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QUANTUM MECHANICAL BOLTZMANN EQUATION FOR A GAS WITH ROTATIONAL STATES

Warren Wollman

(Ph.D. Thesis)

June 1968

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ABSTRACT

A quantum mechanical Boltzmann equation is derived for a dilute diatomic gas by means of scattering theory rather than a many body approach. The classical aspects of molecular motion are heavily relied upon to clarify and relate the quantum-theoretic and semi classical approaches. In particular the limits of validity of the highly successful WCU ansatz are shown to be classical rather than quantal. Finally, an extension of the present technique to account for three and four body collisions is proposed.

1) Introduction

Transport phenomena in dilute gases of spherical molecules without internal structure are quite well described by the Chapman-Enskog (1, 2) method of solving the classical Boltzmann equation. In a dense gas where the volume per molecule is of the same order of magnitude as the volume of a molecule Enskog (2) found a satisfactory (in a practical sense) way to modify Boltzmann's original approach while still considering only binary collisions. However, a thorough-going theoretical account of density effects, including three- and four-body terms, has had very limited success due to certain divergences (3).

Whereas the experimental state of the art has not reached the point where one knows enough to pronounce judgment on the current theoretical approaches for dense gases, it was realized long ago (4) that a theory of heat transport for molecules that ignored their structure would fail badly. Momentum transport or viscosity appeared insensitive to the presence of internal states and the most recent work has not changed this belief (5). A physical but ad hoc theory due to Hirschfelder (6) succeeded in giving a good semi-empirical solution to the problem of heat transport, but what was needed really was a sound theoretical basis which would lead in a natural way toward predicting what was known about transport phenomena for gases with internal states. The first and most successful description was due to Wang-Chang and Uhlenbeck (7) (the WCU equation) which, theoretically, was on the same basis as Boltzmann's original work. Thus it was felt that a treatment starting from more fundamental

principles was still needed in order " to be sure". Mason and co-workers did not wait for such assurances but instead went ahead and found a way to solve the WCU equation not only for the case of a single specie homonuclear diatomic gas, but for polatomic and polar gas mixtures as well (5). Their efforts were highly successful and led them to pursue other lines of research, confident that the problem was, in the main, satisfactorally solved.

The WCU equation and its formal solutions pass smoothly over to the purely classical Taxman equation (8) and its predictions in the limit of classical internal states, i.e., continuous rather than discrete rotational momenta. Taxman's theory was developed with classical models rather than quantal molecules in mind. The great success of the WCU equation strongly suggests that a quantal approach to the problem should take as much advantage as possible of classical-quantal analogues.

The purely quantum theoretical attempts at solving this problem exploited classical analogies with the translational motion only. That is, what was well known and accepted about the solutions to the classical Boltzmann equation was then put to use when approximations were being sought for in handling the position and linear momentum dependence of the quantum expressions. The internal motion was not handled in any manner based on classical analogy. Thus, after forming a density matrix for the gas, both Snider (9) and Waldmann (10) constructed the Wigner function (11) for the translational part but left the internal state density matrix intact. Actually, they started with a density matrix for a one- or

two-molecule system and replaced it with an ensemble averaged matrix without saying much about how this should be done or what exactly happens while it is being done. Of particular concern is what becomes of the off-diagonal terms of the density matrix after averaging. There seemed to be no way of arguing in mathematical detail what might become of them so they were just carried along, repositories perhaps of information the gas could never divulge.

Their efforts resulted in a matrix equation (the Snider-Waldmann or SW equation) which reduced to the WCU equation for the diagonal elements. But when off-diagonal elements were retained, this equation generated incredibly complex and physically opaque solutions (12) in terms of quantities that one should not hope to calculate or measure.

Again what has emerged is the insistent suggestion that one should push as far as possible a classical analogy when handling the internal states and this has been successfully carried out in this thesis. For the diagonal elements of the matrix equation did in fact give the WCU equation and a classical description is complete in terms of the diagonal elements of the density matrix, i.e., classically, interference effects do not survive at the mascroscopic level (sometimes quantum effects do survive of course, the behavior of liquid Helium-3 for example).

The approach to be presented here uses quantum mechanical scattering theory. Classical notions of particles are constantly kept in mind. Thus wave packets were used rather than plane waves and even angular momentum wave packets were considered (with rigid rotators in mind). The latter would be needed to describe the

rotational behaviour of a macroscopic (i.e., classical) rotator or cylinder or loaded sphere (to name a few molecular models). However, it turns out that the unobservability of probabilities for values of the internal angular variables, i.e., their lack of relevance for the transport phenomena in the gas, leads to a crucial simplification of the problem and undercuts the need for angular momentum wave packets. All this became clear once a generalization of the Wigner function could be found for internal states that would allow an exploitation of the quasi-classical rotational behavior. Having found this generalization, a single equation (rather than a matrix equation) was found for the time behaviour of this Wigner function. Had the internal state density matrix been left alone, the procedure developed here would have led to the SW equation. Instead, using the internal Wigner function, one derives the WCU equation and a clear statement of the physical ideas that have led to it and argue for its validity. (Actually there is one stop along the way to the WCU equation, namely an equation written down by Watson (13) which leads to the final result immediately in the absence of preferred orientations of the gas.)

The procedure can be outlined briefly as follows: Consider a collision between two molecules to have taken place and call ψ^+ the wave function of the system. Then

$$\psi^+ = \chi + \psi_{sc}$$

where χ is the original free part and ψ_{sc} the scattered portion of the wave packets. Form the Wigner function f (for transational

states in the usual manner, for internal states in a manner to be described below): f is a particular fourier transform of the density matrix ρ while ρ is $\psi(\alpha)\psi^*(\alpha')$ where α represents the totality of coordinates. Now ψ^+ has two parts so ρ, and hence f, has four: one dependent on χ alone which gives, ultimately, the streaming terms or left hand side of the WCU equation; a second part dependent on ψ_{sc} alone which gives the scattering-in part of the collision integral and two parts due to the interference between χ and ψ_{sc} which, together, give the scattering-out part of the collision integral.

One thus constructs f(t) and then performs an ensemble average to get F(t), the distribution function that appears in the Boltzmann or WCU equation. The equation for F is

$$\frac{F(t) - F(0)}{t} = \frac{\partial F}{\partial t}$$

with the understanding that t is of the order of a mean free time. This way of getting the partial differential equation for F is not new (10, 14) and is equivalent to the "time-smoothing" introduced by Kirkwood (15). As usual, one considers binary collisions only and for times prior to a collision the pair distribution function factors into a product of singlet functions - a statistical assumption which divides past from future and can be said to introduce irreversibility in time into the theory. Compared to other approaches, the one developed here is strikingly simple, physical, and direct. By allowing more generality into the problem, for example by considering three and four body contributions in addition to the binary ones or by allowing a more rapid position

dependence of F to handle denser systems, matters become exceedingly complicated. The method presented here might be better suited than the other approaches for handling the larger questions because of the great need for a simple way of sorting out the various effects. Some thoughts on this are presented among the concluding remarks.

