psi^{(+)}_{\underset{\sim}{k}, i} = \phi_{\underset{\sim}{k}, i} + G^{(+)} V \Psi^{(+)}_{\underset{\sim}{k}, i} \quad . \tag{2-25}$$

The free particle Hamiltonian H_0 which acts on wave functions in position representation is

$$H_0 = \frac{-\hbar^2}{2\mu} \nabla^2_{\underset{\sim}{r}} \quad . \tag{2-26}$$

Formally, the Green's function G is just the inverse of the appropriate differential operator. For example, with respect to Eq. (2-17) G can be written as

$$G = (E-H_0)^{-1} \tag{2-27}$$

where E, an eigenvalue of H_0, is understood to be a multiple of the identity operator. However, when (physical) boundary conditions are incorporated into the Green's function, as they are in Eq. (2-25), then the solution of Eq. (2-17) is chosen to be in the form of Eq. (2-19) and G becomes $G^{(+)}$. The operator expression for $G^{(\pm)}$ is

$$G^{(\pm)} = (E-H_0 \pm i\epsilon)^{-1}. \tag{2-28}$$

Another interesting and important integral equation is that for the scattering amplitude $f_i(\theta, \phi)$ which appeared in the boundary condition for $\Psi^{(+)}_{\underline{k},i}(\underline{r})$, Eq. (2-18). Far away from the influence of the interaction potential $V(\underline{r}')$, i.e., $r \gg r'$, $|\underline{r}-\underline{r}'|$ can be expanded in the following manner:

$$|\mathbf{r}-\mathbf{r}'| = \left[(\mathbf{r}-\mathbf{r}')\cdot(\mathbf{r}-\mathbf{r}')\right]^{1/2}$$

$$= r\left[1 - 2\hat{r}\cdot\frac{\mathbf{r}'}{r} + \left(\frac{r'}{r}\right)^2\right]^{1/2}$$

$$= r\left[1 - \hat{r}\cdot\frac{\mathbf{r}'}{r} - \frac{1}{2}\left(\hat{r}\cdot\frac{\mathbf{r}'}{r}\right)^2 + \cdots\right]$$

$$\simeq r - \hat{r}\cdot\mathbf{r}' \,. \tag{2-29}$$

If this asymptotic expansion is used in Eq. (2-21), then

$$\Psi^{(+)}_{\mathbf{k},i}(\mathbf{r}) = h^{-3/2} e^{i\mathbf{k}\cdot\mathbf{r}}|i\rangle - \frac{2\mu}{4\pi\hbar^2}\int \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} V(\mathbf{r}')\Psi^{(+)}_{\mathbf{k},i}(\mathbf{r}')d\mathbf{r}'$$

$$\simeq h^{-3/2} e^{i\mathbf{k}\cdot\mathbf{r}}|i\rangle + \frac{e^{ikr}}{r}\left(\frac{-2\mu}{4\pi\hbar^2}\right)\int e^{-i\mathbf{k}'\cdot\mathbf{r}'} V(\mathbf{r}')\Psi^{(+)}_{\mathbf{k},i}(\mathbf{r}')d\mathbf{r}' \,,$$

$$r \gg r'$$

(2-30)

where $\underline{k}' \equiv k\hat{r}$. Comparison of Eq. (2-30) with the boundary condition on $\Psi^{(+)}_{\underline{k},i}(\underline{r})$, Eq. (2-18), allows the scattering amplitude f_i (which is still an abstract vector in internal state space) to be identified as

$$f_i = \frac{-2\mu h^{3/2}}{4\pi \hbar^2} \int e^{-i\underset{\sim}{k}'\cdot\underset{\sim}{r}'} V(\underset{\sim}{r}')\, \Psi^{(+)}_{\underset{\sim}{k},i}(\underset{\sim}{r}')\, d\underset{\sim}{r}'$$

$$= \frac{-2\mu}{4\pi\hbar^2} \int h^3 \langle \underset{\sim}{p}'|\underset{\sim}{r}'\rangle\langle \underset{\sim}{r}'|V|\Psi^{(+)}_{\underset{\sim}{k},i}\rangle\, d\underset{\sim}{r}'$$

$$= -2\pi h \mu \langle \underset{\sim}{p}'|V|\Psi^{(+)}_{\underset{\sim}{k},i}\rangle \qquad (2\text{-}31)$$

where Eq. (2-5) was used without internal states. The bra $\langle \underline{p}'|$ represents the asymptotic final state of momentum $\underline{p}'$ into which the particle has been scattered.

Eq. (2-21) can be written in the form

$$\Psi^{(+)}_{\underset{\sim}{k},i} = \Omega^{(+)} \phi_{\underset{\sim}{k},i}$$

$$= \Omega^{(+)} |\underset{\sim}{p},i\rangle \qquad (2\text{-}32)$$

where $\Omega^{(\pm)}$ is the Moeller wave operator. $\Omega^{(+)}$ has the property that it takes the initial incoming plane wave $\langle \underline{r} | \underline{p}, i \rangle$ into the full scattered wave $\Psi^{(+)}_{\underline{k},i}(\underline{r})$. Eq. (2-32) can be used in Eq. (2-31) in order to express the scattering amplitude as a matrix element between the asymptotic incoming and asymptotic outgoing plane wave states, namely

$$
\begin{aligned}
f_i &= -2\pi\mu h \langle \underline{p}' | V\Omega^{(+)} | \underline{p}, i \rangle \\
&\equiv -2\pi\mu h \langle \underline{p}' | t^{(+)} | \underline{p}, i \rangle \\
&\equiv -2\pi\mu h \left(t^{(+)} \right)^{\underline{g}'}_{\underline{g}} | i \rangle .
\end{aligned}
\tag{2-33}
$$

The operator $V\Omega$ is sufficiently important to be given the symbol, t, denoting the transition operator. Note that t is an operator in both momentum space and internal state space while $t^{\underline{g}'}_{\underline{g}}$ is a matrix element in momentum space, but still an operator in internal state space.

If Eq. (2-25) is rewritten in terms of the Moeller wave operator, then the Lippmann-Schwinger integral equation for Ω is obtained, viz.

$$
\Omega = 1 + GV\Omega . \tag{2-34}
$$

An integral equation for t can be written down by substituting Eq. (2-34) into $V\Omega$ to obtain

$$t = V\Omega = V + VGt. \qquad (2\text{-}35)$$

It is vital to notice that the Green's function in Eq. (2-35) contains only the free particle Hamiltonian, H_0, as opposed to the total Hamiltonian.

Now suppose that the potential V is written as a sum of two potentials: one isotropic and denoted by V_0, and the other anisotropic and denoted by V_1. The Schroedinger equation appropriate for describing a system governed by these potentials is

$$\left[E-(H_0+V_0)\right]\Psi_{\underset{\sim}{k},i} = V_1\Psi_{\underset{\sim}{k},i}. \qquad (2\text{-}36)$$

The technique and argument used earlier to solve Eq. (2-15) can be employed again to write a formal solution for Eq. (2-36), namely

$$\Psi^{(+)}_{\underset{\sim}{k},i} = \chi^{(+)}_{\underset{\sim}{k}}|i\rangle + G_0^{(+)}V_1\Psi^{(+)}_{\underset{\sim}{k},i}$$

(2-37)

where $\chi_{\underline{k}}^{(+)}$ is a solution to

$$[E-(H_0+V_0)]\chi_{\underline{k}} = 0 \tag{2-38}$$

with the same kind of boundary condition imposed on $\chi_{\underline{k}}$ as was imposed on $\Psi_{\underline{k},i}^{(+)}$ in Eq. (2-18). The Green's function G_0 satisfies the equation

$$[E-(H_0+V_0)]G_0 = \delta \tag{2-39}$$

where δ is the Dirac delta function.

The physically relevant solution to Eq. (2-38), $\chi_{\underline{k}}^{(+)}$, consists of both a plane wave and an outgoing spherical scattered wave. The scattering is, of course, now due to the isotropic potential. Because the interpretation of $\chi_{\underline{k}}^{(+)}|i\rangle$ in Eq. (2-37) differs from the interpretation of $\phi_{\underline{k},i}$ in the more common representation of $\Psi_{\underline{k},i}^{(+)}$ as given in Eq. (2-25), $\chi_{\underline{k}}^{(+)}|i\rangle$ is often called the "distorted" wave. It is assumed that the effect on $\Psi_{\underline{k},i}$ due to the anisotropic potential, V_1, is small compared to the effect of V_0. Consequently, it is reasonable to solve Eq. (2-37) by iteration. To terms linear in V_1, the distorted-wave Born approximation is obtained, namely

$$\Psi^{(\pm)}_{\underset{\sim}{k},i} = \chi^{(\pm)}_{\underset{\sim}{k}} |i\rangle + G_0^{(\pm)} V_1 \chi^{(\pm)}_{\underset{\sim}{k}} |i\rangle . \qquad (2\text{-}40)$$

Parallel to the decomposition of the potential V into two contributions, the transition operator can be written as a sum of two parts, namely

$$\begin{aligned} t &= t_0 + t_1 \\ &= (V_0 + V_1) + (V_0 + V_1)\, G(t_0 + t_1) \end{aligned} \qquad (2\text{-}41)$$

where G is given by Eq. (2-17). Upon expansion of Eq. (2-41) the "isotropic" transition operator, t_0, and the "anisotropic" transition operator, t_1, can be naturally identified. They are

$$\begin{aligned} t_0 &= V_0 + V_0\, G\, t_0 \\ &\equiv V_0 \Omega_0 \end{aligned} \qquad (2\text{-}42)$$

where Ω_0 is defined as in Eq. (2-34) but with V replaced by V_0, and

$$t_1 = V_1 + V_1\, G\, t_0 + V_0\, G\, t_1 + V_1\, G\, t_1 . \qquad (2\text{-}43)$$

In the DWBA the last term in Eq. (2-43) is dropped on the basis that it is quadratic in V_1. Eq. (2-43) can then be rearranged into the form

$$(1 - V_0\, G)t_1 \;=\; V_1 \Omega_0 \tag{2-44}$$

which implies that

$$t_1 \;=\; (1 - V_0\, G)^{-1}\, V_1 \Omega_0. \tag{2-45}$$

The last equation can be made more useful by obtaining another expression for $(1 - V_0\, G)^{-1}$ or, essentially, for $V_0 G$. If both sides of Eq. (2-42) are multiplied from the right by G and the resulting terms rearranged, then

$$V_0 G \;=\; t_0\, G(1 + t_0 G)^{-1} \tag{2-46}$$

and

$$\begin{aligned}(1 - V_0\, G)^{-1} &= \left[1 - t_0\, G(1 + t_0\, G)^{-1}\right]^{-1} \\ &= 1 + t_0\, G \\ &= \Omega_0^{\,t}.\end{aligned} \tag{2-47}$$

The superscript t on the "isotropic" Moeller wave operator Ω_0 denotes a transpose. At last, Eq. (2-45) can be written in the final form

$$t_1 = \Omega_0^{t}\; V_1 \Omega_0 \tag{2-48}$$

for the DWBA.

An alternative derivation for Eq. (2-48) is given below. The matrix element $t^{(+)\underline{g}'}_{\underline{g}}$ (which is still an operator in internal state space) can be written down from Eq. (2-33) as

$$(t^{(+)})^{g'}_{g}/i\rangle \equiv (-2\pi\mu\hbar)^{-1} f_i \qquad (2\text{-}49)$$
$$= \langle p'|V_0|\Psi^{(+)}_{\underline{k},i}\rangle + \langle p'|V_1|\Psi^{(+)}_{\underline{k},i}\rangle.$$

In the term $\langle \underline{p}'| V_1 | \Psi^{(+)}_{\underline{k},i}\rangle$, $\langle \underline{p}'|$ can be rewritten in terms of the distorted wave $\langle \chi^{(-)}_{\underline{k}'}|$ in the following manner.

First, the solution to Eq. (2-38) can be found analogously to the solution of Eq. (2-15), namely

$$\chi^{(\pm)}_{\underline{k}} = |\underline{p}\rangle + G^{(\pm)}_{\underline{g}} \; V_0 \chi^{(\pm)}_{\underline{k}}. \qquad (2\text{-}50)$$

By means of the algebraic relation

$$A^{-1} - B^{-1} = A^{-1}\,(B-A)\,B^{-1} \qquad (2\text{-}51)$$

the free particle Green's function, $G^{(\pm)}$, can be replaced by the expression

$$G^{(\pm)} \equiv (E - H_0 \pm i\epsilon)^{-1}$$

$$= (E - H_0 - V_0 \pm i\epsilon)^{-1} - (E - H_0 - V_0 \pm i\epsilon)^{-1} V_0 (E - H_0 \pm i\epsilon)^{-1}$$

$$= G_0^{(\pm)} - G_0^{(\pm)} V_0 G^{(\pm)} . \qquad (2\text{-}52)$$

When Eq. (2-52) is substituted back into Eq. (2-50), the distorted wave can be written exclusively in terms of $|\underline{p}\rangle$, viz.

$$\chi_{\underset{\sim}{k}}^{(\pm)} = |p\rangle + G_0^{(\pm)} V_0 \chi_{\underset{\sim}{k}}^{(\pm)} - G_0^{(\pm)} V_0 \left[\chi_{\underset{\sim}{k}}^{(\pm)} - |p\rangle \right]$$

$$= |p\rangle + G_0^{(\pm)} V_0 |p\rangle . \qquad (2\text{-}53)$$

Finally, the substitution of $|\underline{p}\rangle$ from Eq. (2-53) into $\langle \underline{p}' | V_1 | \Psi_{\underline{k},i}^{(+)} \rangle$ of Eq. (2-49) yields

$$(t^{(+)})_{q}^{q'}/i\rangle = \langle p'/V_0/\Psi_{\underset{\sim}{k},i}^{(+)}\rangle + \langle \chi_{\underset{\sim}{k}'}^{(-)}/V_1/\Psi_{\underset{\sim}{k},i}^{(+)}\rangle$$

$$- \langle p'/[G_0^{(-)}V_0]^{\dagger}V_1/\Psi_{\underset{\sim}{k},i}^{(+)}\rangle$$

$$= \langle p'/V_0/\Psi_{\underset{\sim}{k},i}^{(+)}\rangle + \langle \chi_{\underset{\sim}{k}'}^{(-)}/V_1/\Psi_{\underset{\sim}{k},i}^{(+)}\rangle$$

$$- \langle p'/V_0 G_0^{(+)} V_1/\Psi_{\underset{\sim}{k},i}^{(+)}\rangle$$

$$= \langle p'/V_0/\chi_{\underset{\sim}{k},i}^{(+)}\rangle + \langle \chi_{\underset{\sim}{k}'}^{(-)}/V_1/\Psi_{\underset{\sim}{k},i}^{(+)}\rangle$$

(2-54)

where the superscript "$\dagger$" denotes an adjoint. In this case the adjoint is taken in position space, but since $\left[G_0^{(-)}\ V_0\right]^{\dagger}$

is the identity in internal state space, the distinction of which space the adjoint is defined in, is pedagogical. The last step in Eq. (2-54) requires the recognition of Eq. (2-37), namely

$$V_0 \chi_{\underset{\sim}{k}}^{(+)} |i\rangle = V_0 \left[\Psi_{\underset{\sim}{k},i}^{(+)} - G_0^{(+)} V_1 \Psi_{\underset{\sim}{k},i}^{(+)} \right] \tag{2-55}$$

in the first and third terms of the second line of Eq. (2-54).

If Eq. (2-51) is used to express G_0 in terms of G_H, i.e.,

$$G_0 = G_H - G_H V_1 G_0 \tag{2-56}$$

where G_H is the Green's function for the total Hamiltonian $H_0 + V_0 + V_1$, then $\Psi_{\underline{k},i}^{(+)}$ in Eq. (2-37) can be written exclusively in terms of $\chi_{\underline{k}}^{(+)} | i \rangle$, viz.

$$\Psi_{\underset{\sim}{k},i}^{(+)} = \chi_{\underset{\sim}{k}}^{(+)} |i\rangle + G_H^{(+)} V_1 \chi_{\underset{\sim}{k}}^{(+)} |i\rangle . \tag{2-57}$$

This equation (Eq. (2-46)) allows $t^{(+)}{}^{\underline{g}'}_{\underline{g}}$ in Eq. (2-54) to be re-expressed as

$$\left(t^{(+)}\right)_{g}^{g'} = \langle p' | V_0 \Omega_0^{(+)} | p \rangle + \langle \chi_{\underset{\sim}{k}'}^{(-)} | V_1 | \chi_{\underset{\sim}{k}}^{(+)} + G_H^{(+)} V_1 \chi_{\underset{\sim}{k}}^{(+)} \rangle$$

$$\simeq \langle p' | V_0 \Omega_0^{(+)} | p \rangle + \langle \chi_{\underline{k}'}^{(-)} | V_1 | \chi_{\underline{k}}^{(+)} \rangle \tag{2-58}$$

where the DWBA has been used. The operator $V_0 \Omega_0$ can be immediately identified as the "isotropic" transition operator t_0.