2) Some Notions on Distribution Functions

To begin with, all the usual relevent distribution functions need defining and some discussion and this will be done for both the classical and quantal cases. This would be useful in any discussion concerned with finding an equation for a distribution function, but more is needed here than a convenient refreshing of memory. For all attempts at a rigorous derivation of an equation for a one-particle distribution function start with some rigorously correct equation for the N-particle function which is then reduced to an equation describing some averaged single-particle state. The method to be presented here starts at the other end and works back from the properties of one specific particle to some averaged one-particle state. How and where these two approaches intersect is the main result achieved, the question of internal states being handled as an analogous case.

Again, the begin, we define certain classical phase spaces. First, a 6-dimensional space, each point of which is referred to by 6 numbers, $(\underset{\sim}{r}_i, \underset{\sim}{p}_i)$, the subscript i being a particle label. A gas of N molecules appears as a cloud of N points in this μ-space (μ for molecule). The N points appear as a single point in a second construct --

the 6N-dimensional γ-space (γ for gas) whose points are specified by the 6N numbers $(\underset{\sim}{r}_1, \underset{\sim}{p}_1, \underset{\sim}{r}_2, \underset{\sim}{p}_2, \ldots \underset{\sim}{r}_N, \underset{\sim}{p}_N) \equiv (\underset{\sim}{r}^N, \underset{\sim}{p}^N)$.

The case where all N molecules are identical implies certain connections. First of all, interchanging the labels of two points in μ-space leaves the N-point cloud unchanged but alters the location of the system point in γ-space. Thus N! points in γ-space correspond to the N! physically equivalent configurations in μ-space.

Now the probability that a molecule is in $d^3r d^3p$ at $(\underset{\sim}{r}, \underset{\sim}{p})$ in μ-space can not depend on the particle label and so the probability that at time t the volume elements $d^3r_1\, d^3p_1 \ldots d^3r_N d^3p_N \equiv d_r^{3N} d_p^{3N} \equiv d_r^{3N} d_p^{3N}$ at $(\underset{\sim}{r}^N, \underset{\sim}{p}^N)$ are occupied must be a symmetric function of the particle labels. This probability is written as

$$F^{(N)}(\underset{\sim}{r}^N, \underset{\sim}{p}^N, t)\, d^{3N}r\, d^{3N}p$$

The equivalence of the N! configurations obtained by permutation of the particle labels implies that the probability density of a particular arrangement is $F^{(N)}/N!$. Of course, this is also the probability density associated with a particular one of the N! corresponding volume elements in γ-space. This probability density is written $P^{(N)}$, i.e.,

$$P^{(N)}(\underset{\sim}{r}^N, \underset{\sim}{p}^N) = \frac{1}{N!} F^{(N)}(\underset{\sim}{r}^N, \underset{\sim}{p}^N)$$

At once there is a question of normalization and by convention one sets

$$\int_{\underset{\sim}{r}^N} \int_{\underset{\sim}{p}^N} P^{(N)} = 1$$

The probability associated with a configuration of fewer than N molecules is expressed in terms of "reduced" distribution function, defined as follows: The probability that the volume elements $d\underset{\sim}{r}_1 d\underset{\sim}{p}_1 \ldots d\underset{\sim}{r}_m d\underset{\sim}{p}_m$ at $(\underset{\sim}{r}_1 \underset{\sim}{p}_1 \ldots \underset{\sim}{r}_m \underset{\sim}{p}_m)$ are each occupied by some molecule is written as

$$F^{(m)}(\underset{\sim}{r}^m, \underset{\sim}{p}^m)\, d^{3m}r\, d^{3m}p$$

and the probability for a particular assignment of labeled molecules to these volume elements has the smaller probability

$$F^{(m)} d^{3m}r\, d^{3m}p \Big/ \left(N!/(N-m)!\right)$$

since there are $N!/(N-m)!$ different though physically equivalent ways of choosing and ordering the m molecules.

But since a given molecule, the mth say, must lie somewhere in the phase volume, integrating the above over all $\underset{\sim}{r}_m$, $\underset{\sim}{p}_m$ must result in the probability for the remaining particular configuration of (m-1) molecules. We have the equation

$$\frac{(N-m)!}{N!} d^{3(m-1)}r\, d^{3(m-1)}p \int_{\underset{\sim}{r}^m} \int_{\underset{\sim}{p}^m} F^{(m)} = \frac{(N-m+1)!}{N!} d^{3(m-1)}r\, d^{3(m-1)}p\, F^{(m-1)}$$

or

$$\int_{\underset{\sim}{r}_m} \int_{\underset{\sim}{p}_m} F^{(m)} = (N-m+1)\, F^{(m-1)}$$

which, in turn, implies

$$F^{(m)} = \frac{1}{(N-m)!} \int F^{(N)} d^{3(N-m)}r\, d^{3(N-m)}p$$

and so, finally,

$$F^{(1)} = \frac{1}{(N-1)!} \int F^{(N)} d^{3(N-1)}r\, d^{3(N-1)}p = N \int P^{(N)} d^{3(N-1)}r\, d^{3(N-1)}p$$

which gives the one-particle distribution function used in the $\underset{\sim}{r}$-$\underset{\sim}{p}$

Boltzmann equation. (The latter usually is written in terms of velocities and $F(\underset{\sim}{r}, \underset{\sim}{v})$ without a superscript is employed.)

Before one can arrive at a Boltzmann equation, repeated use is made of ensemble and time averages. As a result of such averages, the probabilities in momentum and coordinate space are independent. How to achieve such independence when one starts with a single particle is discussed in the next section.

The quantal function corresponding to $P^{(N)}$ is the density matrix introduced by von Neumann. Defined here in coordinate space in terms of the full N-body wave function $\psi^{(N)}(\underset{\sim}{r}^N, t)$, it is

$$\rho^{(N)}(\underset{\sim}{r}^N, \underset{\sim}{r}^{N\prime}, t) = \psi^{(N)}(\underset{\sim}{r}^N, t)\, \psi^{(N)*}(\underset{\sim}{r}^{N\prime}, t)$$
$$= \langle \underset{\sim}{r}^N | \psi^{(N)}, t\rangle \langle \psi^{(N)}, t | \underset{\sim}{r}^{N\prime}\rangle$$

with $$\int_{\underset{\sim}{r}^N} \rho^{(N)}(\underset{\sim}{r}^N, \underset{\sim}{r}^N, t) \equiv \mathrm{Tr}\,\rho^{(N)} = 1$$

Since $\psi^{(N)}$ is normalized to 1.

One calls $\rho^{(N)}$ the analog of $P^{(N)}$ in the sense that in each function resides all the information that can be mustered to make physical predictions.