A new transition operator t_2 can be defined from Eq. (2-35) by using V_1 as the potential and G_0 as the Green's function, namely

$$\begin{aligned} t_2 &= V_1 + V_1 G_0 t_2 \\ &= V_1 + V_1 (G_H - G_H V_1 G_0) t_2 \\ &= V_1 + V_1 G_H t_2 - V_1 G_H (t_2 - V_1) \\ &= V_1 + V_1 G_H V_1 \end{aligned} \tag{2-59}$$

where G_H is still the Green's function for the total Hamiltonian, $H \equiv H_0 + V_0 + V_1$. Eq. (2-59) appears in Eq. (2-58) in the term $\langle \chi_{\underline{k}'}^{(-)} | V_1 + V_1 G_H V_1 | \chi_{\underline{k}}^{(+)} \rangle$ clarifying its physical interpretation as a matrix element of a transition operator between two distorted waves, each governed by the isotropic potential, V_0, but whose interaction is governed by the anisotropic potential, V_1.

The DWBA of this particular matrix element, namely $\langle \chi_{\underline{k}'}^{(-)} | V_1 | \chi_{\underline{k}}^{(+)} \rangle$ can be further manipulated to yield

$$\begin{aligned}
\langle \chi_{\underset{\sim}{k}'}^{(-)} | V_1 | \chi_{\underset{\sim}{k}}^{(+)} \rangle &= \langle \Omega_0^{(-)} \underset{\sim}{p}' | V_1 | \Omega_0^{(+)} \underset{\sim}{p} \rangle \\
&= \langle \underset{\sim}{p}' | [\Omega_0^{(-)}]^{\dagger} V_1 \Omega_0^{(+)} | \underset{\sim}{p} \rangle \\
&\equiv \langle \underset{\sim}{p}' | t_1^{(+)} | \underset{\sim}{p} \rangle \\
&\equiv \left(t_1^{(+)} \right)_{\underset{\sim}{q}}^{\underset{\sim}{q}'}
\end{aligned} \tag{2-60}$$

where a natural identification of $t_1^{(+)}$ as $\left[\Omega_0^{(-)}\right]^{\dagger} V_1 \Omega_0^{(+)}$ has been made.

The adjoint of $\Omega_0^{(-)}$ can be re-expressed as the transpose of $\Omega_0^{(+)}$ in the following way:

$$\left[\Omega_0^{(-)}\right]^\dagger = \left[1 + G^{(-)}V_0\Omega_0^{(-)}\right]^\dagger$$

$$= \left[1 + (G_0^{(-)} - G_0^{(-)}V_0G^{(-)})V_0\Omega_0^{(-)}\right]^\dagger$$

$$= \left[1 + G_0^{(-)}V_0\right]^\dagger$$

$$= 1 + V_0G_0^{(+)}$$

$$\equiv \left[\Omega_0^{(+)}\right]^t . \tag{2-61}$$

Consequently t_1 becomes $\Omega_0^t V_1 \Omega_0$ which is Eq. (2-48).

CHAPTER III

CALCULATION OF $(t_1^{(+)})_{\underline{g}}^{\underline{g}'}$

In the previous chapter the expression $\Omega\, {}_0^tV_1\Omega_0$, Eq. (2-48) was derived for the DWBA to the anisotropic transition operator for a system with two potentials. Now that Eq. (2-48) or, equivalently, Eq. (2-60) has been established, matrix elements of the anisotropic transition operator in momentum space can be calculated once the isotropic and anisotropic potentials are specified. The overall object of this chapter is to exhibit the calculation of the partial matrix element $(t_1)_{\underline{g}}^{\underline{g}'}$ for a rigid sphere potential V_0, namely

$$V_0(\underline{r}) = \infty\ , \quad r \leq \sigma$$
$$= 0\ , \quad r > \sigma \tag{3-1}$$

where σ is the diameter of the rigid spheres, and for a dipole-dipole nuclear spin interaction potential V_1. The latter potential is given by

$$V_1(\mathbf{r}) = 3\gamma^2\hbar^2\left[\frac{\mathbf{r}\mathbf{r} - (1/3)r^2\mathbf{U}}{r^5}\right] : \left[\frac{\mathbf{I}_1\mathbf{I}_2 + \mathbf{I}_2\mathbf{I}_1}{2} - (1/3)\mathbf{I}_1\cdot\mathbf{I}_2\,\mathbf{U}\right] \tag{3-2}$$

where $\mathbf{I}_1$ and $\mathbf{I}_2$, the nuclear spins of molecules 1 and 2 respectively, are separated by the relative coordinate $\mathbf{r}$.

$(t_1)_{\mathbf{g}}^{\mathbf{g}'}$ from Eq. (2-60) can be written with V_1 in position representation as

$$\begin{aligned}
(t_1^{(\pm)})_{\mathbf{g}}^{\mathbf{g}'} &= \langle \chi_{\mathbf{k}'}^{(\mp)} | V_1 | \chi_{\mathbf{k}}^{(\pm)} \rangle \\
&= \iint d\mathbf{r}\, d\mathbf{r}' \langle \chi_{\mathbf{k}'}^{(\mp)} | \mathbf{r} \rangle \langle \mathbf{r} | V_1 | \mathbf{r}' \rangle \langle \mathbf{r}' | \chi_{\mathbf{k}}^{(\pm)} \rangle \\
&= \iint d\mathbf{r}\, d\mathbf{r}' \langle \mathbf{r} | \chi_{\mathbf{k}'}^{(\mp)} \rangle^{*} \delta(\mathbf{r}-\mathbf{r}') V_1(\mathbf{r}) \langle \mathbf{r}' | \chi_{\mathbf{k}}^{(\pm)} \rangle \\
&= \int d\mathbf{r}\, \chi_{\mathbf{k}'}^{(\mp)*}(\mathbf{r})\, V_1(\mathbf{r})\, \chi_{\mathbf{k}}^{(\pm)}(\mathbf{r}) \\
&= \int d\mathbf{r}\, \chi_{-\mathbf{k}'}^{(\pm)}(\mathbf{r})\, V_1(\mathbf{r})\, \chi_{\mathbf{k}}^{(\pm)}(\mathbf{r})
\end{aligned} \tag{3-3}$$

where the equality

$$\chi^{(\mp)*}_{\underset{\sim}{k}'}(\underset{\sim}{r}) = \chi^{(\pm)}_{-\underset{\sim}{k}'}(\underset{\sim}{r}) \tag{3-4}$$

has been used. Eq. (3-4) can be derived starting from Eq. (2-53) in the following manner, namely

$$\begin{aligned}
\chi^{(\mp)*}_{\underset{\sim}{k}'}(\underset{\sim}{r}) &= \langle \underset{\sim}{r} | \chi^{(\mp)}_{\underset{\sim}{k}'} \rangle^* \\
&= \langle \underset{\sim}{r} | \underset{\sim}{p}' \rangle^* + \iint d\underset{\sim}{r}' d\underset{\sim}{r}'' \langle \underset{\sim}{r} | G^{(\mp)} | \underset{\sim}{r}' \rangle^* \langle \underset{\sim}{r}' | V_0 | \underset{\sim}{r}'' \rangle^* \langle \underset{\sim}{r}'' | \underset{\sim}{p}' \rangle^* \\
&= h^{-3/2} e^{i(-\underset{\sim}{k}')\cdot \underset{\sim}{r}} + \int d\underset{\sim}{r}' \, G^{(\pm)}(\underset{\sim}{r}, \underset{\sim}{r}') V_0(\underset{\sim}{r}') h^{-3/2} e^{i(-\underset{\sim}{k}')\cdot \underset{\sim}{r}'} \\
&= \langle \underset{\sim}{r} | -\underset{\sim}{p}' \rangle + \int d\underset{\sim}{r}' \, G^{(\pm)}(\underset{\sim}{r}, \underset{\sim}{r}') V_0(\underset{\sim}{r}') \langle \underset{\sim}{r}' | -\underset{\sim}{p}' \rangle \\
&= \chi^{(\pm)}_{-\underset{\sim}{k}'}(\underset{\sim}{r}) \; .
\end{aligned} \tag{3-5}$$

It is clear from Eq. (3-1) that the distorted wave $\chi_{\underline{k}}(\underline{r})$ is the solution to a Schroedinger equation with a rigid sphere potential. For $r > \sigma$, $\chi_{\underline{k}}(\underline{r})$ satisfies

$$(\nabla_{\underset{\sim}{r}}^2 + k^2)\,\chi_{\underset{\sim}{k}}(\underset{\sim}{r}) = 0\,. \tag{3-6}$$

Since the rigid sphere (and, in general, any central potential) problem has cylindrical symmetry about the direction of the incoming momentum $\hat{k} \equiv \hat{z}$, the only angle dependence left in $\chi_{\underline{k}}(\underline{r})$ is $\theta \equiv \hat{k}\cdot\hat{r}$. Therefore, for a solution in spherical polar coordinates $\chi_{\underline{k}}(\underline{r})$ can be expanded in terms of Legendre polynomials, $P_\ell(\cos\theta)$, as

$$\chi_{\underset{\sim}{k}}(r,\theta) = \sum_{\ell=0}^{\infty} \zeta_\ell(kr)\,P_\ell(\cos\theta)\,. \tag{3-7}$$

Eq. (3-6) now becomes

$$(\nabla_{r,\theta}^2 + k^2)\,\chi_{\underset{\sim}{k}}(r,\theta)$$

$$= \sum_{\ell=0}^{\infty} P_\ell(\cos\theta)\left[\frac{\partial^2 \zeta_\ell(kr)}{\partial r^2} + \frac{2\,\partial \zeta_\ell(kr)}{r\,\partial r}\right.$$

$$+\left(k^2 - \frac{\ell(\ell+1)}{r^2}\right)\zeta_\ell(kr)\Big]$$

$$= 0 \, . \tag{3-8}$$

Since the P_ℓ's are linearly independent, $\zeta_\ell(kr)$ must satisfy

$$\frac{\partial^2 \zeta_\ell(kr)}{\partial r^2} + \frac{2}{r}\frac{\partial \zeta_\ell(kr)}{\partial r} + \left(k^2 - \frac{\ell(\ell+1)}{r^2}\right)\zeta_\ell(kr) = 0 \tag{3-9}$$

which can be recognized as the differential equation for spherical Bessel functions[6].

In order to satisfy the usual asymptotic boundary condition imposed by a scattering problem (see Eq. (2-18)), it is convenient to write $\zeta_\ell(kr)$, the solution to Eq. (3-9), in the particular form

$$\zeta_\ell(kr) = C_\ell\left[j_\ell(kr) - W_\ell(k\sigma)\, h_\ell^{(1)}(kr)\right]$$

$$\equiv C_\ell\, \chi_\ell(kr) \, . \tag{3-10}$$

$h_\ell^{(1)}(kr)$, the spherical Hankel function of the first kind[7,*], behaves asymptotically as an outgoing spherical wave, i. e.,

$$h_\ell^{(1)}(kr) \xrightarrow[r\to\infty]{} (-kr)^{-1}\left[\exp i(kr-(\ell+1)\pi/2)\right], \tag{3-11}$$

while the spherical Hankel function of the second kind, $h_\ell^{(2)}(kr)$, represents an incoming spherical wave. The latter function is, in fact, the complex conjugate of $h_\ell^{(1)}(kr) \equiv h_\ell(kr)$. The plane wave portion of the asymptotic boundary condition on $\chi_\ell(kr)$ is fulfilled by the particular linear combination of spherical Hankel functions which is regular at the origin, namely

$$(1/2)\left[h_\ell(kr) + h_\ell^*(kr)\right] \equiv j_\ell(kr) \tag{3-12}$$

---

* Note that the spherical Hankel functions of the first kind appear to be defined differently in Messiah[7] and in Morse and Feshbach, Vol. II, p.1573, but, in fact, the $h_\ell^{(1)}(z)$ and $h_\ell(z)$ respectively, are exactly the same. It is in the definition of the spherical Neumann functions that the two books differ by a minus sign.

where $j_\ell(kr)$ is the spherical Bessel function. The other obvious real, linearly independent linear combination of $h_\ell(kr)$ and $h_\ell^*(kr)$, namely

$$(i/2)\left[h_\ell(kr) - h_\ell^*(kr)\right] \equiv n_\ell(kr), \tag{3-13}$$

defines the spherical Neumann function $n_\ell(kr)$, which is irregular at the origin. The constants C_ℓ and W_ℓ in Eq. (3-10) are chosen to satisfy the boundary conditions on the rigid sphere radial wavefunction, $\zeta_\ell(kr)$, both at infinity and at $r = \sigma$.

The former constant, C_ℓ, can be determined by comparing the asymptotic form of the partial wave expansion of $\exp(i\underline{k}\bullet\underline{r})$ in

$$\chi_{\underset{\sim}{k}}^{(+)}(\underset{\sim}{r}) \xrightarrow[r\to\infty]{} r^{-3/2}\left[e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} + f(\theta)\frac{e^{ikr}}{r}\right] \tag{3-14}$$

with the asymptotic expansion of $j_\ell(kr)$ from Eq. (3-10) in $\chi_{\underline{k}}^{(+)}(r,\theta)$. The partial wave expansion of a plane wave is

$$e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} = \sum_{l=0}^{\infty} i^{l}(2l+1)\, j_{l}(kr)\, P_{l}(\cos\theta),$$

(3-15)

and as r approaches infinity, $e^{i\underline{k}\cdot\underline{r}}$ becomes

$$e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} \xrightarrow[r\to\infty]{} \sum_{l=0}^{\infty} i^{l}(2l+1)(kr)^{-1}\left[\cos\left(kr-(l+1)\frac{\pi}{2}\right)\right] P_{l}(\cos\theta).$$

(3-16)

The term $(kr)^{-1}\left[\cos\left(kr-(l+1)\frac{\pi}{2}\right)\right]$ describes the asymptotic form of the spherical Bessel function $j_{l}(kr)$.