The analog of $F^{(N)}$ is the Wigner function which is the density matrix in a mixed representation and is given by

$$f^{(N)}(\underset{\sim}{R}^N, \underset{\sim}{P}^N, t) = \frac{1}{(2\pi\hbar)^{3N}} \int_{\underset{\sim}{x}^N} e^{-\frac{i}{\hbar}\underset{\sim}{P}\underset{\sim}{x}^N} \rho^{(N)}(\underset{\sim}{R}^N + \tfrac{1}{2}\underset{\sim}{x}^N, \underset{\sim}{R}^N - \tfrac{1}{2}\underset{\sim}{x}^N, t)$$

with the highly suggestive properties

$$\int_{\underset{\sim}{P}^N} f^{(N)} = \rho^{(N)}(\underset{\sim}{R}^N, \underset{\sim}{R}^N, t) = \left| \psi^{(N)}(\underset{\sim}{R}^N, t) \right|^2$$

$$\int_{\underset{\sim}{R}^N} f^{(N)} = \left| \Phi^{(N)}(\underset{\sim}{P}^N, t) \right|^2$$

where $\Phi^{(N)}(\underset{\sim}{P}^N, t) = \langle \underset{\sim}{P}^N | \psi^N, t \rangle$ is the momentum space wave function. Thus the densities in coordinate and momentum space are extraced from $f^{(N)}$ just as they are from $F^{(N)}$ in the classical case. The uncertainty principle prevents us from interpreting $f^{(N)}$ as the probability density for the simultaneous occupation of $\underset{\sim}{R}^N$ and $\underset{\sim}{P}^N$. Other problems arise when one pushes the classical interpretation. For example, $f^{(N)}$ is not necessarily real everywhere. Still, the preceding equations are more than an anomaly and the equation for expectation values in terms of $f^{(N)}$ is written precisely the same way as is the phase space average of classical variables.

The sweeping generality of these remarks might make a specialist on the Wigner function wince. My remarks are those of a layman, by comparison, using only what he needs to understand a related problem. In this respect I am no different than others who have tackled this problem. If they have had more specialized knowledge of the Wigner function, they at least have not had to display it.

To return, we define reduced functions $f^{(m)}$, $m < N$ analogously to the $F^{(m)}$. Since $f^{(N)}$ is normalized to 1 instead of N! we have

$$f^{(m)}(\underset{\sim}{r}^m, \underset{\sim}{p}^m) = \frac{N!}{(N-m)!} \int f^{(N)} d^{3(N-m)}r \, d^{3(N-m)}p \qquad m < N$$

The function $f^{(1)}(\underset{\sim}{r}, \underset{\sim}{p})$ must undergo necessary but often vaguely defined changes before it becomes useful. All derivations of the classical Boltzmann equation from the equation for $f^{(1)}$ must somewhere along the way and usually more than once employ emsemble and time averages on $f^{(1)}$(or products of $f^{(1)}$'s) before it can emerge in the place occupied by Boltzmann's f. Even the quantum-Boltzmann equations involve an averaged $f^{(1)}$ although just where or how the averaging has taken place often is not specified. One can get away with this because the solution to the classical part of the problem is known from the outset. Whatever else it might be, $f^{(1)}$ must be made to be smoothly and slowly varying in coordinate space and time. Previous derivations assume this to be true which implies great simplifications. In working out the consequences of such an assumption, the procedure is asserted to be justified by a demonstration of self-consistency.

We close with some observations on the equations governing the time evolution of these distribution functions. First consider how $P^{(N)}$ is related to the notion of an ensemble. The probability that the system point in γ-space is in a certain volume element is proportional to the number of members of an

ensemble whose system point is found in that element. In the limit of an enormous number of systems, $P^{(N)}$ is a continuous distribution. The points move through γ-space along trajectories determined by the classical Hamiltonian $H(\underset{\sim}{r}^N, \underset{\sim}{p}^N)$. Consider an arbitrary point on one such trajectory as representing the initial conditions in a solution of Hamilton's equations. Each trajectory is in a one-to-one correspondence with such a point. Thus two trajectories never intersect at a single point only, the point uniquely determining the trajectories henceforth (and by the time reversibility of the equations of motion, the trajectories are also determined for all previous times). The points of the ensemble are often likened to a gas of non-interacting particles. Such interactions are meaningless in this context as are the notions of sources and sinks. Thus the continuity equation for these points is simply

$$\frac{\partial P^{(N)}}{\partial t} + \nabla_{\underset{\sim}{r}^N}\left(\dot{\underset{\sim}{r}}^N P^{(N)}\right) + \nabla_{\underset{\sim}{p}^N}\left(\dot{\underset{\sim}{p}}^N P^{(N)}\right) = 0$$

and since

$$\dot{\underset{\sim}{r}}^N = \nabla_{\underset{\sim}{p}^N} H \quad , \qquad \dot{\underset{\sim}{p}}^N = -\nabla_{\underset{\sim}{r}^N} H$$

we get the Liouville equation

$$\frac{\partial P^{(N)}}{\partial t} + \nabla_{\underset{\sim}{r}^N} P^{(N)} \cdot \nabla_{\underset{\sim}{p}^N} H - \nabla_{\underset{\sim}{p}^N} P^{(N)} \cdot \nabla_{\underset{\sim}{r}^N} H = 0$$

or

$$\frac{\partial P^{(N)}}{\partial t} = \left\{ H, P^{(N)} \right\}$$

where $\{\ ,\ \}$ is shorthand for what is called the Poisson bracket, written here because of the striking similarity of this equation with the quantal result.

From the Schrodinger equation one quickly derives the equation for the density matrix:

$$\frac{\partial \rho^{(N)}}{\partial t} = \frac{[H, \rho^{(N)}]}{i\hbar}$$

where $[H, \rho^{(N)}] = (H(\underset{\sim}{r}^N) - H(\underset{\sim}{r}'^N))\, \rho^{(N)}(\underset{\sim}{r}^N, \underset{\sim}{r}^{N'})$.

These two equations are the traditional starting points in both the classical and quantal many-body approaches to the kinetic equations.

Performing the appropriate fourier transform on the above equation gives the equation for $f^{(N)}$:

$$0 = \frac{i}{\hbar} \frac{1}{(2\pi\hbar)^{3N}} \int_{\underset{\sim}{p}^{N'}} \int_{\underset{\sim}{x}^N} e^{\frac{i}{\hbar}(\underset{\sim}{p}^N - \underset{\sim}{p}^{N'})\underset{\sim}{x}^N} \left[V(\underset{\sim}{R}^N + \frac{\underset{\sim}{x}^N}{2}) - V(\underset{\sim}{R}^N - \frac{\underset{\sim}{x}^N}{2})\right] f^{(N)}(\underset{\sim}{R}^N, \underset{\sim}{p}^{N'})$$

$$+ \frac{\partial f^{(N)}}{\partial t} + \frac{1}{m} \underset{\sim}{p}^N \cdot \nabla_{\underset{\sim}{r}^N} f^{(N)}(\underset{\sim}{r}^N, \underset{\sim}{p}^N, t)$$

Expanding the potential terms $V(\underset{\sim}{R}^N \pm \frac{1}{2}\underset{\sim}{X}^N)$ about $V(\underset{\sim}{R}^N)$ allows the third term to be written

$$-\frac{2}{\hbar} \sin\left(\frac{\hbar}{2} \nabla_{\underset{\sim}{R}^N} \cdot \nabla_{\underset{\sim}{p}^N}\right) V(\underset{\sim}{R}^N) f^{(N)}(\underset{\sim}{R}^N, \underset{\sim}{p}^N, t)$$

where $\nabla_{\underset{\sim}{R}^N}$ acts on $V(\underset{\sim}{R}^N)$ only.

If the particles experienced no potential, the equation would reduce to the Liouville equation for an $H = (p^N)^2/2m$. If there was instead only an external potential we would then expect the full Liouville equation. However only if $V(\underset{\sim}{R}^N)$ varies slowly enough over molecular dimensions can we obtain the classical result. The same thing comes about if we simply pass to the classical limit $\hbar \to 0$, equivalent to retaining lowest order gradients of V. But the classical equation accounts for collisions between particles so requiring V to be external in the quantal equation is too restrictive if one wants to examine the classical limit. If an internal V did not vary much over molecular dimensions the classical form of the equation would result. This restriction on the potential proves equivalent to the condition needed that a quantal object obey classical equations. Classically an analog is the short wavelength limit of optics. With such a potential, molecules are well described by localized wave packets whose detailed shape is irrelevant.

Since the external force $\underset{\sim}{F}^{ext.}$ doesnot depend on $\underset{\sim}{r}^N$ while the internal force $\underset{\sim}{F}^{int.}$ does, a reduction of the quantal equation to $f^{(1)}$ appears as

$$\frac{\partial f^{(1)}}{\partial t} + \frac{1}{m} p_1 \cdot \nabla_{R_1} f^{(1)} + \underset{\sim}{F}^{ext.} \cdot \nabla_{p_1} f^{(1)} = - \iint d^{3(N-1)}R \, d^{3(N-1)}p \; \underset{\sim}{F}^{int.} \cdot \nabla_{p_1} f^{(N)}$$

with a similar classical equation. For two-body forces $\underset{\sim}{F}^{int.} = \sum_{i<j} \underset{\sim}{F}_{ij}$ and there are (N-1) identical integrals, a typical one being

$$-\iint d^{3(N-1)}R\, d^{3(N-1)}p \frac{1}{(N-1)!} \underset{\sim}{F}_{12} \cdot \nabla_{p_N} f^{(N)} = -\iint_{\underset{\sim}{R}_2 p_2} \frac{\underset{\sim}{F}_{12}}{(N-1)!} \cdot \nabla_{p_1} \iint d^{3(N-2)}R\, d^{3(N-2)}p\, f^{(N)}$$

$$= -\iint_{\underset{\sim}{R}_2 p_2} \frac{\underset{\sim}{F}_{12}}{(N-1)!} \cdot \nabla_{p_1} \left[(N-2)!\, f^{(2)}(\underset{\sim}{R}_1 p_1; \underset{\sim}{R}_2 p_2) \right]$$

resulting in

$$-\iint_{\underset{\sim}{R}_2 p_2} \underset{\sim}{F}_{12} \cdot \nabla_{p_1} f^{(2)}$$

for the sum of these (N-1) integrals.

This can further be reduced so that only $f^{(1)}$'s are involved by invoking the principle of molecular chaos -- prior to a collision, two particles are unrelated -- and the assumption of binary encounters only. Expressions arise in the classical equation which are interpreted in classical terms only. A semi-classical (or semi-quantal) result is achieved merely by substituting in the classical equation for all expressions or quantities with a quantal analog, e.g., cross-sections. The question remains as to whether a treatment based solely on the quantal equation would have led to the same result. The answer is yes if one makes the additional demand that $\hbar \to 0$.

From another point of view we note that at high temperatures, the effects of molecules of very low energy are negligible. If then we had expanded $f^{(N)}(\underset{\sim}{p}^{N\prime})$ about $\underset{\sim}{p}^{N}$ keeping only the first non-vanishing contribution, instead of expanding V about $\underset{\sim}{R}^{N}$, we

again would come up with the classical equation for $f^{(N)}$. At low enough temperatures small velocities count and the procedure needs modification at the very least. Moreover, the thermal deBroglie wavelength becomes large enough that one can no longer assume the intermolecular potential constant across molecular dimensions. In other words, when the wave packets overlap, representing their interaction by a function of the separation of their centers of mass is simply anachronistic and fruitless. Still one can push the equations by carrying out the expansion of V to higher terms to see if lower temperature effects can be handled. Something is gained but there are limits of course and when they are exceeded, the classical equation is quite wrong and one must start again with the quantal equation. But this time as the limit $\hbar = 0$ is reached, terms proportional to $\hbar^2$ are retained and with such terms a much improved description results. Still, this method, expansion in powers of $\hbar^2$, is itself limited and fails at sufficiently low temperatures since the correction terms are proportional to powers of $\beta = 1/kT$ as well and diverge badly. Also, but for He, all substances crystallize at low temperatures (H at 14°) so He offers the only possibility for observing macroscopic quantum effects in a fluid. Below the λ-point the expansion in $\hbar^2$ diverges and another approach is required. A semi-classical method using an expansion in powers of the coupling constant in an assumed form of the intermolecular potential leads to a theory valid below the λ-point but other techniques less closely allied in spirit with the classical approach are currently proving more useful.

With all these limitations in mind, we can begin describing a procedure valid at high temperatures for dilute gases which makes full use of our knowledge of such systems to derive quite simply a quantum-Boltzmann equation which accounts for internal molecular states.

The procedure starts with a description of a single molecule in the gas in order that the left hand side or streaming terms of the Boltzmann equation be derived. The right hand side or collision integral results from a description of a particular binary collision. In either the single- or two-particle case, a wave function for the system, strictly speaking, does not exist if the system is in statistical interaction with another one. The interaction prevents a factorization of the total system wave function into parts relating only to one subsystem or the other. The density matrix for the subsystem always exists however but it must be derived from the full density matrix. Once so reduced the matrix will not explicitly depend on the coordinates of the rest of the gas but it will depend on the state of the system as a whole through the form of the total wave function remaining in the reduced matrix.

If a wave function did exist, we could expand it in terms of energy eigenfunctions (we consider a canonical ensemble, for example). The wave function for such a state (called a "pure" state, i.e., describable by a single wave function) is

$$\psi(\underset{\sim}{x},t) = \sum_n c_n e^{-\frac{i}{\hbar}E_n t} \xi_n(\underset{\sim}{x})$$

$$H\xi_n = E_n \xi_n$$

and ρ is

$$\rho(\underset{\sim}{x},\underset{\sim}{x}',t) = \psi(\underset{\sim}{x},t)\,\psi^*(\underset{\sim}{x}',t) = \sum_{n,m} c_n c_m^* e^{-\frac{i}{\hbar}(E_n - E_m)t} \xi_n(\underset{\sim}{x})\xi_m^*(\underset{\sim}{x}')$$

If instead we are dealing with a "mixed" state for which there is no single wave function, only a density matrix, a double expansion of is still allowed, but instead of $c_n c_m^*$ we would have c_{nm}. One should not think that the non-factorable c_{nm} arises from an ensemble average of the $c_n c_m^*$ since the latter simply do not exist unless the state is pure to begin with (18).