Thus the two specific terms to be compared are

$$\chi_{\underset{\sim}{k}}^{(+)}(\underset{\sim}{r}) \xrightarrow[r\to\infty]{} h^{-3/2}\left[e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} + (\ldots)\right]$$

$$\xrightarrow[r\to\infty]{} h^{-3/2}\sum_{l=0}^{\infty}\left[\left\{i^{l}(2l+1)\left[\cos\left(kr-(l+1)\frac{\pi}{2}\right)\right]+(\ldots)\right\}\right.$$

$$\left.\times\, P_{l}(\cos\theta)\right]$$

(3-17)

and

$$\chi^{(+)}_{\underset{\sim}{k}}(\underset{\sim}{r},\theta) \xrightarrow[r\to\infty]{} \sum_{\ell=0}^{\infty}\left[\left\{C_\ell\,(kr)^{-1}\left[\cos\left(kr-(\ell+1)\frac{\pi}{2}\right)\right]+(\cdots)\right\}\right.$$

$$\left.\times P_\ell(\cos\theta)\right]. \quad (3\text{-}18)$$

From these last two expressions C_ℓ can be identified as

$$C_\ell = k^{-3/2}\, i^\ell (2\ell+1). \quad (3\text{-}19)$$

The second constant W_ℓ is found from the condition that for a rigid sphere potential, the wavefunction must vanish at the molecular diameter, i.e.,

$$\chi_\ell(k\sigma) = 0$$

$$= k^{-3/2}\, i^\ell (2\ell+1)\left[j_\ell(k\sigma) - W_\ell(k\sigma)\, h_\ell(k\sigma)\right].$$

(3-20)

Consequently, $W_{\ell}(k\sigma)$ is the quotient

$$W_{\ell}(k\sigma) = \frac{j_{\ell}(k\sigma)}{h_{\ell}(k\sigma)} \quad . \tag{3-21}$$

Now from Eqs. (3-19) and (3-21), the complete expression for $\chi_{\underline{k}}^{(+)}(\underline{r})$ for a rigid sphere potential is

$$\chi_{\underset{\sim}{k}}^{(+)}(\underset{\sim}{r}) = h^{-3/2} \sum_{\ell=0}^{\infty} i^{\ell}(2\ell+1)\left[j_{\ell}(kr) - W_{\ell}(k\sigma)h_{\ell}(kr)\right] P_{\ell}(\cos\theta)$$

$$= h^{-3/2} \sum_{\ell=0}^{\infty} i^{\ell}(2\ell+1)\,\chi_{\ell}(kr)\,P_{\ell}(\cos\theta). \tag{3-22}$$

It is convenient to write $(t_1^{(+)})_{\underline{g}}^{\underline{g}'}$ from Eqs. (3-3) and (3-2) as*

$$\left(t_1^{(+)}\right)_{\underset{\sim}{g}}^{\underset{\sim}{g}'} \doteq \underset{\approx}{D} : 3\gamma^2 \hbar^2 \left[\underset{\sim}{I}_1 \underset{\sim}{I}_2\right]^{(2)} \tag{3-23}$$

where $\underset{\approx}{D}$ is explicitly given (with the use of Eq. (3-22) in Eq. (3-3) by

$$\underset{\approx}{D} \equiv \int d\underset{\sim}{r}\, \chi_{-\underset{\sim}{k}'}^{(+)}(\underset{\sim}{r}) \left[\frac{\hat{r}\hat{r} - 1/3\,\underset{\approx}{U}}{r^3}\right] \chi_{\underset{\sim}{k}}^{(+)}(\underset{\sim}{r})$$

$$= k^{-3} \sum_{\ell,\ell'=0}^{\infty} \Bigg[i^{(\ell'+\ell)} (2\ell'+1)(2\ell+1) \int_{\sigma}^{\infty} \chi_{\ell'}(kr)\chi_{\ell}(kr)\, \frac{dr}{r}$$

$$\times \iint d\hat{r}\, P_{\ell'}(-\hat{k}'\cdot\hat{r}) P_{\ell}(\hat{k}\cdot\hat{r}) (\hat{r}\hat{r} - 1/3\,\underline{\underline{U}}) \Bigg] \tag{3-24}$$

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* The notation $\left[\underset{-}{I}_1 \underset{-}{I}_2\right]^{(2)}$ means the completely symmetrized and traceless part of the general second rank tensor $\underset{-}{I}_1 \underset{-}{I}_2$. $\left[\underset{-}{I}_1 \underset{-}{I}_2\right]^{(2)}$ is written out explicitly in Eq. (3-2). For a general discussion of Cartesian tensors, see reference 8.

where $\hat{r}$ is the unit vector in the $\underline{r}$ direction. Because the collisions are elastically energetic, the magnitudes (but not the directions) of the wave vectors $-\underline{k}'$ and $\underline{k}$ are the same. The second rank tensor[8] $\underset{\approx}{D}$ breaks up naturally into two integrations: one, over angles and the other, over the magnitude r. The radial integral $\int_{\sigma}^{\infty} \chi_{\ell'}(kr)\chi_{\ell}(kr)\frac{dr}{r}$ will be evaluated first.

Consider the following two differential equations for spherical Bessel functions, namely

$$\frac{1}{r^2}\frac{d}{dr}\left[\frac{r^2 d f_m(k'r)}{dr}\right] + \left[(k')^2 - \frac{m(m+1)}{r^2}\right] f_m(k'r) = 0$$

(3-25a)

and

$$\frac{1}{r^2}\frac{d}{dr}\left[\frac{r^2 d g_n(kr)}{dr}\right] + \left[k^2 - \frac{n(n+1)}{r^2}\right] g_n(kr) = 0.$$

(3-25b)

If Eq. (3-25a) is multiplied through by $g_n(kr)$, and Eq. (3-25b) by $f_m(k'r)$, then after subtraction of the two resulting equations, a simple integration yields

$$\int \left(f_m [r^2 g_n'] - g_n [r^2 f_m'] \right) dr$$

$$= \int \left[(k')^2 - \frac{m(m+1)}{r^2} - k^2 + \frac{n(n+1)}{r^2} \right] g_n f_m r^2 dr$$

$$= r^2 \left[f_m g_n' - g_n f_m' \right] .$$

(3-26)

The prime denotes differentiation with respect to r, and the arguments of f_m and g_n are understood to be k'r and kr respectively. For elastic scattering (k' = k) this last equation becomes

$$\int g_n(kr) f_m(kr) dr = \left[\frac{r^2}{n(n+1) - m(m+1)} \right] \left(f_m g_n' - g_n f_m' \right) .$$

(3-27)

The following equation[6]

$$\frac{(2\ell+1)}{kr} g_\ell(kr) = g_{\ell-1}(kr) + g_{\ell+1}(kr)$$

(3-28)

is valid for all spherical Bessel functions and for those linear combinations of spherical Bessel functions whose coefficients are independent of both ℓ and kr. Thus from this recursion relation, $\chi_\ell(kr)$ in Eq. (3-22) can be rewritten as

$$r^{-1}\chi_\ell(kr) = (2\ell+1)^{-1}k\Big[\chi_{\ell-1} + \chi_{\ell+1} + (W_{\ell-1} - W_\ell)h_{\ell-1} + (W_{\ell+1} - W_\ell)h_{\ell+1}\Big]. \tag{3-29}$$

The form of $\chi_\ell(kr)$ as given in the last equation breaks up the radial integral $\int_\sigma^\infty \chi_{\ell'}(kr)\chi_\ell(kr)\frac{dr}{r}$ into four other integrals, each of which can be easily integrated by means of Eq. (3-27). These four integrals are:

$$\frac{k}{(2\ell+1)}\int_\sigma^\infty \chi_{\ell'}(kr)\chi_{\ell-1}(kr)\,dr = \frac{k}{(2\ell+1)}\left[\frac{r^2}{\ell'(\ell'+1)-\ell(\ell-1)}\right]\left(\chi_{\ell-1}\chi'_{\ell'} - \chi_{\ell'}\chi'_{\ell-1}\right)\Big|_\sigma^\infty, \tag{3-30a}$$

$$\frac{k}{(2\ell+1)}\int_\sigma^\infty \chi_{\ell'}(kr)\,\chi_{\ell+1}(kr)\,dr$$

$$=\frac{k}{(2\ell+1)}\left[\frac{r^2}{\ell'(\ell'+1)-(\ell+1)(\ell+2)}\right]\left(\chi_{\ell+1}\chi'_{\ell'}-\chi_{\ell'}\chi'_{\ell+1}\right)\Bigg|_\sigma^\infty ,$$

(3-30b)

$$\frac{k}{(2\ell+1)}\left[W_{\ell-1}(k\sigma)-W_\ell(k\sigma)\right]\int_\sigma^\infty \chi_{\ell'}(kr)\,h_{\ell-1}(kr)\,dr$$

$$=\frac{k}{(2\ell+1)}\left[\frac{r^2\left(W_{\ell-1}-W_\ell\right)}{\ell'(\ell'+1)-\ell(\ell-1)}\right]\left(h_{\ell-1}\chi'_{\ell'}-\chi_{\ell'}h'_{\ell-1}\right)\Bigg|_\sigma^\infty ,$$

(3-31a)

and

$$\frac{k}{(2\ell+1)}\left[W_{\ell+1}(k\sigma)-W_\ell(k\sigma)\right]\int_\sigma^\infty \chi_{\ell'}(kr)\,h_{\ell+1}(kr)\,dr$$

$$=\frac{k}{(2\ell+1)}\left[\frac{r^2\left(W_{\ell+1}-W_\ell\right)}{\ell'(\ell'+1)-(\ell+1)(\ell+2)}\right]\left(h_{\ell+1}\chi'_{\ell'}-\chi_{\ell'}h'_{\ell+1}\right)\Bigg|_\sigma^\infty .$$

(3-31b)

It is to be understood for the remainder of this chapter that if χ_ℓ, j_ℓ, and h_ℓ appear with no functional dependence, as they have just been written, then the argument is kr. Similarly, W_ℓ will be a shorthand notation for $W_\ell(k\sigma)$.

The first thing to notice about Eqs. (3-30 a) and (3-30 b) is that there is no contribution to the integrals at their lower limit because of the boundary condition on $\chi_\ell(kr)$ at $r=\sigma$ for a rigid sphere potential (See Eq. (3-20)). For the same reason $\chi_{\ell'}(kr)h'_{\ell-1}(kr)$ and $\chi_{\ell'}(kr)h'_{\ell+1}(kr)$ in Eqs. (3-31a) and (3-31 b) respectively, vanish at $r=\sigma$. The evaluation of the set of equations Eqs. (3-30a), (3-30b), (3-31a), and (3-31b) at infinity requires more effort.

The right hand side of Eq.(3-30a) in the limit as r approaches infinity will be discussed first. Another recursion relation[6], this time for the derivative of spherical Bessel functions and appropriate linear combinations thereof, is given below

$$\frac{d g_n(z)}{dz} = g_{n-1}(z) - \left(\frac{n+1}{z}\right) g_n(z) . \tag{3-32}$$

Eq. (3-32) is used to rewrite $\chi_{\ell-1}\chi'_{\ell'} - \chi_{\ell'}\chi'_{\ell-1}$ from Eq. (3-30a) so that the limit can be evaluated, i. e.,

$$\lim_{r\to\infty} \frac{k}{(2\ell+1)} \cdot \frac{r^2}{M(\ell',\ell)} \left[\chi_{\ell-1} \chi'_{\ell'} - \chi_{\ell'} \chi'_{\ell-1} \right]$$

$$= \lim_{r\to\infty} \frac{k}{(2\ell+1)} \cdot \frac{r^2}{M(\ell',\ell)} \left\{ \chi_{\ell-1} \left[k\left(j_{\ell'-1} - W_{\ell'} h_{\ell'-1}\right) + \frac{\ell}{r} \chi_{\ell'} \right] \right.$$

$$\left. - \chi_{\ell'} \left[\frac{(\ell'+1)}{r} \chi_{\ell-1} + k\left(j_{\ell-2} - W_{\ell-1} h_{\ell-2}\right) \right] \right\}$$

$$= \frac{1}{(2\ell+1) M(\ell',\ell)} \left[i^{-\ell'+\ell} \left(\tfrac{1}{2} - W_{\ell'}\right) + i^{-\ell+\ell'} \left(\tfrac{1}{2} - W_{\ell-1}\right) \right]$$

(3-33)

where $M(\ell',\ell)$ is defined as

$$M(\ell',\ell) \equiv \ell'(\ell'+1) - \ell(\ell-1) \,. \qquad (3\text{-}34)$$

In order to actually calculate the limit in Eq. (3-33) the asymptotic expressions for $h_\ell(kr)$ and $j_\ell(kr)$ as given in Eqs. (3-11) and (3-16) respectively, are needed. Now the right hand side of Eq. (3-30b) can be written down by inspection, for r approaching infinity, from Eq. (3-33), namely

$$\lim_{r\to\infty} \frac{k}{(2\ell+1)} \cdot \frac{r^2}{N(\ell',\ell)} \left[\chi_{\ell+1} \chi'_{\ell'} - \chi_{\ell'} \chi'_{\ell+1} \right]$$

$$= \frac{-1}{(2\ell+1)N(\ell',\ell)} \left[i^{\ell'-\ell}\left(\tfrac{1}{2} - W_{\ell+1}\right) + i^{\ell-\ell'}\left(\tfrac{1}{2} - W_{\ell'}\right) \right]$$

(3-35)

where

$$N(\ell',\ell) \equiv \ell'(\ell'+1) - (\ell+1)(\ell+2). \qquad (3\text{-}36)$$

The recursion relation Eq. (3-32) is used again to find the limit at infinity of the right hand side of Eq. (3-31a), i. e.,

$$\lim_{r\to\infty} \frac{k}{(2\ell+1)} \left[\frac{r^2\left(W_{\ell-1} - W_{\ell}\right)}{M(\ell',\ell)} \right] \left(h_{\ell-1} \chi'_{\ell'} - \chi_{\ell'} h'_{\ell-1} \right)$$

$$= \lim_{r\to\infty} \frac{k}{(2\ell+1)} \left[\frac{r^2\left(W_{\ell-1} - W_{\ell}\right)}{M(\ell',\ell)} \right] \left[h_{\ell-1} \left\{ \left[\frac{\ell}{r} - \frac{(\ell'+1)}{r} \right] \chi_{\ell'} \right.\right.$$

$$\left.\left. + k\left[j_{\ell'-1} - W_{\ell'} h_{\ell'-1} \right] \right\} - k\, h_{\ell-2}\, \chi_{\ell'}(kr) \right]$$

$$= \frac{i^{-\ell+\ell'}}{(2\ell+1)M(\ell',\ell)}(W_{\ell-1} - W_\ell). \tag{3-37}$$

By inspection of Eq. (3-37) the last upper limit, that in Eq. (3-31b), can be written down. The result is

$$\lim_{r\to\infty} \frac{k}{(2\ell+1)}\left[\frac{r^2(W_{\ell+1} - W_\ell)}{N(\ell',\ell)}\right]\left(h_{\ell+1}\chi'_{\ell'} - \chi_{\ell'}h'_{\ell+1}\right)$$

$$= \frac{-i^{-\ell+\ell'}}{(2\ell+1)N(\ell',\ell)}\left(W_{\ell+1} - W_\ell\right). \tag{3-38}$$

The only remaining evaluations are the two trivial calculations on the non-zero lower limits of Eqs. (3-31a) and (3-31b), namely

$$\frac{k}{(2\ell+1)}\left[\frac{r^2(W_{\ell-1} - W_\ell)}{M(\ell',\ell)}\right] h_{\ell-1}\chi'_{\ell'}\Big|_\sigma$$

$$= \frac{-k^2\sigma^2}{(2\ell+1)M(\ell',\ell)}\left[j_{\ell-1}(k\sigma) - W_\ell h_{\ell-1}(k\sigma)\right]\left[j_{\ell'-1}(k\sigma) - W_{\ell'}h_{\ell'-1}(k\sigma)\right],$$

(3-39)

and

$$\frac{k}{(2\ell+1)}\left[\frac{r^2\left(W_{\ell+1}-W_{\ell}\right)}{N(\ell',\ell)}\right] h_{\ell+1}\,\chi'_{\ell'}\Big|_{\sigma}$$

$$=\frac{-k^2\sigma^2}{(2\ell+1)N(\ell',\ell)}\left[j_{\ell'-1}(k\sigma)-W_{\ell'}h_{\ell'-1}(k\sigma)\right]\left[j_{\ell+1}(k\sigma)-W_{\ell}h_{\ell+1}(k\sigma)\right].$$

(3-40)

Eq. (3-32) has been used again in the above two equations.

Finally the radial integral in Eq. (3-24) can be written down from Eqs. (3-33), (3-35), (3-37), (3-38) (3-39), and (3-40) as

$$\int_{\sigma}^{\infty}\chi_{\ell'}(kr)\chi_{\ell}(kr)\frac{dr}{r}$$

$$=(MN)^{-1}\left[i^{-\ell+\ell'}(2W_{\ell-1}-1)+i^{-\ell'+\ell}(2W_{\ell'}-1)\right]$$

$$-\frac{k^2\sigma^2}{(2\ell+1)}\left[j_{\ell'-1}(k\sigma)-W_{\ell'}h_{\ell'-1}(k\sigma)\right]$$

$$\times\left\{N^{-1}\left[j_{\ell+1}(k\sigma)-W_{\ell}h_{\ell+1}(k\sigma)\right]+M^{-1}\left[j_{\ell-1}(k\sigma)-W_{\ell}h_{\ell-1}(k\sigma)\right]\right\}$$

(3-41)

with the following two restrictions, namely

$$\ell' \neq \ell-1 \tag{3-42a}$$

and

$$\ell' \neq \ell+1 \,. \tag{3-42b}$$

The reason that Eqs. (3-42a) and (3-42b) must be satisfied is to keep the denominator in Eqs. (3-30a,b) and (3-31a,b) finite. Eq. (3-41) can be further simplified by looking at the Wronskian of the spherical Bessel function with a spherical Neumann function.