But the facts of the matter are that in a dilute gas each molecule leads a fairly solitary existence, only rarely encountering another, almost never engaging in triple or more complicated collisions. The assumptions of only binary encounters and no prior correlations allow the state to be considered pure. This becomes less well justified for dense gases and not at all for liquids. Still, the errors introduced by this assumption in applications to dense gases are less important than those incurred by assuming negligible changes in $f^{(1)}$ over distances comparable to molecular dimensions. When the latter approximation is dispensed with, one can give a good semi-empirical account of phenomena in dense gases both in theory and practice. The assumption

of binary encounters is quite difficult to supplant and this is one of the most pressing current problems in many-body physics. Some thoughts on this question will be presented later.

In view of the above remarks, one should not expect disaster if one starts by assuming a pure state and then performs an ensemble average. In other words, if one makes physical assumptions leading to a disregard of certain strict tenets of quantum mechanics, the implications should still be valid to the extent that are the assumptions. It turns out that proceeding in this way gives a very practical solution to the problem. What is perhaps a little surprising is that this procedure is so very simple and effortless in comparison with the other more rigorous treatments. However, my method is tailored to fit a specific problem. The approximations limit the generalization of the original problem the method is designed to handle. Thus while a more direct path toward a particular end is achieved, adjacent goals may be without access though they may still be reached by the other more general theoretical approaches.

In the next section, the single particle description in terms of wave packets is developed and the notion of an ensemble average is made precise in order to derive the streaming terms in the Boltzmann equation. Accounting for external forces results in a precise specification of the limits of a "classical" wave packet's usefulness. The commutability of the operations "ensemble average" and $\frac{\partial}{\partial t}$ are also discussed.

3) Wave Packets

The problem at hand is simply to discover how the presence of internal molecular states modify the Boltzmann equation of an otherwise classical gas. What is meant by classical will be detailed in the next section in quantal terms. For now we turn our attention on how to describe an object both localized and with well-defined energy. A molecule in a gas at roughly NTP is best described by a wave packet for our present purposes, there being intuitively more useful information conveyed here by the word particle rather than wave. Having argued for particles, I proceed by discussing waves.

We represent a plane wave in $\underset{\sim}{k}$-space (momentum $=\hbar \underset{\sim}{k}$) by

$$\langle \underset{\sim}{p} | \underset{\sim}{k} \rangle = \delta(\underset{\sim}{p} - \underset{\sim}{k})$$

and by

$$\langle \underset{\sim}{r} | \underset{\sim}{k} \rangle = \frac{1}{(2\pi)^{3/2}} e^{i \underset{\sim}{k} \underset{\sim}{r}}$$

in coordinate space. With the free Hamiltonian $H_o = -\frac{1}{2m}\nabla^2$ a solution to the time-dependent wave equation is

$$\chi_{\underset{\sim}{k}}(\underset{\sim}{r}, t) = e^{-iH_o t} \chi_{\underset{\sim}{k}}(\underset{\sim}{r}, 0) = \frac{1}{(2\pi)^{3/2}} e^{i \underset{\sim}{k} \underset{\sim}{r} - i E_k t}$$

$$E_k = k^2/2m \quad , \quad \hbar \to 1$$

A particle can be "created" from a superposition of such waves and information on the initial conditions of its trajectory built in at the same time. With weighting function $a_{\underset{\sim}{k}}$, a superposition of the $\chi_{\underset{\sim}{k}}$ leads to the packet $\int_{\underset{\sim}{k}} a_{\underset{\sim}{k}} \chi_{\underset{\sim}{k}}$ with momentum

localized about $\underset{\sim}{k} = \underset{\sim}{p}$ if $a_{\underset{\sim}{k}}$ is. Moreover, if $\chi_{\underset{\sim}{k}}$ is multiplied by $e^{-i\underset{\sim}{k}\underset{\sim}{r}_o + iE_k t_o}$, the packet becomes with $a_{\underset{\sim}{k}} \equiv a(\underset{\sim}{k} - \underset{\sim}{p})$

$$X_{\underset{\sim}{p}} = \frac{1}{(2\pi)^{3/2}} \int_{\underset{\sim}{k}} a(\underset{\sim}{k}-\underset{\sim}{p})\, e^{i\underset{\sim}{k}(\underset{\sim}{r}-\underset{\sim}{r}_0) - iE_k(t-t_0)}$$

Expanding E_k about E_p to first order in $(\underset{\sim}{k} - \underset{\sim}{p})$, changing dummy variable from $\underset{\sim}{k}$ to $\underset{\sim}{\rho} \equiv \underset{\sim}{k} - \underset{\sim}{p}$, we get

$$X_{\underset{\sim}{p}} = \frac{1}{(2\pi)^{3/2}} e^{i\underset{\sim}{p}(\underset{\sim}{r}-\underset{\sim}{r}_0) - iE_p(t-t_0)} \int_{\underset{\sim}{\rho}} a(\underset{\sim}{\rho})\, e^{i\underset{\sim}{\rho}(\underset{\sim}{r}-\underset{\sim}{r}_0 - \frac{1}{m}\underset{\sim}{p}(t-t_0))}$$

$$= \chi_{\underset{\sim}{p}}\, G(\underset{\sim}{r} - \underset{\sim}{r}_0 - \tfrac{1}{m}\underset{\sim}{p}(t-t_0))$$

where

$$G(\underset{\sim}{r}) \equiv \int_{\underset{\sim}{\rho}} a(\underset{\sim}{\rho})\, e^{i\underset{\sim}{\rho}\underset{\sim}{r}}$$

The function $a(\underset{\sim}{\rho})$ has width w^{-1} which implies G has width w. The wave enevelope G is appreciably different from zero when $\underset{\sim}{r} \cong \underset{\sim}{r}_o + \underset{\sim}{v}(t - t_o)$, $\underset{\sim}{v} = \frac{1}{m}\underset{\sim}{p}$. The group velocity of the packet is $\underset{\sim}{v}$. Using $X_{\underset{\sim}{p}}$, we find $\langle \underset{\sim}{r} \rangle (t) = \underset{\sim}{r}_{cl}(t)$ = classical $\underset{\sim}{r}(t)$ to within an uncertainty w. The width w is many times larger than the mean de Broglie wavelength in order that the packet be so well defined. These statements need not be made more precise at this time (16). Normalization of $X_{\underset{\sim}{p}}$ to unity implies

$$\int_{\underset{\sim}{r}} \frac{1}{(2\pi)^3} |G|^2 = 1$$

$$\int_{\underset{\sim}{p}} |a(\underset{\sim}{p})|^2 = 1$$

The corrections to $X_{\underset{\sim}{p}}$ arising from the neglect of the ρ^2 term in the expansion of $E_{\underset{\sim}{k}}$ about $E_{\underset{\sim}{p}}$ lead to the conclusion that the true envelope spreads in time and ceases to be localized. For the times of interest here, the mean free time or collision time, the spreading is utterly negligible.