The Wronskian is

$$j_\ell(z)n'_\ell(z) - j'_\ell(z)n_\ell(z) = -z^2 \tag{3-43 }$$

where the prime now denotes differentiation with respect to z. From the recursion relation Eq. (3-32), and from Eqs. (3-12) and (3-13) for $j_\ell(z)$ and $n_\ell(z)$ respectively, Eq. (3-43) can be re-expressed in terms of spherical Hankel functions as

$$\begin{aligned} -z^2 &= j_\ell(z)n_{\ell-1}(z) - j_{\ell-1}(z)n_\ell(z) \\ &= i/2\left[h_{\ell-1}(z)h^*_\ell(z) - h^*_{\ell-1}(z)h_\ell(z)\right]. \end{aligned} \tag{3-44}$$

An example of how the Wronskian from Eq. (3-44) can be used in Eq. (3-41) is

$$j_{\ell+1}(k\sigma) - W_\ell(k\sigma)h_{\ell+1}(k\sigma)$$

$$= (1/2)\left[h_{\ell+1}(k\sigma) + h^*_{\ell+1}(k\sigma)\right]$$

$$- \frac{(1/2)\left[h_\ell(k\sigma) + h^*_\ell(k\sigma)\right]h_{\ell+1}(k\sigma)}{h_\ell(k\sigma)}$$

$$= \frac{i}{k^2\sigma^2 h_\ell(k\sigma)} . \qquad (3\text{-}45)$$

Furthermore, the entire second term in Eq. (3-41) can be rewritten by means of Eq. (3-44), i. e.,

$$\frac{-k^2\sigma^2}{(2\ell+1)}\left[j_{\ell'-1} - W_{\ell'} h_{\ell'-1}\right]\left[\frac{1}{N(\ell',\ell)}\left(j_{\ell+1} - W_\ell h_{\ell+1}\right) + \frac{1}{M(\ell',\ell)}\left(j_{\ell-1} - W_\ell h_{\ell-1}\right)\right]$$

$$= \frac{1}{M(\ell',\ell)N(\ell',\ell)} \cdot \frac{(-k^2\sigma^2)}{(2\ell+1)} \cdot \frac{(-i)}{k^2\sigma^2 h_{\ell'}}\left[\frac{iM(\ell',\ell)}{k^2\sigma^2 h_\ell} - \frac{iN(\ell',\ell)}{k^2\sigma^2 h_\ell}\right]$$

$$= \frac{1}{M(\ell',\ell)N(\ell',\ell)}\left[\frac{-2}{k^2\sigma^2 h_{\ell'} h_\ell}\right] \qquad (3\text{-}46)$$

where the arguments of j_ℓ, W_ℓ, and h_ℓ are, of course, $k\sigma$.

Now if the expression $(2W_\ell - 1)$, which also appears in Eq. (3-41), is re-expressed in terms of spherical Hankel functions only, namely

$$2W_\ell - 1 = \frac{2j_\ell(k\sigma)}{h_\ell(k\sigma)} - 1$$

$$= \frac{h_\ell^*(k\sigma)}{h_\ell(k\sigma)}, \tag{3-47}$$

where Eq. (3-12) for j_ℓ has been used again, then Eq. (3-41) can be written as a quotient of spherical Hankel functions. Finally, from Eqs. (3-46) and (3-47), Eq. (3-41) becomes

$$\int_\sigma^\infty \chi_{\ell'}(kr)\chi_\ell(kr)\frac{dr}{r}$$

$$= \frac{1}{M(\ell',\ell)N(\ell',\ell)}\left[i^{\ell'-\ell}\frac{h_\ell^*(k\sigma)}{h_\ell(k\sigma)} + i^{\ell-\ell'}\frac{h_{\ell'}^*(k\sigma)}{h_{\ell'}(k\sigma)} - \frac{2}{k^2\sigma^2 h_\ell(k\sigma)h_{\ell'}(k\sigma)}\right]$$

(3-48)

with the restrictions in Eqs. (3-42a) and (3-42b) still valid.

The integrations over angles which remain in $\underset{\approx}{D}$ of Eq. (3-24) could be carried out here explicitly. The calculations would involve the following expression, namely

$$\iint P_{\ell'}(\widehat{-k'}\cdot\hat{r})\,P_{\ell}(\hat{k}\cdot\hat{r})\,(\hat{r}\hat{r}-1/3\,\underset{\approx}{U})\,d\hat{r}$$

$$= A(\widehat{-k'}\,\widehat{-k'} - 1/3\,\underset{\approx}{U}) + B(\hat{k}\hat{k} - 1/3\,\underset{\approx}{U})$$

$$+ C\left[\frac{\widehat{-k'}\,\hat{k} + \hat{k}\,\widehat{-k'}}{2} - \frac{\hat{k}\cdot\widehat{-k'}}{3}\,\underset{\approx}{U}\right], \qquad (3\text{-}49)$$

and then contracting each side of Eq. (3-49) with each of the three $\hat{k}$, $\widehat{-k'}$ second rank tensors in order to find the constants A, B, and C. The three contractions into the right hand side of Eq. (3-49) are straightforward. The contractions into the left hand side of the same equation require that the Addition Theorem for spherical harmonics be used to uncouple $\widehat{-k'}\cdot\hat{r}$ and $\hat{k}\cdot\hat{r}$ so that the $\hat{r}$-integration can be done. However it will be shown in the next chapter that Eq. (3-49) is not needed, and the angle integrations can be carried out in a different, and simpler, manner.

Now Eq. (3-23) can be fully written out as

$$\left(t_1^{(+)}\right)_{g}^{g'} = \underset{\approx}{D} : 3\gamma^2 \hat{k}^2 \left[\underset{\sim}{I}_1 \underset{\sim}{I}_2\right]^{(2)}$$

$$= h^{-3/2} \sum_{\ell',\ell=0}^{\infty} \Bigg\{ i^{\ell'+\ell} (2\ell'+1)(2\ell+1)$$

$$\times \frac{1}{M(\ell',\ell)N(\ell',\ell)} \left[i^{\ell'-\ell} \frac{h_\ell^*(k\sigma)}{h_\ell(k\sigma)} + i^{\ell-\ell'} \frac{h_{\ell'}^*(k\sigma)}{h_{\ell'}(k\sigma)} - \frac{2}{k^2\sigma^2 h_\ell(k\sigma) h_{\ell'}(k\sigma)} \right]$$

$$\times \iint P_{\ell'}(-\hat{k}'\cdot\hat{r}) P_\ell(\hat{k}\cdot\hat{r}) (\hat{r}\hat{r} - 1/3\underset{=}{U}) d\hat{r} \Bigg\} : 3\gamma^2 \hat{k}^2 \left[\underset{\sim}{I}_1 \underset{\sim}{I}_2\right]^{(2)}$$

(3-50)

where $\left[\underline{I}_1 \underline{I}_2\right]^{(2)}$ denotes the completely symmetrized, traceless tensor.

CHAPTER IV

RELAXATION TIME - T_1^{-1}

Chen and Snider have derived an expression for the spin-lattice relaxation time T_1^{-1} for a dilute monatomic gas. This expression for T_1^{-1} contains the partial matrix element $t_{\underset{\sim}{g}}^{\underset{\sim}{g}'}$ of the transition operator whose interaction potential makes it possible for the relaxation phenomenon to occur. In this thesis the intermolecular potential for the monatomic gas will be approximated by a rigid sphere potential and a dipole-dipole nuclear spin interaction. Thus, $(t_1^{(+)})_{\underset{\sim}{g}}^{\underset{\sim}{g}'}$ from Chapter III will be inserted into the equation of Chen and Snider, namely

$$T_1^{-1} = T_2^{-1}$$

$$= \frac{(2\pi)^2 n \hbar^2 m (\pi m k T)^{1/2}}{\langle I^2 \rangle Q^2} \times$$

$$\times\Bigg\{ Tr_1 Tr_2 \iint \exp\left(-v^2 - \frac{(\mathcal{H}_1+\mathcal{H}_2)}{kT}\right)$$

$$\times\, v' \Bigg[(\underset{\sim}{I}_1+\underset{\sim}{I}_2)^2 \left(t_1^{(+)}\right)_{g}^{g'} \left(t_1^{(+)}\right)_{g}^{g'\,+'}$$

$$- (\underset{\sim}{I}_1+\underset{\sim}{I}_2)\cdot\left(t_1^{(+)}\right)_{g}^{g'} (\underset{\sim}{I}_1+\underset{\sim}{I}_2)\left(t_1^{(+)}\right)_{g}^{g'\,+'} \Bigg] d\underset{\sim}{v}\, d\hat{v}' \Bigg\},$$

(4-1)

and the relaxation time will be approximately evaluated by analytical methods. The symbols which appear in Eq. (4-1) are as follows: n is the number density; m is the mass of one molecule; k is Boltzmann's constant (which is to be distinguished from the wavenumber k); $\langle I^2 \rangle$ is the expectation value of the spin operator I^2; T is the absolute temperature; $Q = Q_1 = Q_2$ is the internal state partition function for one molecule; and $\underset{\sim}{v}$ is the reduced relative velocity. The last quantity is appropriately defined in terms of the relative velocity $\underset{\sim}{g}$ as

$$\underset{\sim}{v} \equiv \left(\frac{m}{4kT}\right)^{1/2} \underset{\sim}{g} = \frac{\hbar}{(mkT)^{1/2}} \underset{\sim}{k}, \quad (4\text{-}2)$$

while the internal state partition function for molecule 1, Q_1, is given by

$$Q_1 = Tr_1\left[\exp\left(-\frac{\mathcal{H}_1}{k T} + \gamma\hbar\frac{\underset{\sim}{H}\cdot\underset{\sim}{I}_1}{k T}\right)\right].$$

(4-3)

$\underset{\sim}{H}$ is the external magnetic field, and $\mathcal{H}_1$ and $\underset{\sim}{I}_1$ have been defined previously in Chapter II. The trace Tr_1 is over the internal states of molecule 1.

Now in order to derive Eq. (4-1) Chen and Snider used the following high temperature approximation, i. e.,

$$\gamma\hbar H \ll kT \tag{4-4}$$

where H is the magnitude of the applied magnetic field. Eq. (4-4) can be used to justify expanding the exponential, exp $\left(\frac{\gamma\hbar}{kT}\underset{\sim}{H}\cdot\underset{\sim}{I}_1\right)$, from Eq. (4-3) in a power series about zero and keeping only the first term. Because, in general, the internal state Hamiltonian $\mathcal{H}_1$ has a much larger energy associated with it than does the nuclear Zeeman Hamiltonian, $\underset{\sim}{H}\cdot\underset{\sim}{I}_1$, the term exp $(-\mathcal{H}_1/kT)$ is not expanded in a power series. Consequently, Q_1 is

$$Q_1 \simeq Tr_1 \exp(-\mathcal{H}_1/k_T)$$

$$= (2I_1+1)\, Q_{el} \qquad (4\text{-}5)$$

where Q_{el} is the electronic partition function and $(2I_1 + 1)$ is the degeneracy of the nuclear spin space.

The factor Q_{el}^2 also arises from the exponential term $\exp\left(\frac{-\mathcal{H}_1-\mathcal{H}_2}{k_T}\right)$ in the numerator of Eq. (4-1). Consequently, Eq. (4-1) becomes

$$T_1^{-1} = T_2^{-1}$$

$$= \frac{(2\pi)^2 n m \hbar^2 (\pi m k_T)^{1/2}}{I(I+1)(2I+1)^2}$$

$$\times \left\{ Tr_1 Tr_2 \iint e^{-v^2} v' \left[(\underset{\sim}{I}_1+\underset{\sim}{I}_2)^2 (t_1^{(+)})_g^{g'} (t_1^{(+)})_g^{g'\dagger} \right.\right.$$

$$\left.\left. - (\underset{\sim}{I}_1+\underset{\sim}{I}_2)\cdot(t_1^{(+)})_g^{g'} (\underset{\sim}{I}_1+\underset{\sim}{I}_2)(t_1^{(+)})_g^{g'\dagger} \right] d\underset{\sim}{v}\, d\hat{v}' \right\}.$$

(4-6)

$(t_1^{(+)})_{\underline{g}}^{\underline{g}'\dagger'}$ is the adjoint of $(t_1^{(+)})_{\underline{g}}^{\underline{g}'}$ in spin space. For the particular case of Eq. (3-50), $\underset{\approx}{D}$ acts as a coefficient in front of the operator $\left[\underset{\sim}{I}_1\underset{\sim}{I}_2\right]^{(2)}$. Since both $\underset{\sim}{I}_1$ and $\underset{\sim}{I}_2$ are Hermitian operators, they are unaffected by the adjoint $\dagger'$ while the coefficient $\underset{\approx}{D}$ is changed to $\underset{\approx}{D}^*$.

The traces over the spin states of molecules 1 and 2 in Eq. (4-6) can be carried out by writing $(t_1^{(+)})_{\underline{g}}^{\underline{g}'}$ and $(t_1^{(+)})_{\underline{g}}^{\underline{g}'\dagger'}$ in terms of $\underset{\approx}{D}$ and $\left[\underset{\sim}{I}_1\underset{\sim}{I}_2\right]^{(2)}$ as in Eq. (3-23). Then the result is

$$
\begin{aligned}
Tr_1 Tr_2 \Big\{ & (\underset{\sim}{I}_1+\underset{\sim}{I}_2)^2 \left[\underset{\sim}{I}_1\underset{\sim}{I}_2\right]^{(2)} \left[\underset{\sim}{I}_1\underset{\sim}{I}_2\right]^{(2)} \\
& - (\underset{\sim}{I}_1+\underset{\sim}{I}_2)\cdot \underset{\approx}{\left(\left[\underset{\sim}{I}_1\underset{\sim}{I}_2\right]^{(2)}\right)} \cdot (\underset{\sim}{I}_1+\underset{\sim}{I}_2)\left[\underset{\sim}{I}_1\underset{\sim}{I}_2\right]^{(2)} \Big\} \\
&= (1/3) I_1(I_1+1)(2I_1+1) I_2(I_2+1)(2I_2+1) \\
&\quad \times \left(1/2\left[\underset{\approx}{U}\underset{\approx}{U} + \underset{=}{(\overset{U}{\approx})}\right] - 1/3\, \underset{\approx}{U}\underset{\approx}{U}\right) \\
&= (1/3) I^2(I+1)^2(2I+1)^2\left(1/2\left[\underset{\approx}{U}\underset{\approx}{U} + \underset{=}{(\overset{U}{\approx})}\right] - 1/3\, \underset{\approx}{U}\underset{\approx}{U}\right).
\end{aligned}
\tag{4-7}
$$

Consequently, Eq. (4-6) is further reduced to

$$T_1^{-1} = 3nm(2\pi)^2 \gamma^4 \hbar^6 I(I+1)(\pi m k_x T)^{1/2}$$

$$\times \iint e^{-v^2} v' \underline{\underline{D}}\,\underline{\underline{D}}^* \vdots \left[1/2 \left(\underline{\underline{\underline{\underline{W}}}} + \underline{\underline{\underline{\underline{U}}}} \right) - \tfrac{1}{3} \underline{\underline{U}}\,\underline{\underline{U}} \right] d\underset{\sim}{v}\, d\hat{v}'$$

$$= 12 \frac{nI(I+1)}{k_x T} \pi^2 \gamma^4 \hbar^{10} \left(\frac{\pi}{m k_x T} \right)^{1/2}$$

$$\times \left\{ \iiint k^3 \sigma^3 e^{\left(\frac{-\hbar^2 k^2 \sigma^2}{m k_x T \sigma^2} \right)} \right.$$

$$\times \langle \chi_{-\underset{\sim}{k}'}^{(+)*}(\underset{\sim}{r}) \left| \frac{\hat{r}\hat{r} - 1/3 \underline{\underline{U}}}{r^3} \right| \chi_{\underset{\sim}{k}}^{(+)}(\underset{\sim}{r}) \rangle \langle \chi_{-\underset{\sim}{k}'}^{(+)*}(\underset{\sim}{r}') \left| \frac{\hat{r}'\hat{r}' - 1/3 \underline{\underline{U}}}{(r')^3} \right| \chi_{\underset{\sim}{k}}^{(+)}(\underset{\sim}{r}') \rangle^*$$

$$\left. \vdots \left[1/2 \left(\underline{\underline{\underline{\underline{W}}}} + \underline{\underline{\underline{\underline{U}}}} \right) - \tfrac{1}{3} \underline{\underline{U}}\,\underline{\underline{U}} \right] d\left(\frac{k\sigma}{\sigma} \right) d\hat{k}\, d\hat{k}' \right\}$$

(4-8)

where Eq. (4-2) has been used to write the reduced relative velocities in terms of the wave vectors.

As was mentioned at the end of the previous chapter, it is possible to perform the $\hat{r}$-integration in $\underset{\approx}{D}$ in more than one way. The alternative method to that associated with Eq. (3-49) uses the property of the isotropic, symmetric traceless tensor which appears in Eq. (4-8), i. e.,

$$(\hat{r}\hat{r} - \tfrac{1}{3}\underset{\approx}{U})(\hat{r}'\hat{r}' - \tfrac{1}{3}\underset{\approx}{U}) \vdots \left[\tfrac{1}{2}\left(\underset{\approx\approx}{UU} + \underset{\approx}{\overset{U}{=}}\right) - \tfrac{1}{3}\underset{\approx}{U}\,\underset{\approx}{U}\right]$$

$$= (\hat{r}\hat{r} - \tfrac{1}{3}\underset{\approx}{U}) : (\hat{r}'\hat{r}' - \tfrac{1}{3}\underset{\approx}{U})$$

$$= (\hat{r}\cdot\hat{r}')^2 - \tfrac{1}{3}$$

$$= (\tfrac{2}{3})\, P_2(\hat{r}\cdot\hat{r}') \tag{4-9}$$

or, equivalently, that

$$\iint \underset{\approx}{D}\,\underset{\approx}{D}^{*} \vdots \left[\tfrac{1}{2}\left(\underset{\approx\approx}{UU} + \underset{\approx}{\overset{U}{=}}\right) - \tfrac{1}{3}\underset{\approx}{U}\,\underset{\approx}{U}\right] d\hat{k}\, d\hat{k}'$$

$$= \iint \left\langle \chi^{(+)*}_{-\underset{\sim}{k}'}(\underset{\sim}{r}) \middle| \frac{\hat{r}\hat{r} - \frac{1}{3}\underset{\approx}{U}}{r^3} \middle| \chi^{(+)}_{\underset{\sim}{k}}(\underset{\sim}{r}) \right\rangle : \left\langle \chi^{(+)*}_{-\underset{\sim}{k}'}(\underset{\sim}{r}') \middle| \frac{\hat{r}'\hat{r}' - \frac{1}{3}\underset{\approx}{U}}{(r')^3} \middle| \chi^{(+)}_{\underset{\sim}{k}}(\underset{\sim}{r}') \right\rangle^{*} d\hat{k}\, d\hat{k}'. \tag{4-10}$$

Eq. (4-10) will be integrated out completely in the following paragraphs.

The Addition Theorem for spherical harmonics[7] is used to separate the wave vector angle dependence from the relative coordinate angle dependence in the Legendre functions in the $\chi^{(+)}_{\underline{k}}(\underline{r})$'s. Thus Eq. (4-10) becomes

$$\iint \left\langle \chi^{(+)*}_{-\underline{k}'}(\underline{r}) \left| \frac{\hat{r}\hat{r}-\frac{1}{3}\underline{U}}{r^3} \right| \chi^{(+)}_{\underline{k}}(\underline{r}) \right\rangle \left\langle \chi^{(+)*}_{-\underline{k}'}(\underline{r}') \left| \frac{\hat{r}'\hat{r}'-\frac{1}{3}\underline{U}}{(r')^3} \right| \chi^{(+)}_{\underline{k}}(\underline{r}') \right\rangle^* d\hat{k}\, d\hat{k}'$$

$$= k^{-6} \sum_{\ell,\ell',L,L'=0}^{\infty} \left\{ \frac{1}{m(\ell',\ell)\, n(\ell',\ell)\, M(L',L)\, N(L',L)} \right.$$

$$\times \left[(-1)^{\ell'} \frac{h^*_{\ell}}{h_{\ell}} + (-1)^{\ell} \frac{h^*_{\ell'}}{h_{\ell'}} - \frac{2i^{\ell+\ell'}}{z^2 h_{\ell} h_{\ell'}} \right]$$

$$\times \left[(-1)^{L'} \frac{h_{L}}{h^*_{L}} + (-1)^{L} \frac{h_{L'}}{h^*_{L'}} - \frac{2(-i)^{L+L'}}{z^2 h^*_{L} h^*_{L'}} \right]$$

$$\times \int \left(\left(\left[(4\pi)^2 \sum_{m'=-\ell'}^{\ell'} \sum_{m=-\ell}^{\ell} Y^{m'*}_{\ell'}(-\hat{k}')\, Y^{m*}_{\ell}(\hat{k})\, Y^{m'}_{\ell'}(\hat{r})\, Y^{m}_{\ell}(\hat{r}) \right] \right.\right.$$

$$\times\left[(4\pi)^2 \sum_{M'=-L'}^{L'} \sum_{M=-L}^{L} Y_{L'}^{M'^*}(-\hat{k}') Y_L^{M^*}(\hat{k}) Y_{L'}^{M'}(\hat{r}') Y_L^{M}(\hat{r}')\right]$$

$$\times\left[\frac{8\pi}{15} \sum_{m''=-2}^{2} Y_2^{m''^*}(\hat{r}) Y_2^{m''}(\hat{r}')\right]\Bigg) d\hat{r}\, d\hat{r}'\, d\hat{k}\, d\hat{k}'\Bigg\}.$$

(4-11)

Now if $\hat{r}$ is chosen as the fixed reference axis, then Eq. (4-11) can be further simplified to

$$\iint \underset{\approx}{D}\underset{\approx}{D}^* \vdots \left[\tfrac{1}{2}\left(\underset{\approx}{\underset{\approx}{W}} + \underset{\approx}{\overset{\approx}{U}}\right) - \tfrac{1}{3}\underset{\approx}{U}\underset{=}{U} \right] d\hat{k}\, d\hat{k}'$$

$$= h^{-6} \sum_{\ell,\ell',L,L'=0}^{\infty} \left\{ \frac{1}{m(\ell',\ell)\, n(\ell',\ell)\, M(L',L)\, N(L',L)} \right.$$

$$\times\left[(-1)^{\ell'} \frac{h_\ell^*}{h_\ell} + (-1)^{\ell} \frac{h_{\ell'}^*}{h_{\ell'}} - \frac{2i^{\ell+\ell'}}{z^2 h_\ell h_{\ell'}} \right]$$

$$\times\left[(-1)^{L'}\frac{h_L}{h_L^*} + (-1)^{L}\frac{h_{L'}}{h_{L'}^*} - \frac{2(-i)^{L+L'}}{z^2 h_L^* h_{L'}^*} \right]$$

$$\times (4\pi)^4 (4/3)\sqrt{\pi/5} \iint \Bigg[\sum_{M'=-L'}^{L'} \sum_{M=-L}^{L} Y_{\ell'}^{0}(-\hat{k}') Y_{L'}^{M'^*}(-\hat{k}')$$

$$\times Y_{\ell}^{0}(\hat{k}) Y_{L}^{M^*}(\hat{k}) Y_{L'}^{M'}(\hat{r}') Y_{L}^{M}(\hat{r}') Y_{2}^{0}(\hat{r}') Y_{\ell'}^{0}(\hat{r}) Y_{\ell}^{0}(\hat{r}) \Bigg]$$

$$\times d\hat{r}\, d\hat{r}'\, d\hat{k}\, d\hat{k}' \Big\} . \qquad (4\text{-}12)$$

In order to complete the next step the following two results are needed, namely

$$Y_{\ell'}^{0}(-\hat{k}') Y_{L'}^{M'^*}(-\hat{k}') = (-1)^{\ell'} Y_{\ell'}^{0}(\hat{k}') Y_{L'}^{M'^*}(\hat{k}') (-1)^{L'}$$

(4-13)

and

$$Y_{\ell'}^{0}(\hat{r})\,Y_{\ell}^{0}(\hat{r}) = \left(\frac{2\ell'+1}{4\pi}\right)^{1/2}\left(\frac{2\ell+1}{4\pi}\right)^{1/2} P_{\ell'}(\cos 0)\,P_{\ell}(\cos 0)$$

$$= (4\pi)^{-1}\left[(2\ell'+1)(2\ell+1)\right]^{1/2}. \tag{4-14}$$

Use of Eqs. (4-13) and (4-14) further facilitates the calculation in Eq, (4-12), i. e.,

$$\int \sum_{M'=-L'}^{L'} \sum_{M=-L}^{L} \Big[Y_{\ell'}^{0}(-\hat{k}')\,Y_{L'}^{M'*}(-\hat{k}')\,Y_{\ell}^{0}(\hat{k})\,Y_{L}^{M*}(\hat{k})\,Y_{L'}^{M'}(\hat{r}')\,Y_{L}^{M}(\hat{r}')$$

$$\times Y_{2}^{0}(\hat{r}')\,Y_{\ell'}^{0}(\hat{r})\,Y_{\ell}^{0}(\hat{r})\Big]\,d\hat{r}\,d\hat{r}'\,d\hat{k}\,d\hat{k}'$$

$$= \sum_{M'=-L'}^{L'} \sum_{M=-L}^{L} \Bigg(\left[(-1)^{\ell'+L'}\delta_{0M'}\,\delta_{\ell'L'}\right]\left[\delta_{0M}\,\delta_{\ell L}\right]$$

$$\times\left[(5/4\pi)^{1/2}(2L'+1)^{1/2}(2L+1)^{1/2}\begin{pmatrix} L' & L & 2 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L' & L & 2 \\ M' & M & 0 \end{pmatrix}\right]$$

$$\times\left[(2\ell'+1)(2\ell+1)\right]^{1/2}\Bigg)$$

$$= (-1)^{\ell'+L'}\left[(5/4\pi)(2L'+1)(2\ell'+1)(2L+1)(2\ell+1)\right]^{1/2}\begin{pmatrix} L' & L & 2 \\ 0 & 0 & 0 \end{pmatrix}^2$$

$$\times\, \delta_{\ell' L'}\, \delta_{\ell L}\,. \qquad (4\text{-}15)$$

With Eq. (4-15), Eq. (4-11) finally becomes

$$\iint \left\langle \chi_{-\underset{\sim}{k}'}^{(+)*}(\underset{\sim}{r}) \left| \frac{\hat{r}\hat{r}-1/3\underset{=}{U}}{r^3} \right| \chi_{\underset{\sim}{k}}^{(+)}(\underset{\sim}{r}) \right\rangle : \left\langle \chi_{-\underset{\sim}{k}'}^{(+)*}(\underset{\sim}{r}') \left| \frac{\hat{r}'\hat{r}'-1/3\underset{=}{U}}{(r')^3} \right| \chi_{\underset{\sim}{k}}^{(+)}(\underset{\sim}{r}') \right\rangle^* d\hat{k}\, d\hat{k}'$$

$$= h^{-6} \sum_{\ell',\ell=0}^{\infty} \Bigg\{ (2/3)(4\pi)^4 \left[m(\ell',\ell)\, n(\ell',\ell)\right]^{-2}$$

$$\times \left[(-1)^{\ell'} \frac{h_\ell^*}{h_\ell} + (-1)^{\ell} \frac{h_{\ell'}^*}{h_{\ell'}} - \frac{2 i^{\ell+\ell'}}{z^2 h_\ell h_{\ell'}} \right]$$

$$\times \left[(-1)^{\ell'} \frac{h_\ell^*}{h_\ell} + (-1)^{\ell} \frac{h_{\ell'}^*}{h_{\ell'}} - \frac{2 i^{\ell+\ell'}}{z^2 h_\ell h_{\ell'}} \right]^*$$

$$\times (2\ell'+1)(2\ell+1)\begin{pmatrix} \ell' & \ell & 2 \\ 0 & 0 & 0 \end{pmatrix}^2 \Bigg\}$$

$$= k^{-6}\left[\sum_{\ell=1}^{\infty} A_{\ell,\ell}(z) + 2\sum_{\ell=0}^{\infty} A_{\ell,\ell+2}(z)\right] \tag{4-16}$$

where the argument, $k\sigma$, of the spherical Hankel functions will be denoted by z from now on, viz.

$$k\sigma \equiv z. \tag{4-17}$$

The function $A_{\ell,\ell}(z)$ is defined as

$$A_{\ell,\ell}(z) = \frac{128\pi^4}{3}\,\frac{(2\ell+1)}{(2\ell+3)(\ell+1)\ell(\ell-1)}\left[\frac{z^2 h_\ell^*(z)h_\ell(z)-1}{z^2 h_\ell^*(z)\,h_\ell(z)}\right]^2 \tag{4-18}$$

and will henceforth be referred to as a "diagonal" contribution to Eq. (4-16). The "non-diagonal" contribution $A_{\ell,\ell+2}(z)$ is defined as

$$A_{\ell,\ell+2}(z) = \frac{128\pi^4}{9}\,\frac{1}{(2\ell+3)(\ell+2)(\ell+1)}\,\frac{\left[z^2\left(\mathrm{Re}\, h_\ell(z)h_{\ell+2}^*(z)\right)+1\right]^2}{\left[z^2 h_\ell(z)h_{\ell+2}^*(z)z^2 h_\ell^*(z)h_{\ell+2}(z)\right]}. \tag{4-19}$$

The restriction on ℓ-values as stated in Eqs. (3-42a) and (3-42b) is automatically accounted for in the $A_\ell(z)$'s because of the 3-j symbol[7] which appears in Eq. (4-16). That is, for $\ell' = \ell \pm 1$

$$\begin{pmatrix} \ell' & \ell & 2 \\ 0 & 0 & 0 \end{pmatrix} = \begin{pmatrix} \ell \pm 1 & \ell & 2 \\ 0 & 0 & 0 \end{pmatrix} = 0 \tag{4-20}$$

because $\ell \pm 1 + \ell + 2$ is odd for every value of ℓ.

Now the only integration left in the equation for the relaxation time is that over the energy parameter z, namely

$$T_1^{-1} = \frac{3}{16}\left(\frac{\gamma\hbar}{\pi\sigma}\right)^4 \frac{n I(I+1)}{k T}\left(\frac{\pi}{m k T}\right)^{1/2}$$

$$\times \int_0^\infty z^3 e^{-c^2 z^2}\left[\sum_{\ell=1}^{\infty} A_{\ell,\ell}(z) + 2\sum_{\ell=0}^{\infty} A_{\ell,\ell+2}(z)\right] dz \tag{4-21}$$

where the constant c^2 is defined as

$$c^2 \equiv \left[\frac{\hbar}{(m k T)^{1/2}\,\sigma}\right]^2 . \tag{4-22}$$

In order to complete the calculation of T_1^{-1} the ℓ's must be summed over and the z-parameter must be integrated out explicitly.

It is appropriate at this point to discuss the parameter c^2 which is defined in Eq. (4-22). If an estimate of its magnitude could be made, then the magnitude of c^2 could serve as a guide in choosing the type of approximation with which to carry out the energy integration (i. e., z-integration) in the relaxation time. Thus, for example, for a ^{129}Xe atom at 300°K., c^2 is approximately 1.25 × 10^{-4}, i. e.,

$$c^2 \equiv \frac{\hbar^2}{m k T \sigma^2}$$

$$\simeq \frac{1 \times 10^{-54}\ \text{ergs}^2\ \text{sec}^2}{\dfrac{129\ \text{gms. mole}^{-1}}{6 \times 10^{23}\ \dfrac{\text{molecules}}{\text{mole}}} \times 1.38 \times 10^{-16}\ \dfrac{\text{ergs}}{\text{deg.}} \times 300\ \text{deg.} \times (3 \times 10^{-8})^2\ \text{cm}^2}$$

$$\simeq 1.25 \times 10^{-4}\ . \qquad (4\text{-}23)$$

CHAPTER V

A LINEAR APPROXIMATION TO T_1^{-1}

The central issue in this and the next chapter is to find a decent approximation to the quotient of spherical Hankel functions which appears in the $A_\ell(z)$'s of Eqs. (4-18) and (4-19). Originally, an attempt was made to rigorously integrate Eq. (4-21) for each ℓ-value from 0 to 10 inclusive. The justification for terminating the infinite series at $\ell = 10$ came from the fact that the general ℓ'th term in each series behaves basically like ℓ^{-3} and for the Riemann-Zeta function, namely $\sum_{\ell=1}^{\infty} 1/\ell^3$, the first nine terms constitute 99.5 % of the value of the entire infinite sum. Unfortunately, it soon became apparent that the particular quotients involved in Eq. (4-21) were diverging, rather than converging, after each succeeding integration. The decision to approximate the quotient of spherical Hankel functions was made after further fruitless investigations into rigorous methods for solving Eq. (4-21). At the same time, a further decision to approximate the infinite sums by integrations was made. The remainder of this chapter, then, will deal with a "linear-in-w" approximation to the products $z^2 h_\ell(z) h_\ell^*(z)$ and $z^2 h_\ell(z) h_{\ell+2}^*(z)$ in Eq. (4-18) and (4-19) respectively, and with the Euler-Maclaurin sum formula[9] in order to facilitate an approximate evaluation of T_1^{-1}.

The Euler-Maclaurin sum formula is given by

$$\sum_{\ell=0}^{n} g(x_0+\ell h) = (1/h)\int_{x_0}^{x_0+nh} g(\ell)\,d\ell + (1/2)\left[g(x_0+nh)+g(x_0)\right]$$

$$+ \text{ more correction terms} \qquad (5\text{-}1)$$

where the summation is replaced by an integration. Eq. (5-1) is valid for n approaching infinity and, in fact, in this thesis n can be directly replaced by infinity. The constant h is equal to one since consecutive values of ℓ, the summation parameter, differ by one; and the constant x_0 is the lowest value of ℓ in the sum.