The density matrix associated with the free packet is

$$\rho(\underset{\sim}{r}, \underset{\sim}{r}', t) = X_{\underset{\sim}{p}}(\underset{\sim}{r}) X^*_{\underset{\sim}{p}}(\underset{\sim}{r}')$$
$$= \frac{1}{(2\pi)^3} e^{i\underset{\sim}{p}(\underset{\sim}{r}-\underset{\sim}{r}')} G(\underset{\sim}{r} - \underset{\sim}{v}(t-t_0) - \underset{\sim}{r}_0) G^* \Big]_{\underset{\sim}{r} = \underset{\sim}{r}'}$$

From what is known of G, ρ cannot be much different from zero for $|\underset{\sim}{r} - \underset{\sim}{r}'| > w$. The center of mass of the molecule is like a piece of classical apparatus showing no non-local effects over macroscopic distances.

Defining new variables

$$\underset{\sim}{R} = \frac{1}{2}(\underset{\sim}{r} + \underset{\sim}{r}') \quad , \quad \underset{\sim}{x} = \underset{\sim}{r} - \underset{\sim}{r}'$$

the Wigner function is

$$f(\underset{\sim}{R},\underset{\sim}{P},t)=\frac{1}{(2\pi)^3}\int_{\underset{\sim}{x}} e^{-i\underset{\sim}{P}\underset{\sim}{x}}\frac{1}{(2\pi)^3}e^{i\underset{\sim}{p}\underset{\sim}{x}}\,G\,G^{*\prime}$$

If the G's are insensitive to $\underset{\sim}{x}$ over the range of $\underset{\sim}{x}$ where $GG^{*\prime}$ is non-vanishing, we get

$$f(\underset{\sim}{R},\underset{\sim}{P},t)=\frac{1}{(2\pi)^3}\delta(\underset{\sim}{P}-\underset{\sim}{p})\,|G(\underset{\sim}{R}-\underset{\sim}{v}(t-t_0)-\underset{\sim}{r}_0)|^2$$

A better approximation appears when we rewrite the G's in terms of integrals over the $a(\underset{\sim}{\rho})$'s. The result is to replace the $\delta(\underset{\sim}{P}-\underset{\sim}{p})$ by $|a(\underset{\sim}{P}-\underset{\sim}{p})|^2$ so

$$f(\underset{\sim}{R},\underset{\sim}{P},t)=\frac{1}{(2\pi)^3}|a(\underset{\sim}{P}-\underset{\sim}{p})|^2\,|G(\underset{\sim}{R}-\underset{\sim}{V}(t-t_0)-\underset{\sim}{r}_0)|^2$$

Thus the uncertainty $\underset{\sim}{x}$ in the G's is retained to the extent that it produces a corresponding uncertainty in $\underset{\sim}{P}$. The interpretation of this f is straightforward in classical terms. The corrections to it are proportional to gradients of the G's. Anything involving the detailed shape of the packets will be neglected since all measurements of properties of the gas are independent of such information. To carry along the gradient terms would not improve our description of the gas. This approximation is equivalent to retaining only gradient terms on the left side of the Boltzmann equation.

An ensemble average of this f is written as $\bar{f}$:

$$\bar{f} = \int_{\underset{\sim}{r}_0} \int_{\underset{\sim}{p}} F(\underset{\sim}{r}_0, \underset{\sim}{p}, t_0) f(\underset{\sim}{R}, \underset{\sim}{P}, t) = F(\underset{\sim}{R} - \underset{\sim}{V}(t - t_0), \underset{\sim}{P}, t_0)$$

where $F(\underset{\sim}{r}_o, \underset{\sim}{p}, t_o)$ is proportional to the probability that at $t = t_o$ there was a molecule at $\underset{\sim}{r}_o$ with momentum $\underset{\sim}{p}$. Clearly we have

$$\frac{\partial \bar{f}}{\partial t} + \underset{\sim}{V} \cdot \nabla_{\underset{\sim}{R}} \bar{f} = 0$$

so $\bar{f}$ satisfies the Boltzmann equation for a gas without external forces or interactions. Also it is assumed that F does not vary over distances and momenta of the order of the quantum mechanical uncertainties. F is the classical distribution function and in its argument, the coordinate is associated with the time (as is the momentum). In this case the "classical" argument corresponds to $\underset{\sim}{R} - \frac{1}{m} \underset{\sim}{P}(t - t_o)$ - where the particle is at $t = t_o$, call it $\underset{\sim}{R}(t_o)$. The solution to the above equation satisfies the relationship

$$\bar{f}(\underset{\sim}{r}, \underset{\sim}{p}, t + \tau) = \bar{f}(\underset{\sim}{r} - \underset{\sim}{v}\tau, \underset{\sim}{p}, t)$$

an obvious result considering that no forces or interactions are present, so we have

$$\bar{f} = F(\underset{\sim}{R}, \underset{\sim}{P}, t)$$

or $\bar{f}$ is free of "initial" conditions and the coordinate argument is independent of the momentum.

What have we done? We have assumed the existence of the Boltzmann F and used it to perform an ensemble average of the f of a single molecule to find that the averaged f obeys an equation implying that it is identical to the classical F if the usual classical approximations are retained. Since rotational energies of molecules are so small (with respect to kT), the internal motion is nearly classical, characterized by high angular momentum quantum numbers. The distribution function should describe such internal states in a manner approximating the description of a statistical ensemble of classical rotators. The procedure of assuming a classical type F to average the rotational part of a quantum mechanical f should result, as in the simple case just considered, in a useful generalization of the Boltzmann equation to account for rotational states. For internal modes of high energy such as vibrational states, such a procedure would not be expected to work. But only at extremely high temperatures are the effects of the vibrational modes felt. An equation ignoring them is thus expected to be valid over a wide temperature range.

If the ensemble averaging had been carried out after taking the $\partial/\partial t$, the final result would have been the same, although in order to get there, the approximation of neglecting effects due to quantum mechanical uncertainties would appear in a different place. It was used to write $\bar{f}$ = F plus no gradient terms due to uncertainties. The equation for $\partial\bar{f}/\partial t$ followed at once. Taking $\partial/\partial t$ first would lead to the equation

$$\frac{\partial \bar{f}}{\partial t} + \frac{1}{m}(\underset{\sim}{P} + \bar{p}) \cdot \nabla_{\underset{\sim}{R}} \bar{f} = 0$$

where

$$\bar{p} = \int_{p} p \, |a(p)|^2$$

and $\bar{f}$ is the same as before. Higher derivatives of $\bar{f}$ are consistently dropped. Here we neglect $\underset{\sim}{\bar{p}}$ with respect to $\underset{\sim}{P}$.

These considerations tell us which results of this method are to be regarded as spurious and are to be systematically ignored. After all, the approximations involved in choosing the arguments of the distribution functions come up only in the collision integral, the form of the streaming terms being exact. The usual approximations arise where expected when the collision integral is derived. The averaging procedure then becomes analogous to a time (as well as space) smoothing and the notion of a time derivative comes in for closer scrutiny. The streaming terms are well behaved. They always come out the same regardless of the averaging procedure.