It is convenient at this point to define a new diagonal term $\bar{A}_\ell(z)$ by

$$\bar{A}_\ell(z) \equiv \frac{3}{128\pi^4}\,\frac{(2\ell+3)(\ell+1)\ell(\ell-1)}{(2\ell+1)}\,A_{\ell,\ell}(z)$$

$$= \left[\frac{z^2 h_\ell(z)\,h_\ell^*(z) - 1}{z^2 h_\ell(z)\,h_\ell^*(z)}\right]^2 \qquad (5\text{-}2)$$

and, similarly, a new non-diagonal term $\bar{A}_{\ell,\ell+2}(z)$ by

$$\bar{A}_{\ell,\ell+2}(z) \equiv \frac{\left[\left(\mathrm{Re}\, z^2 h_\ell(z) h_\ell^*(z)\right) + 1\right]^2}{z^2 h_\ell(z) h_{\ell+2}^*(z)\, z^2 h_\ell^*(z) h_{\ell+2}(z)} \,. \tag{5-3}$$

An approximation to $\bar{A}_\ell(z)$ will be considered first.

The product of the power series expansions for $zh_\ell(z)$ and $zh_\ell^*(z)$,[7] namely

$$z^2 h_\ell(z) h_\ell^*(z) = \sum_{r,r'=0}^{\ell} \frac{(-1)^{r'} i^{r+r'}}{2^{r+r'} r!\, r'!} \frac{(\ell+r)!(\ell+r')!}{(\ell-r)!(\ell-r')!} z^{-r-r'} , \tag{5-4}$$

up to terms quadratic in $(1/z)$, allows $\bar{A}_\ell(z)$ to be expressed as

$$\bar{A}_\ell(w) \simeq \frac{\left[(1/2)\ell(\ell+1)\right]^2}{\left[(1/2)\ell(\ell+1) + w\right]^2} \tag{5-5}$$

where w is defined by

$$w \equiv z^2 \equiv (k\sigma)^2 \,. \tag{5-6}$$

The approximation which is exhibited in Eq. (5-5) will be called the "linear" approximation to the diagonal term $\overline{A}_{\ell}$. Now, of course, Eq. (5-5) can be substituted into the whole diagonal term $A_{\ell,\ell}(w)$ which, upon keeping only the main term in the Euler-Maclaurin sum formula, becomes

$$\frac{3}{128\pi^4}\sum_{\ell=1}^{\infty} A_{\ell,\ell}(W) \simeq \int_1^{\infty} \frac{\ell(\ell+1)(2\ell+1)\,d\ell}{(2\ell+3)(2\ell-1)4\left[W+(1/2)\ell(\ell+1)\right]^2}$$

$$= \int_2^{\infty} \frac{x\,dx}{4(4x-3)(W+x/2)^2}$$

$$= \int_2^{\infty} \frac{dx}{16(W+x/2)^2}\left[1+\frac{3}{4x}+O\left(\frac{1}{x^2}\right)\right]$$

$$\simeq \int_2^{\infty} \frac{dx}{16(W+x/2)^2}$$

$$= \frac{1}{8(W+1)} \qquad (5\text{-}7)$$

where x is defined by

$$x \equiv \ell(\ell+1). \tag{5-8}$$

The result in Eq. (5-7) can be put back into the diagonal term of Eq. (4-21) in order that the w-integration be completed.

Consequently, the diagonal contribution to the relaxation time is

$$\int_0^\infty z^3 e^{-c^2 z^2}\left[\sum_{\ell=1}^{\infty} A_{\ell,\ell}(z)\right] dz$$

$$= (1/2)\int_0^\infty W e^{-c^2 W}\left[\frac{128\pi^4}{3} \times \frac{1}{8(W+1)}\right] dW$$

$$= \frac{8\pi^4}{3}\left[\frac{1}{c^2} - e^{c^2}\{-Ei(-c^2)\}\right]. \tag{5-9}$$

The exponential integral $\{-\ Ei\ (-y)\}$[10] is defined by

$$\{-Ei(-y)\} \equiv \int_y^\infty \frac{e^{-t}}{t} dt$$

$$= -\ln\gamma - \ln y - \sum_{n=1}^{\infty} \frac{(-1)^n y^n}{n!\, n}, \quad 0 < y < \infty \tag{5-10}$$

where γ, the Euler-Mascheroni constant[10], has the numerical value 0.577215... .

The linear approximation to the non-diagonal term $\bar{A}_{\ell,\ell+2}(z)$ is performed analogously to that of the diagonal term; that is, the power series of $zh_\ell(z)zh^*_{\ell+2}(z)$, namely

$$z^2 h_\ell(z) h^*_{\ell+2}(z) = \sum_{r=0}^{\ell} \sum_{r'=0}^{\ell+2} \frac{(-1)^{r'+1}\, i^{r+r'}\, (\ell+2+r')!\,(\ell+r)!\, z^{-r-r'}}{2^{r+r'}\, r!\, r'!\, (\ell+2-r')!\,(\ell-r)!}, \tag{5-11}$$

is cut off at terms quadratic in $(1/z)$. Similarly, the power series expression for $\mathrm{Re}\left[z^2 h_\ell(z) h^*_{\ell+2}(z)\right]$ is cut off at $1/z^2$. Consequently, $\bar{A}_{\ell,\ell+2}(w)$ becomes

$$\bar{A}_{\ell,\ell+2}(w) \simeq \frac{(9/4)(\ell+1)^2(\ell+2)^2}{\left[w+(1/2)\ell(\ell+1)\right]\left[w+(1/2)(\ell+2)(\ell+3)\right]} \tag{5-12}$$

where again $w \equiv z^2$ and the "linear" approximation actually refers to the parameter w rather than z. Now the full non-diagonal term $A_{\ell,\ell+2}$, with the first term of the Euler-Maclaurin sum formula, becomes

$$\frac{9}{128\pi^4}\sum_{\ell=0}^{\infty} A_{\ell,\ell+2}(W)$$

$$\simeq \frac{9}{4}\int_0^{\infty}\frac{(\ell+1)(\ell+2)}{(2\ell+3)^2}\left[\frac{d\ell}{W+(1/2)\ell(\ell+1)} - \frac{d\ell}{W+(1/2)(\ell+2)(\ell+3)}\right]$$

$$\simeq \frac{9}{8}\int_0^{\infty} d\ell\left[\frac{1}{2W+\ell^2+\ell} - \frac{1}{2W+\ell^2+5\ell+6}\right]$$

$$= \frac{9}{8(1-8W)^{1/2}}\left[\ln\left(\frac{5-(1-8W)^{1/2}}{5+(1-8W)^{1/2}}\right) - \ln\left(\frac{1-(1-8W)^{1/2}}{1+(1-8W)^{1/2}}\right)\right]$$

$$\simeq \frac{9}{8W} \; . \tag{5-13}$$

From Eq. (5-13), the non-diagonal contribution to the relaxation time, Eq. (4-21), is

$$(1/2)\int_0^{\infty} W e^{-c^2 W}\left[\frac{16\pi^4}{W}\right]dW = \frac{8\pi^4}{c^2} \; . \tag{5-14}$$

Thus the complete evaluation of T_1^{-1} from Eq. (4-21) for the linear-in-w approximation is

$$T_1^{-1} = \frac{1}{2}\left(\frac{\gamma\hbar}{\sigma}\right)^4 \frac{n I(I+1)}{k T}\left(\frac{\pi}{m k T}\right)^{1/2}\left[\frac{7}{c^2} - e^{c^2}\{-Ei(-c^2)\}\right]. \tag{5-15}$$

For the diagonal contribution, the first correction term, namely $1/2\left[g(\infty) + g(x_0)\right]$, from Eq. (5-1) of the Euler-Maclaurin sum formula is

$$\frac{3}{128\pi^4} \times \frac{1}{2}\left[A_\infty(w) + A_1(w)\right]$$

$$= \frac{1}{2}\left[0 + \frac{3}{10(w+1)^2}\right]. \tag{5-16}$$

And similarly the first correction term of the non-diagonal contribution as given in the integrand of the first line of Eq. (5-13) is

$$\frac{9}{128\pi^4} \times \frac{1}{2}\left[A_\infty(W) + A_0(W)\right]$$

$$= \frac{1}{2}\left[0 + \frac{3}{2W(W+3)}\right]. \qquad (5\text{-}17)$$

Eqs. (5-16) and (5-17) can be put back into the expression for the relaxation time, Eq. (4-21), to find the magnitude of the correction terms. The result is

$$(T_1^{-1})_{corr} = 3\left(\frac{\gamma\hbar}{\sigma}\right)^4 \frac{n\,I(I+1)}{k_{\chi}T}\left(\frac{\pi}{m k_{\chi} T}\right)^{1/2}$$

$$\times\Big[\,1/5 + (1/5)(1+c^2)\,e^{c^2}\{-Ei(-c^2)\}$$

$$+ (2/3)\,e^{3c^2}\{-Ei(-3c^2)\}\Big].$$

(5-18)

None of the terms in Eq. (5-18) contribute to the dominant $1/c^2$ term in the main contribution, Eq. (5-15), to the relaxation time. This fact is considered to be sufficient justification for using the Euler-Maclaurin sum formula to change the infinite sums in the original problem to integrations.

CHAPTER VI

A QUADRATIC APPROXIMATION TO T_1^{-1}

In this chapter the polynomials of $z^2 h_\ell(z) h^*_\ell(z)$ and $z^2 h_\ell(z) h^*_{\ell+2}(z)$ in Eqs. (5-4) and (5-11) respectively, will be terminated at z^{-4} rather than at z^{-2}. Then a procedure analogous to that used in the previous chapter will be carried out in order to obtain a better approximation to the relaxation time T_1^{-1} from Eq. (4-21).

The quadratic-in-w diagonal term can be found from Eq. (5-4), namely

$$\bar{A}_\ell(w) \simeq \left[(1/2)\ell(\ell+1)\right]^2 \times \left[\frac{w + (3/4)(\ell+2)(\ell-1)}{w^2 + (1/2)\ell(\ell+1)w + (3/8)(\ell+2)(\ell+1)\ell(\ell-1)}\right]^2 . \tag{6-1}$$

If Eq. (6-1) is put into the full diagonal term $A_{\ell,\ell}(w)$ and if only the main term of the Euler-Maclaurin sum formula, Eq. (5-1), is kept, then the result is

$$\frac{3}{128\pi^4}\sum_{\ell=1}^{\infty} A_{\ell,\ell}(W)$$

$$\simeq \int_1^{\infty} \frac{\ell(\ell+1)(2\ell+1)}{4[4\ell(\ell+1)-3]} \frac{[W+(3/4)[\ell(\ell+1)-2]]^2\, d\ell}{[W^2+(1/2)\ell(\ell+1)W+(3/8)\ell(\ell+1)[\ell(\ell+1)-2]]^2}$$

$$= \int_2^{\infty} \frac{x}{4(4x-3)} \frac{[W+(3/4)(x-2)]^2\, dx}{[W^2+(1/2)xW+(3/8)x(x-2)]^2}$$

$$= (1/16)\int_2^{\infty} \frac{[W+(3/4)(x-2)]^2}{[W^2+(1/2)xW+(3/8)x(x-2)]^2}\left[1+\frac{3}{4x}+\cdots\right]dx$$

$$\simeq (1/16)\int_2^{\infty} dx \left[\frac{W+(3/4)(x-2)}{W^2+(1/2)xW+(3/8)x(x-2)}\right]^2$$

$$= \frac{1}{8(W+1)} - \frac{3W(W+3/2)}{16(W+1)(5W^2+3W-9/4)}$$

$$- \frac{9W^2}{16[(-)(5W^2+3W-9/4)]^{3/2}}\left(\ln\left[\frac{W+3/2+\sqrt{-(5W^2+3W-9/4)}}{W+3/2-\sqrt{-(5W^2+3W-9/4)}}\right]\right)$$

(6-2)

where x is defined as in Eq. (5-8). The integration from the second last line to the last line of Eq. (6-2) is exact. The integral is of the general form

$$\bar{I} \equiv \int \frac{ds}{(a' + b's)^m S^n} \tag{6-3}$$

where S is defined as

$$S \equiv a + bs + cs^2 . \tag{6-4}$$

Integral (6-3) can be found in any book[11] which lists tables of integrals. The integration over energy of the first term in the last line of Eq. (6-2) is straightforward. The integration of the remaining two terms, however, requires more effort. The aforementioned energy integration will be discussed in the following paragraphs.

For convenience the following definition will be made, namely

$$f(w) \equiv \frac{w}{2}\left\{ \frac{-3w(w+3/2)}{16(w+1)(5w^2+3w-9/4)} - \frac{9w^2}{16\left[(-)(5w^2+3w-9/4)\right]^{3/2}}\left(\ln\left[\frac{w+3/2+\sqrt{(-)(5w^2+3w-9/4)}}{w+3/2-\sqrt{-(5w^2+3w-9/4)}}\right]\right)\right\}. \tag{6-5}$$

The energy integration over f(w) cannot be done exactly in a straightforward manner. Thus f(w) must be approximated. Because the factor $[-(5w^2 + 3w - 9/4)]^{\frac{1}{2}} / (w + 3/2)$ appears both in the argument for the logarithm and in the other term of f(w), it was found to be convenient to expand f(w) in an inverse power series in

$$y \equiv w + 3/2 \quad . \tag{6-6}$$

Thus f(w) can be written in terms of y in the form

$$f(y) = a + b/y + d/y^2 + F(y) \tag{6-7}$$

Where the remainder F(y) is, obviously,

$$F(y) = f(y) - a - b/y - d/y^2 . \tag{6-8}$$

Consequently the complete energy integral of Eq. (6-5) in terms of Eqs. (6-7) and (6-8) is

$$\int_0^\infty e^{-c^2 w} f(w)\,dw = e^{\frac{3c^2}{2}} \int_{3/2}^\infty dy\, e^{-c^2 y} \left[a + \frac{b}{y} + \frac{d}{y^2} \right] + \int_0^\infty e^{-c^2 w} F(w)\,dw. \tag{6-9}$$

In the integral $\int_0^\infty \exp\,(-c^2 w)\, F(w)dw$ the exponential is unnecessary for convergence since F(w) behaves, at least, as y^{-2}. Therefore the exponential can be expanded in a power series. Because the parameter c^2 is so small (see Eq. (4-23)), the power series can be cut off explicitly at terms linear in c^2. That is,

$$\begin{aligned} \int_0^\infty e^{-c^2 w} F(w)\,dw &= \int_0^\infty \left[(1 - c^2 w) + (e^{-c^2 w} - 1 + c^2 w) \right] F(w)\,dw \\ &= \int_0^\infty F(w)\,dw - c^2 \int_0^\infty w F(w)\,dw + O(c^4) \end{aligned} \tag{6-10}$$

since $\left[\exp(-c^2w) - 1 + c^2w\right]$ is of the order of c^4. Thus Eq. (6-9) becomes

$$\int_0^\infty e^{-c^2W} f(W)\,dW$$

$$= \frac{a}{c^2} + b e^{\frac{3c^2}{2}} \left\{-Ei\left(-3c^2/2\right)\right\}$$

$$- d c^2 e^{\frac{3c^2}{2}} \left\{-Ei\left(-3c^2/2\right)\right\} + \int_0^\infty \left[f(W) - a - \frac{b}{W+3/2}\right] dW$$

$$- c^2 \int_0^\infty W \left[f(W) - a - \frac{b}{W+3/2} - \frac{d}{(W+3/2)^2}\right] dW$$

$$+ O(c^4).$$

(6-11)

The constants a, b, and d must be calculated explicitly, and the magnitude of the two integrals, namely

$$I_1 \equiv \int_0^\infty \left[f(W) - a - \frac{b}{W + 3/2} \right] dW \qquad (6\text{-}12)$$

and

$$I_2 \equiv c^2 \int_0^\infty W \left[f(W) - a - \frac{b}{W + 3/2} - \frac{d}{(W + 3/2)^2} \right] dW$$

(6-13)

must be estimated. The calculation of a, b, and d will be exhibited first.

a, b, and d are found from the asymptotic form of f(y) in Eq. (6-7), i. e.,

$$f(y) \xrightarrow[y \to \infty]{} a + b/y + d/y^2 \ . \qquad (6\text{-}14)$$

In order to identify a, b, and d it is useful to notice that various powers of the quotient

$$-\chi^2 \equiv \frac{5W^2 + 3W - 9/4}{(W + 3/2)^2}$$

$$= 5 - \frac{12}{W + 3/2} + \frac{9}{2(W + 3/2)^2} \qquad (6\text{-}15)$$

appear in the expression for f(w) in Eq. (6-5). Now for w approaching infinity, x itself can be approximated in the following manner:

$$x = \sqrt{5}\, i \left[1 - \frac{12}{5(w+3/2)} + \frac{9}{10(w+3/2)^2} \right]^{1/2}$$

$$= \sqrt{5}\, i \left[1 - \frac{6}{5(w+3/2)} - \frac{27}{100(w+3/2)^2} + O\left(\frac{1}{y^3}\right) \right]$$

$$\simeq \sqrt{5}\, i\, (1+u) \qquad (6\text{-}16)$$

where u is given by

$$u \equiv -6 / 5(w + 3/2) \quad . \qquad (6\text{-}17)$$

This approximation for x can be used to simplify the argument of the logarithm in Eq. (6-5), namely

$$\ln\left(\frac{1+x}{1-x}\right) \simeq \ln\left[\frac{1+\sqrt{5}\, i(1+u)}{1-\sqrt{5}\, i(1+u)}\right] \qquad (6\text{-}18)$$

$$= \ln\left[\frac{1+i\sqrt{5}}{1-i\sqrt{5}}\right] + \ln\left[1 + \frac{i\sqrt{5}u}{1+i\sqrt{5}}\right] - \ln\left[1 - \frac{i\sqrt{5}u}{1-i\sqrt{5}}\right]$$

$$\simeq \ln\left[\frac{1+i\sqrt{5}}{1-i\sqrt{5}}\right] + \frac{i\sqrt{5}u}{3} - \frac{i5\sqrt{5}u^2}{18} + O(u^3)$$

where the fact that u approaches zero as w approaches infinity is used in the expansion of the logarithmic terms. Thus the whole second term in Eq. (6-5) can be approximated by

$$\frac{-9w^3}{32x^3(w+3/2)^3}\left(\ln\left[\frac{1+x}{1-x}\right]\right)$$

$$=\frac{9w^3}{160i\sqrt{5}(w+3/2)^3(1+u)^3}$$

$$\times\left[2i(\arctan\sqrt{5})+\frac{i\sqrt{5}u}{3}-\frac{i5\sqrt{5}u^2}{18}+O(u^3)\right]$$

$$\simeq\frac{9}{160\sqrt{5}}\left[1-\frac{3}{2(w+3/2)}\right]^3$$

$$\times\left[1-3u+6u^2+O(u^3)\right]\left[2i(\arctan\sqrt{5})+\frac{\sqrt{5}u}{3}\right.$$

$$\left.-\frac{5\sqrt{5}u^2}{18}+O(u^3)\right]$$

$$\simeq \frac{9}{160\sqrt{5}}\left[1-\frac{9}{2(W+3/2)}+\frac{27}{4(W+3/2)^2}+O\left(\frac{1}{w^3}\right)\right]$$

$$\times\left[1-3u+6u^2+O(u^3)\right]$$

$$\times\left[2i\left(\arctan\sqrt{5}\right)+\frac{\sqrt{5}}{3}u-\frac{5\sqrt{5}}{18}u^2+O(u^3)\right]$$

$$=\frac{9}{160\sqrt{5}}\left[2\left(\arctan\sqrt{5}\right)+\frac{(-1/5)\left[9\left(\arctan\sqrt{5}\right)+2\sqrt{5}\right]}{W+3/2}\right.$$

$$\left.-\frac{(1/25)\left[(81/2)\left(\arctan\sqrt{5}\right)+\sqrt{5}\right]}{(W+3/2)^2}+O\left(\frac{1}{w^3}\right)\right].$$

(6-19)

By precisely the same techniques, the first term of f(w) in Eq. (6-5), for w approaching infinity, can be expressed as

$$\frac{3W^2}{32(W+1)(W+3/2)x^2} = \frac{\left(\frac{-3}{160}\right)\left[1 - \frac{3}{2(W+3/2)}\right]^2}{\left[1 - \frac{1}{2(W+3/2)}\right](1+\mu)^2}$$

$$\simeq (-3/160)\left[1 - 2\left[\frac{3}{2(W+3/2)}\right] + \frac{9}{4(W+3/2)^2} + O\left(\frac{1}{y^3}\right)\right]$$

$$\times\left[1 + \frac{1}{2(W+3/2)} + \frac{1}{4(W+3/2)^2} + O\left(\frac{1}{y^3}\right)\right]$$

$$\times\left[1 + \frac{12}{5(W+3/2)} + \frac{108}{25(W+3/2)^2} + O\left(\frac{1}{y^3}\right)\right]$$

$$= \left(\frac{-3}{160}\right)\left[1 - \frac{1}{10(W+3/2)} - \frac{17}{25(W+3/2)^2} + O\left(\frac{1}{y^3}\right)\right]. \tag{6-20}$$

The two results in Eqs. (6-19) and (6-20) constitute the explicit evaluation of the constants in the asymptotic expansion for f(y) in Eq. (6-14). Therefore, a, b, and d can be identified as

$$a = (3/160)\left[\frac{6(\arctan (5)^{\frac{1}{2}})}{(5)^{\frac{1}{2}}} - 1\right] = 0.0391, \qquad (6\text{-}21a)$$

$$b = -(3/800)\left[\frac{11}{2} + \frac{27(\arctan (5)^{\frac{1}{2}})}{(5)^{\frac{1}{2}}}\right]$$

$$= -0.0726, \qquad (6\text{-}21b)$$

and

$$d = (3/2000)\left[7 - \frac{243(\arctan (5)^{\frac{1}{2}})}{4(5)^{\frac{1}{2}}}\right]$$

$$= -0.0363. \qquad (6\text{-}21c)$$

In order to complete the evaluation of the right hand side of Eq. (6-11) the magnitudes of the integrals I_1 and I_2 in Eqs. (6-12) and (6-13) respectively, must be investigated. It was concluded after several numerical integrations on I_1, and after several graphs of the exact integral were drawn, that the contribution of I_1 to Eq. (6-11) is negligible (of the order of 10^{-3}) compared to, for example, the main term $(a/c^2) \approx 3 \times 10^2$. Firstly, because of the similarity of the integrand in I_2 to that in I_1 and secondly, because of the fact that c^2 multiplies I_2, it was similarly concluded that the integral I_2 contributes negligibly to Eq. (6-11). Therefore, the complete energy integration for the quadratic-in-w approximation to the diagonal term, Eq. (6-2), in the relaxation time is

$$\int_0^{\infty} z^3 e^{-c^2 z^2} \left[\sum_{\ell=1}^{\infty} A_{\ell,\ell}(z) \right] dz$$

$$= \frac{1}{2} \int_0^{\infty} W e^{-c^2 W} \frac{128\pi^4}{3} \left[\frac{1}{8(W+1)} + \frac{2}{W} f(W) \right] dW$$

$$= \frac{128\pi^4}{3} \left[\frac{(a + 1/16)}{c^2} - \frac{e^{c^2}\{-Ei(-c^2)\}}{16} + e^{\frac{3c^2}{2}}\left\{-Ei\left(\frac{-3c^2}{2}\right)\right\}(b - dc^2) \right].$$

(6-22)

In order to complete the calculation for the relaxation time, the quadratic-in-w approximation to the non-diagonal term

$\bar{A}_{\ell,\ell+2}(z)$ must also be obtained. From Eq. (5-11), $\bar{A}_{\ell,\ell+2}(w)$ becomes

$$\bar{A}_{\ell,\ell+2}(w) \tag{6-23}$$

$$\simeq (1/4)(\ell+2)^2(\ell+1)^2$$

$$\times \frac{\left[9w^2+(15/2)\ell(\ell+3)w+(25/16)\ell^2(\ell+3)^2\right]}{\left[w^2+(\frac{1}{2})\ell(\ell+1)w+(\frac{3}{8})(\ell+2)(\ell+1)\ell(\ell-1)\right]\left[w^2+(\frac{1}{2})(\ell+2)(\ell+3)w+(\frac{3}{8})(\ell+4)(\ell+3)(\ell+2)(\ell+1)\right]}.$$

The denominator in Eq. (6-23) is such a complicated function of ℓ that the main term of the Euler-Maclaurin sum formula cannot be rigorously integrated. Consequently both factors in the denominator were approximated by the same expression, namely $[w + (3/8)^{\frac{1}{2}}(\ell + 2)(\ell + 1)]^2$. Now the whole non-diagonal term can be further approximated by the principal term in the Euler-Maclaurin sum formula to become

$$\frac{9}{128\pi^4}\left[\sum_{\ell=0}^{\infty} A_{\ell,\ell+2}(w)\right]$$

$$\simeq \int_0^\infty \frac{9}{16}\left[(2\ell+3) - \frac{1}{(2\ell+3)}\right] \frac{\left[w + (5/12)\,\ell(\ell+3)\right]^2 d\ell}{\left[w + \sqrt{3/8}\,(\ell+2)(\ell+1)\right]^4}$$

$$= \int_0^\infty d\ell \, \frac{9}{16}\left[(2\ell+3) - \frac{1}{(2\ell+3)}\right]\left\{\frac{25}{54}\left(\frac{1}{w+\sqrt{3/8}\,(\ell+2)(\ell+1)}\right)^2\right.$$

$$\left. + \frac{(5/3)\sqrt{\frac{2}{3}}\left[\left(1-\frac{5}{6}\sqrt{\frac{2}{3}}\right)w - \frac{5}{6}\right]}{\left[w+\sqrt{3/8}\,(\ell+2)(\ell+1)\right]^3} + \frac{\left[\left(1-\frac{5}{6}\sqrt{\frac{2}{3}}\right)w - \frac{5}{6}\right]^2}{\left[w+\sqrt{3/8}\,(\ell+2)(\ell+1)\right]^4}\right\}.$$

(6-24)

In Eq. (6-24) the three integrals with the factor $(2\ell + 3)$ have straightforward ℓ- and w-integrations. Each of these three integrals is of the form $\overline{I}$ given in Eq. (6-3). The ℓ-integrations and their subsequent w-integrations yield the following results:

$$\frac{128\pi^4}{9} \times \frac{1}{2}\int_0^\infty W e^{-c^2 W}\left\{\left[\frac{(25/48)(\sqrt{2/3})}{W+\sqrt{3/2}}\right]\right.$$

$$+\frac{5}{8}\left[\frac{(1-\frac{5}{6}\sqrt{\frac{2}{3}})}{W+\sqrt{3/2}} - \frac{\sqrt{3/2}}{(W+\sqrt{3/2})^2}\right]$$

$$\left.+\frac{3\sqrt{8}}{16\sqrt{3}}\left[\frac{(1-\frac{5}{6}\sqrt{\frac{2}{3}})^2}{W+\sqrt{3/2}} - \frac{\sqrt{6}(1-\frac{5}{6}\sqrt{\frac{2}{3}})}{(W+\sqrt{3/2})^2} + \frac{3/2}{(W+\sqrt{3/2})^3}\right]\right\} dW$$

$$= (8\pi^4/9)(1/c^2)\left[(25\sqrt{6}/18) + (1/3)\left(1-\frac{5\sqrt{6}}{18}\right)(10+3\sqrt{6})\right]$$

$$+ (8\pi^4/9)(c^2)^0\left[\sqrt{6} - 7/6\right]$$

$$+ (8\pi^4/9)\, c^2 \left[3\sqrt{6}/4\right]$$

$$+ (8\pi^4/9)\, e^{\sqrt{\frac{3}{2}}c^2}\left\{-Ei\left(-\sqrt{\tfrac{3}{2}}c^2\right)\right\}\left[(1/3)\left(\frac{311}{6}-26\sqrt{6}\right)+\left(\frac{31}{2}\right)\left(\frac{\sqrt{6}}{3}-3\right)c^2\right].$$

(6-25)

The three remaining integrals, preceded by the factor $(2\ell + 3)^{-1}$, also have ℓ-integrations which are straightforward. The integrals are of the type $\bar{I}$ given in Eq. (6-3). In each of the three succeeding w-integrations an integral in the form of

$$I(c^2) \equiv \int_{-\beta}^{\infty} e^{-c^2 y} \ln(1+\alpha y)\frac{dy}{y}, \quad \alpha, \beta > 0 \tag{6-26}$$

appears. Eq. (6-26) still must be estimated in order to complete the evaluation of the quadratic approximation to the non-diagonal contribution to the relaxation time.

A brief discussion of the integrand in Eq. (6-26) will clarify the method used to carry out the integration. First of all, there is no problem at the origin because, by l'Hôpital's rule, the limit as y approaches zero is finite, i. e.,

$$\lim_{y\to 0} \frac{\ln(1+\alpha y)}{y} = \lim_{y\to 0} \frac{\frac{\alpha}{1+\alpha y}}{1} = \alpha . \tag{6-27}$$

Secondly, as long as the exponential exp $(-c^2y)$ is left alone and not expanded in a power series in c^2, the integral in Eq. (6-26) is finite. Finally, it would facilitate the integration if the logarithm, $\ln(1 + \alpha x)$, could be replaced by a power series expansion in x. Unfortunately, with such an expansion the powers of $(1 / c^2)$ would increase after the w-integration, and from the linear-in-w approximation in Chapter V, the main contribution to the relaxation time should be no larger than $(1 / c^2)$.

A method which avoids the aforementioned difficulties entails splitting the integral $I(c^2)$ into two parts, namely

$$\int_{-\beta}^{\infty} e^{-c^2 y} \ln(1+\alpha y) \frac{dy}{y}$$

$$= \int_{-\frac{\alpha\beta}{2}}^{1} e^{-\frac{2c^2}{\alpha}u} \ln(1+2u) \frac{du}{u} + \int_{1}^{\infty} e^{-\frac{2c^2}{\alpha}u} \ln(1+2u) \frac{du}{u} \tag{6-28}$$

and expanding each integral in a different manner. u is defined by

$$2u \equiv \alpha y. \tag{6-29}$$

The first integral which appears on the right hand side of

Eq. (6-28) can now be evaluated by expanding the exponential in powers of c^2, i. e.,

$$\int_{-\frac{\alpha\beta}{2}}^{1} e^{-2qu}\ln(1+2u)\frac{du}{u}$$

$$= \int_{-\frac{\alpha\beta}{2}}^{1}(1-2qu)\ln(1+2u)\frac{du}{u} + \int_{-\frac{\alpha\beta}{2}}^{1}\left(e^{-2qu}-1+2qu\right)\ln(1+2u)\frac{du}{u} \tag{6-30}$$

where

$$q \equiv (c^2/\alpha). \tag{6-31}$$

Because the first coefficient in front of the second integral on the right hand side of Eq. (6-30) is c^4 ($\simeq 10^{-8}$), and because the succeeding coefficients increase in powers of c^2 starting from c^6, Eq. (6-30) can be reduced to

$$\int_{-\frac{\alpha\beta}{2}}^{1} e^{-2qu}\ln(1+2u)\frac{du}{u} \simeq \int_{-\frac{\alpha\beta}{2}}^{1}(1-2qu)\ln(1+2u)\frac{du}{u}$$

$$= Li_2(\alpha\beta) - Li_2(-2) - q\left[-2-\alpha\beta+3\ln 3-(1-\alpha\beta)\ln(1-\alpha\beta)\right]. \tag{6-32}$$

The dilogarithm function[12] $\mathrm{Li}_2(y)$ is defined by

$$Li_2(s) \equiv -\int_0^s \ln(1-u)\,\frac{du}{u}\,. \qquad (6\text{-}33)$$

Now the second integral which appears on the right hand side of Eq. (6-28) is more difficult to evaluate. If the logarithm is rewritten, then the integral under consideration can be split into two contributions, viz.,

$$\int_1^\infty e^{-2gu}\ln(1+2u)\,\frac{du}{u}$$

$$= \int_1^\infty e^{-2gu}(\ln 2u)\,\frac{du}{u} + \int_1^\infty e^{-2gu}\ln\left(1+\frac{1}{2u}\right)\frac{du}{u}$$

$$= (\ln 2)\{-Ei(-2g)\} + \int_1^\infty e^{-2gu}(\ln u)\,\frac{du}{u}$$

$$+ (1/2)(e^{-2g}-1) - Li_2(1/2)$$

$$- g\left[1 + \{-Ei(-2g)\} - 3\ln(3/2)\right] + O(g^2 \ln g).$$

(6-34)

Thus the problem has been shifted to evaluating the integral

$$I(q) \equiv \int_1^{\infty} \left[\exp\,(-2qu)\right] (\ln u) \frac{du}{u} . \qquad (6\text{-}35)$$

The next few paragraphs will deal with the evaluation of I(q).