The effects of external forces, discussed next, modify the streaming terms and are also involved with the limitations of the classical approximation.

4) The Classical Approximation, Stationary States, and the Streaming Terms

The trajectories of the molecules between collisions will be classical if the external potential V satisfies certain requirements. The situation encountered in practice is one in which

external forces can be considered constant over distances of the order of a mean free path and external potentials constant across the extent of a molecule. In terms of the potential, the Hamiltonian is thus considered at most a linear function of the coordinates of the center of mass of the molecule.

Quite generally, Ehrenfest's theorem states, for any wave function, that

$$\frac{d}{dt}\langle \underset{\sim}{p} \rangle = -\langle \nabla H \rangle$$

For example, in the absence of a magnetic field

$$-\nabla H = \underset{\sim}{F}(\underset{\sim}{r})$$

and the classical trajectory is followed if we can replace $\underset{\sim}{F}(\underset{\sim}{r})$ by $\underset{\sim}{F}(\langle \underset{\sim}{r} \rangle)$. An expansion of $\underset{\sim}{F}$ about $\underset{\sim}{r} = \langle \underset{\sim}{r} \rangle$ when substituted into Ehrenfest's equation yields

$$\frac{d}{dt}\langle \underset{\sim}{p} \rangle = \underset{\sim}{F}(\langle \underset{\sim}{r} \rangle) + \frac{1}{2}\sum_{ij}\left[\langle r_i r_j \rangle - \langle r_i \rangle \langle r_j \rangle\right]\frac{\partial^2 \underset{\sim}{F}}{\partial r_i \partial r_j}\Bigg|_{\underset{\sim}{r} = \langle r \rangle} + \cdots$$

so a classical trajectory will result if the second term is negligible compared to the first. The quantity in square brackets is of the order of w^2 (w as before is the width of the packet) so the condition reads

$$\left| w^2 \partial^3 V / \partial r_i \partial r_j \partial r_k \right| \ll \left| \frac{\partial V}{\partial r_\ell} \right|$$

This is always satisfied under the physical conditions we are concerned with.

An elegant derivation of the conditions for classical motion proceeds from a reduction of the Schrodinger equation to the Hamilton-Jacobi equation by assuming the phase of the wave function to be slowly varying in space. Writing

$$\psi(\underset{\sim}{r}, t) = \exp\left[\frac{i}{\hbar} S(\underset{\sim}{r}, t)\right] ,$$

Schrodinger's equation becomes an equation for S:

$$-\frac{\partial S}{\partial t} = \frac{1}{2m}\left[(\nabla S)^2 + \frac{\hbar}{i}\nabla^2 S\right] + V$$

Letting $\hbar \to 0$ so $S \to S_o$ (since S can depend on $\hbar$) gives the H-J equation for S_o, a particular solution of which completely describes a classical orbit. The same follows if

$$\hbar|\nabla^2 S| << |\nabla S|^2$$

The classical momentum is derived from S_o via

$$\underset{\sim}{p}(t) = \nabla S_o(\underset{\sim}{r}, t)$$

To estimate the limitations of this result, expand S to first order in $\hbar$:

$$S = S_o + \frac{\hbar}{i} S_1$$

Substitute into the equation for S and equate coefficients of $\hbar$, the remaining terms vanishing by virtue of satisfying the H-J equation. The inclusion of S_1 allows the probability density to be written $\rho = \exp(2S_1)$, the probability current as

$$\underset{\sim}{j}(\underset{\sim}{r},t) = \frac{\hbar}{m} \operatorname{Im} \psi^* \nabla \psi = \frac{1}{m} e^{2S_1} \nabla S_0 = \frac{1}{m} e^{2S_1} \underset{\sim}{p} = \rho \underset{\sim}{v}$$

and ρ and $\underset{\sim}{j}$ satisfy the continuity equation by implication of the equation for S_1:

$$-\frac{\partial S_1}{\partial t} = \frac{1}{m} \left(\nabla S_0 \cdot \nabla S_1 + \frac{1}{2} \nabla^2 S_0 \right)$$

Thus, to the extent that $\psi = e^{S_1} e^{\frac{i}{\hbar} S_0}$ is valid, ψ describes a continuous mass distribution moving according to the classical equations.

The neglect of wave packet spreading is equivalent to considering this description valid.

When the Hamiltonian is not a function of time, one can make the separation $S = W(\underset{\sim}{r}) - Et$. In the one-dimensional case, the equation for $W(x)$

$$\left(\frac{dW}{dx}\right)^2 = 2m(E-V) = \left(\frac{\hbar}{\lambda\!\!\!^{-}}\right)^2, \quad \lambda\!\!\!^{-} = \frac{\hbar}{(2m(E-V))^{1/2}}$$

can be integrated to give

$$W(x) = \pm \int^x dx' \, \hbar / \lambda\!\!\!^{-}(x')$$

so that, except for normalization, the stationary wave function is

$$\psi(x,t) = \exp\left[\pm i \int^{x} dx'/\chi(x')\right] e^{-\frac{i}{\hbar}Et}$$

and the necessary conditions that the motion be classical are still

$$\hbar\left|\frac{d^2W}{dx^2}\right| \ll \left(\frac{dW}{dx}\right)^2 \quad \text{or} \quad \left|\frac{d\chi}{dx}\right| \ll 1 \quad , \quad \chi \not\to \infty$$

The latter is fulfilled in the absence of classical turning points which can occur at very low energies, i.e., precisely when contributions to transport are negligible. Thus the condition is generally assumed to be satisfied. When the former is satisfied as well, a superposition of the ψ's can be used to build a wave packet executing classical behavior. This will now be done in the one-dimensional case. In the general case, the coordinate x becomes the location of a point on the classical trajectory and the condition that the gradient of χ along the trajectory be much less than 1 is sufficient to insure the validity of the approach.

We now consider a molecule having just suffered a collision and which is now out of range of any other molecules. The potential is written V = - Fx, the zero being chosen at the last point of collision so that x is the distance traveled since that collision. The Schrodinger equation reads

$$\psi'' + \frac{2m}{\hbar^2}(E + Fx)\psi = 0$$

In terms of the dimensionless variable

$$\xi \equiv x\,(1+E/Fx)\,(2mF/\hbar^2)^{1/3} \doteq x\left(1-\frac{E}{V}\right)\left(\frac{2mF}{\hbar^2}\right)^{1/3}$$

the equation becomes

$$\psi'' + \xi\psi = 0$$

For $\xi \gg 1$, i.e., far from a classical turning point (where E = V), the wave function is quasi-classical, for in this region the stationary solution for ψ is

$$\psi(\xi) = (2m)^{1/3}\,\pi^{-1/2}\,F^{-1/6}\,\hbar^{-2/3}\,\xi^{-1/4}\sin\left(\frac{2}{3}\xi^{3/2} + \pi/4\right), \quad \xi \gg 1$$

where

$$\frac{2}{3}\xi^{3/2} = \frac{1}{\hbar}\int^{x} \lambda^{-1}dx' = W/\hbar + \text{const.}, \quad S = W - Et$$

The normalization of ψ was determined by requiring that when ψ be written as a sum of two traveling waves, each shall be normalized to a current of $(2\pi\hbar)$. We will come back to this point later. The corresponding momentum space wave function is

$$a_E(p) = (2\pi\hbar F)^{-1/2}\exp\left[\frac{i}{\hbar F}(E - p^2/6m)p\right]$$

normalized as

$$\int_p a_E\, a_{E'}^* = \delta(E - E')$$

These ideas which are briefly discussed and accepted as a starting point here are developed in detail in standard references (e.g., 17). The point here is that the following is justified.