By means of the following tabulated integral[13], namely

$$\int_1^{\infty} e^{-2qu} \left(\ln\left[2u\left(1-\frac{1}{2u}\right)\right]\right) \frac{du}{u}$$

$$= \frac{1}{2}\left\{-Ei(-q)\right\}^2$$

$$= (\ln 2)\left\{-Ei(-2q)\right\} + \int_1^{\infty} e^{-2qu} (\ln u) \frac{du}{u}$$

$$+ \int_1^{\infty} e^{-2qu} \ln\left(1-\frac{1}{2u}\right) \frac{du}{u} ,$$

(6-36)

I(q) can be expressed in terms of the exponential integral

$\{-\text{Ei }(-q)\}$ and the integral $\int_1^\infty [\exp(-2qu)] \ln(1-(2u)^{-1}) \frac{du}{u}$.
The latter quantity is explicitly calculated as follows:

$$\int_1^\infty e^{-2qu}\left[\ln\left(1-\frac{1}{2u}\right)\right]\frac{du}{u}$$

$$= \frac{-1}{2}\int_1^\infty \frac{e^{-2qu}}{u^2}\,du + \int_1^\infty e^{-2qu}\left[\ln\left(1-\frac{1}{2u}\right)+\frac{1}{2u}\right]\frac{du}{u}$$

$$= (-1/2)e^{-2q} + q\{-Ei(-2q)\}$$

$$+\int_1^\infty e^{-2qu}\left[\ln\left(1-\frac{1}{2u}\right)+\frac{1}{2u}\right]\frac{du}{u}. \qquad (6\text{-}37)$$

The last integral in Eq. (6-37) can be approximately evaluated by the usual trick of adding and subtracting (1 - 2qu) to the integrand, namely

$$\int_1^{\infty} e^{-2qu}\left[\ln\left(1-\frac{1}{2u}\right)+\frac{1}{2u}\right]\frac{du}{u}$$

$$=\int_1^{\infty}(1-2qu)\left[\ln\left(1-\frac{1}{2u}\right)+\frac{1}{2u}\right]\frac{du}{u}$$

$$+\int_1^{\infty}\left(e^{-2qu}-1+2qu\right)\left[\ln\left(1-\frac{1}{2u}\right)+\frac{1}{2u}\right]\frac{du}{u}$$

(6-38)

so that one (the last one on the right hand side of Eq. (6-38)) of the integrals can be eliminated on the basis of the argument that the leading coefficient of this integral is of the order of c^4. There is no problem about the integrand in $\int_1^{\infty}(\exp(-2qu) - 1 + 2qu)\left[\ln(1-(2u)^{-1}) + (2u)^{-1}\right]\frac{du}{u}$ at infinity since the factor $(u)^{-1}(\exp(-2qu) - 1 + 2qu)$ multiplied by the term-by-term expansion of the logarithm behaves at least as $(u)^{-3}(\exp(-2qu) - 1 + 2qu)$ at infinity.

The integral $\int_1^{\infty}(1-2qu)\left[\ln\left(1-\frac{1}{2u}\right)+\frac{1}{2u}\right]\frac{du}{u}$ from Eq. (6-38) remains to be evaluated. It can be done exactly, namely

$$\int_1^\infty (1-2qu)\left[\ln\left(1-\frac{1}{2u}\right)+\frac{1}{2u}\right]\frac{du}{u}$$

$$=\int_0^1\left[1-\frac{2q}{y}\right]\left[\ln\left(1-\frac{y}{2}\right)+\frac{y}{2}\right]\frac{dy}{y}$$

$$=\int_0^{1/2}\frac{\ln(1-t)}{t}\,dt+\frac{1}{2}-2q\int_0^1\left[\ln\left(1-\frac{y}{2}\right)+\frac{y}{2}\right]\frac{dy}{y^2}$$

$$=-Li_2(1/2)+1/2+q(1-\ln 2).$$

(6-39)

Now I(q) from Eq. (6-35) can be expressed in terms of Eqs. (6-36), (6-37), and (6-39) as

$$I(q)=\int_1^\infty e^{-2qu}(\ln u)\frac{du}{u}$$

$$\simeq -1/2+Li_2(1/2)+(1/2)e^{-2q}+\tfrac{1}{2}\{-Ei(-q)\}^2$$

$$-q\left[1-\ln 2+\{-Ei(-2q)\}\right]$$

$$-(\ln 2)\{-Ei(-2q)\}.$$

(6-40)

Finally, $I(c^2)$ from Eq. (6-26) can be written down from Eqs. (6-32), (6-34), and (6-40) as

$$I(c^2) \equiv \int_{-\beta}^{\infty} e^{-c^2 y} \ln(1+\alpha y) \frac{dy}{y}$$

$$\simeq Li_2(1/2) - Li_2(-1/2) + Li_2(\alpha\beta) - Li_2(-2) - 1$$
$$+ e^{-2q} + q\left[-2(\ln 2) + \alpha\beta + (1-\alpha\beta)\ln(1-\alpha\beta)\right]$$
$$+ (1/2)\{-Ei(-q)\}^2 - 2q\{-Ei(-2q)\}$$

(6-41)

where, of course, $q \equiv c^2/\alpha$.

Now the energy integrations of the set of three integrals preceded by the factor $(2\ell + 3)^{-1}$ in Eq. (6-24) are given by

$$\frac{128\pi^4}{9} \times \frac{1}{2} \int_0^\infty dW \; W e^{-c^2 W} \times \left[- \int_0^\infty dl \; \frac{9}{16(2l+3)} \right.$$

$$\times \left\{ (25/54) \left[W + \sqrt{\tfrac{3}{8}} (l+2)(l+1) \right]^{-2} \right.$$

$$+ \frac{(5/3)\sqrt{2/3}\left[\left(1 - \frac{5}{6}\sqrt{\frac{2}{3}}\right) W - \frac{5}{6} \right]}{\left[W + \sqrt{\frac{3}{8}} (l+2)(l+1) \right]^3}$$

$$\left. \left. + \frac{\left[\left(1 - \frac{5}{6}\sqrt{\frac{2}{3}}\right) W - 5/6 \right]^2}{\left[W + \sqrt{\frac{3}{8}} (l+2)(l+1) \right]^4} \right\} \right]$$

$$= \frac{128\pi^4}{18} \left\{ \frac{5}{4608} \left[29\sqrt{6} - \frac{2329}{2} \right] + (\ln 9/8) \left[\frac{2711}{768} - \frac{47\sqrt{6}}{12} \right] \right.$$

$$+ c^2 (1/1024) \left(-5 - \frac{17\sqrt{6}}{4} \right) + c^2 (\ln 9/8) \left(\frac{-225}{1024} + \frac{75 \times 745\sqrt{6}}{4096} \right)$$

$$+ e^{\sqrt{\frac{3}{2}} c^2} \left\{ -Ei\left(-\sqrt{\tfrac{3}{2}} c^2 \right) \right\} \left[\left(\frac{569}{128 \times 18} - \frac{5\sqrt{6}}{6 \times 64} \right) + c^2 \left(\frac{25}{384} + \frac{187\sqrt{6}}{24 \times 48} \right) \right]$$

$$\left. + e^{\frac{-c^2}{4}\sqrt{\frac{3}{8}}} I\left(c^2, \alpha = \tfrac{4}{9}\sqrt{\tfrac{8}{3}}, \beta = \tfrac{1}{4}\sqrt{\tfrac{3}{8}} \right) \left[\frac{-57}{512} + c^2 \left(\frac{-875}{3072} + \frac{137\sqrt{6}}{6144} \right) \right] \right\}.$$

(6-42)

It is interesting to notice that there is no $(1 / c^2)$ contribution to the relaxation time from Eq. (6-42).

The numerical value of the relaxation time for the quadratic-in-w approximation can be obtained by using Eqs. (6-22), (6-25), and (6-42) in Eq. (4-21). The portion of the quadratic evaluation of T_1^{-1} in Eq. (4-21) that is of principal interest is the $(1 / c_2)$ contribution which comes from Eqs. (6-22) and (6-25), namely

$$T_1^{-1} = 8\left(\frac{\gamma\hbar}{\sigma}\right)^4 \frac{n I(I+1)}{kT}\left(\frac{\pi}{m k T}\right)^{1/2}\left[0.320\ \bar{c}^{-2} + \ldots\right].$$

(6-43)

The only calculations which remain to be done are those pertaining to the first correction term of the Euler-Maclaurin sum formula, Eq, (5-1), for the diagonal and non-diagonal contributions to the relaxation time. The correction term for $A_{\ell,\ell}(w)$ in Eq. (6-2) is

$$\frac{3}{128\pi^4} \times \frac{1}{2}\left[A_\infty(w) + A_1(w)\right] = \frac{1}{2}\left[0 + \frac{3}{10(w+1)^2}\right]$$

(6-44)

which is exactly the same as that for the correction term to the linear diagonal contribution to the relaxation time, namely Eq. (5-16). The correction term for $A_{\ell,\ell+2}(w)$ in Eq. (6-24) is

$$\frac{9}{128\pi^4} \times \frac{1}{2}\left[A_\infty(W) + A_0(W)\right] = \frac{1}{2}\left[0 + \frac{(3/2)W^2}{(W+\sqrt{3/2})^4}\right].$$

(6-45)

After the energy integrations are performed on the last two equations and the results are multiplied by the appropriate factors, then the correction to the relaxation time, $(T_1^{-1})_{corr}$, can be written down as

$$(T_1^{-1})_{corr} = 3\left(\frac{\gamma\hbar}{\sigma}\right)^4 \frac{nI(I+1)}{kT}\left(\frac{\pi}{mkT}\right)^{1/2}$$

$$\times\left[-46/45 + (1/5)(1+c^2)\{-Ei(-c^2)\}\right.$$

$$+ (1/9 - \sqrt{6}/2)c^2$$

$$\left. + (1/3 + \sqrt{\tfrac{3}{2}}\,c^2)e^{\sqrt{\frac{3}{2}}c^2}\{-Ei(-\sqrt{\tfrac{3}{2}}\,c^2)\}\right].$$

(6-46)

Use of the Euler-Maclaurin sum formula in Eqs. (6-2) and (6-24) has thus been justified by the fact that the first correction terms do not yield a contribution in the form of $(1/c^2)$ to the relaxation time.

CHAPTER VII

SUMMARY

A comparison of the results for the principal term $1/c^2$ between the linear and quadratic approximations to the relaxation time, is made below. In the linear approximation discussed in Chapter V, the energy integration of the diagonal contribution, Eq. (5-9), yields a numerical factor of $(8/3)\pi^4$ for the $1/c^2$ term. The analogous result from the non-diagonal contribution, Eq. (5-14), is $8\pi^4$. From the complete expression for T_1^{-1}, Eq. (4-21), it is seen that there exists a factor of 2 in front of the non-diagonal portion of the relaxation time. This fact, combined with the evidence that $8\pi^4$ is already larger than $(8/3)\pi^4$, means that any weakness in the approximations used to evaluate the non-diagonal term is to be reflected in the significance that can be attached to the estimated value of T_1^{-1}.

In contrast to the linear approximation, the results from the quadratic evaluation given in Chapter VI are $(8/3)\pi^4(1.625)$ and $8\pi^4(0.583)$ for the diagonal, Eq. (6-22), and non-diagonal, Eq. (6-25), terms respectively. Again, the latter number must be multiplied by 2 before the relative contributions to the relaxation time can be compared. Now with this factor, the non-diagonal term contributes twice as much as the diagonal one to T_1^{-1}.

With respect to the quadratic approximation, it is felt that more confidence can be attached to the value from the diagonal term than to the one from the non-diagonal term because of the way in which certain approximations are made in the two expressions. In the Euler-Maclaurin approximation to the diagonal contribution, the factor $\left[4 - \frac{3}{\ell(\ell+1)}\right]^{-1}$, Eq. (6-2), is expanded for large ℓ in the obvious manner. However, in the non-diagonal term, the approximation to the denominators in Eq. (6-23) is, in a sense, forced on the problem by practical considerations rather than arising in an obvious, natural manner. Thus the two rigorous, distinct denominators were replaced by a single expression $\left[w + \sqrt{(3/8)}(\ell + 1)(\ell + 2)\right]^2$ which was selected after several other equally reasonable choices had been investigated. Unfortunately, the integrations with these other denominators either diverged or gave c^{-4} contributions.

Because there exists a factor of c^2 in the coefficient $\frac{3}{16}\left(\frac{\gamma\hbar}{\sigma\pi}\right)^4 \frac{n I(I+1)}{k T}\left(\frac{\pi}{m k T}\right)^{1/2}$ which appears in Eq. (4-21) for T_1^{-1}, the $1/c^2$ terms from the diagonal and non-diagonal portions of T_1^{-1} are effectively c^0 terms. Now for $c^2 = 0$, it is obvious that the whole contribution to T_1^{-1} comes from these terms. Thus, again for $c^2 = 0$, it was found that the value of the numerical factor in front of the expression for the total relaxation time decreased from 7/2 in the linear approximation to 2.56 in the quadratic approximation. No such corresponding decrease is exhibited from the linear to the quadratic approximations in the diagonal contribution itself. In fact, the latter approximation to the diagonal term yields a result which is 1.625 times larger than that from the linear approximation. An explanation for this increase is given below.

In the exact expression for $\bar{A}_\ell(z)$, Eq, (5-2), the quotient can be written down as

$$\bar{A}_\ell(z) = \left[1 - \frac{1}{1 + \frac{a}{z^2} + \frac{b}{z^4} + \cdots}\right]^2$$

$$\geqslant \left[1 - \frac{1}{1 + \frac{a}{z^2} + \frac{b}{z^4}}\right]^2$$

$$\geqslant \left[1 - \frac{1}{1 + \frac{a}{z^2}}\right]^2 \qquad (7\text{-}1)$$

where it has been assumed that a, b, etc. are <u>all</u> positive. Now if it is true that all the coefficients in the first line of Eq. (7-1) are non-negative, then the result given by the linear approximation to the diagonal term is a lower bound for the diagonal contribution to T_1^{-1}. This substantiates the aforementioned increase from the linear to the quadratic evaluations of the diagonal term. Although no proof has been exhibited here to show that all the coefficients are in fact positive, investigation has shown that, at least for the lower powers of $1/z^2$, the assumption in Eq. (7-1) is valid.

In contrast to the diagonal term, the decrease in the numerical factor multiplying T_1^{-1} is reflected in the values obtained from the linear and quadratic approximations to the non-diagonal term. This decrease is almost by a factor of 1/2. Because of the nature of the approximations to the quadratic non-diagonal term as discussed above, there exists an uncertainty as to whether the numerical factor should have increased or decreased.

At this point, the obvious question to ask is how the results in this thesis can be improved or further substantiated. It seems that rather than calculating more correction terms and/or rather than keeping more powers of $1/z^2$ in both $z^2 h_\ell(z) h_\ell^*(z)$ and $z^2 h_\ell(z) h_{\ell+2}^*(z)$, it would be more useful to find an entirely different analytical approximation to the quotient of polynomials in Eqs. (5-2) and (5-3). Then perhaps a good estimate of the upper and lower bounds to the relaxation time could be found.

As they now stand, the results for T_1^{-1} from this thesis can be compared with the result of Chen and Snider. First, c^2 must be put equal to zero. Then from Eqs. (5-15) and (6-43), the relaxation times corresponding to the linear and quadratic approximations are

$$T_1^{-1} = (7/2)\, I(I+1) \frac{\hbar^2 \gamma^4}{\sigma^2}\, n \left(\frac{\pi m}{kT}\right)^{1/2} \tag{7-2}$$

and

$$T_1^{-1} = 2.56\; I(I+1) \frac{\hbar^2 \gamma^4}{\sigma^2}\, n \left(\frac{\pi m}{kT}\right)^{1/2} \tag{7-3}$$

respectively. Chen and Snider obtain

$$T_1^{-1} = 2\; I(I+1) \frac{\hbar^2 \gamma^4}{d^2}\, n \left(\frac{\pi m}{kT}\right)^{1/2} \tag{7-4}$$

where their d is to be identified with σ here. It would appear from Eqs, (7-2) and (7-3) that the value obtained by the other workers is good, especially considering their crude approximation which consisted of replacing the distorted wave by a plane wave.

In conclusion, it can be said that this thesis exhibits the feasibility of using analytical methods to estimate the relaxation time for a specific system.

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