We want to build a wave packet from the $a_E(p)$ of the ψ and the question arises as to the spread of energies that is admissible. If two waves of energy E, E' are in phase at x, then we want a phase difference of π at x + w if E - E' is to be the maximum admissible energy spread. The phase difference at time t for the waves ψ is set equal to π to give the equation

$$\pi = -(E-E')t + \frac{2}{3}\left(\frac{2mF}{\hbar^2}\right)^{1/2}\left[\left(x+w+\frac{E}{F}\right)^{3/2} - \left(x+w+\frac{E'}{F}\right)^{3/2}\right]$$

Using the fact that $Fw \ll E, E'$ and setting $E' = E - \Delta E$, we assume $\Delta E \ll E$ to find the self-consistent result

$$\frac{\Delta E}{E} \cong \frac{2\pi F^{1/2}}{Ew} \cdot \frac{(x+E/F)^{1/2}}{(2m/\hbar^2)^{1/2}}$$

The external potential is a small perturbation of the motion, i.e., $Fx \ll E$ where x is of the order of a mean free path. Thus we get

$$\frac{\Delta E}{E} \simeq \frac{2\pi\hbar}{w(2mE)^{1/2}} \simeq \lambda/w \,, \quad \lambda = \text{de Broglie w.l.}$$

Since the width of a packet, w, is much larger than the mean de Broglie wavelength we have found $\Delta E \ll E$ as was assumed. In terms of the width w_p of the momentum space wave function, we have

$$\frac{\Delta E}{E} \simeq \frac{\omega_p}{p} \quad , \quad p = (2mE)^{1/2}$$

The wave packet will be formed from traveling waves rather than stationary ones of energy E. First the normalization must be changed to conform with previous formulae. To get traveling waves of current density $v/2\pi\hbar$ the above normalization must be multiplied by the factor $\sqrt{v} = (m/(E + Fx)2)^{-1/4}$. Then the coefficient squared of the wave $e^{i(\frac{2}{3}\xi^{3/2} + \frac{\pi}{4})}$ gives

$$\left[\frac{1}{2}\left(\frac{2E}{m}\right)^{1/4} \frac{(2m)^{1/3}}{\pi^{1/2} F^{1/6} \hbar^{2/3} \xi^{1/4}}\right]^2 = \frac{1}{2\pi\hbar}$$

corresponding to normalization to a δ-function in momentum instead of energy for the wave function ψ. The phase

$$\frac{2}{3}\xi^{3/2} + \frac{\pi}{4} = \frac{2}{3}(E+Fx)^{3/2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\frac{1}{F} + \frac{\pi}{4}$$

can be approximated, since E >> Fx, by

$$\left(\frac{2mE}{\hbar^2}\right)^{1/2} x + \frac{2}{3}\frac{E^{3/2}}{F}\left(\frac{2m}{\hbar^2}\right)^{1/2} + \frac{\pi}{4} \equiv kx + C$$

or kx plus a constant which can be absorbed by the phase of the normalization constant. In the limit $F \to 0$, ψ becomes a sum of plane waves

$$\psi \propto (2\pi\hbar)^{-1/2}\left[e^{ikx} - e^{-ikx}\right]$$

so what we must packet is that part of ψ which reduces to exp(ikx) when $F \to 0$. Call it ψ^+ so we packet

$$\psi^+(\xi) = \frac{1}{2}\left[\frac{2(E+Fx)}{m}\right]^{1/4} \frac{(2m)^{1/3}}{\pi^{1/2} F^{1/6} \hbar^{2/3} \xi^{1/4}} e^{i\left(\frac{2}{3}\xi^{3/2} + \frac{\pi}{4} - C\right)}$$

ψ^+ is also a solution to the problem if ψ is, and to the same degree of approximation.

The coefficient of the exponential is $(2\pi\hbar)^{-1/2}$. With the time included, the argument of the exponent is

$$\frac{2}{3}\left[(E+Fx)^{3/2}\left(\frac{2m}{\hbar^2}\right)^{1/2}\frac{1}{F} - \frac{E^{3/2}}{F}\left(\frac{2m}{\hbar^2}\right)^{1/2}\right] - \frac{Et}{\hbar}$$

Call $E = p_o^2/2m$ and packet with weighting function $a(p_o - \bar{p})$. Once again we expand about $p_o = \bar{p}$ dropping terms of order $(p_o - \bar{p})^2$. The exponent becomes

$$\left(\bar{p}x + \bar{p}\frac{Fx^2}{4\bar{E}} - \bar{E}\frac{t}{\hbar}\right) + \left[\frac{x}{\hbar}(1 - Fx/4\bar{E}) - \bar{v}t\right](p_o - \bar{p})$$

Now $Fx^2/4\bar{E} = \frac{1}{2} g (x/\bar{v})^2$, $g = \dot{\bar{v}}$

and setting $x/\bar{v} \equiv \Delta t$ we have as a result of packeting

$$\psi(x) = \frac{1}{(2\pi\hbar)^{1/2}} \exp\left[i\left(\bar{p}\left(x + \frac{1}{2}g(\Delta t)^2\right) - \bar{E}t\right)\right] G\left(x - \bar{v}t - \frac{1}{2}g(\Delta t)^2\right)$$

G is non-zero when x is within w of the value

$$x = \bar{v}t + \frac{1}{2}gt^2$$

and $\langle \Delta t \rangle = t$ to the same degree of approximation, i.e., to within w/v.

The Wigner function constructed in the same way as before is (dropping bars on mean values)

$$f = \frac{1}{(2\pi)^2} \int_r e^{-iPr + ipr + ip\frac{g}{2v^2}\left[(R+\frac{r}{2})^2 - (R-\frac{r}{2})^2\right]} G\left(R + \frac{r}{2} - vt - \frac{1}{2}g(\Delta t)^2\right) G^* \Big]_{x = R - \frac{r}{2}}$$

That part of the exponent proportional to p is

$$p(1 + gR/v^2)r$$

and the coefficient of r is an approximation to

$$p(R) \equiv (p^2 + 2m^2 gR)^{1/2}$$

since p = mv, which is the familiar kinematical relationship for the momentum as a function of position under the influence of a constant acceleration. Thus we have, in the spirit of previous approximations,

$$f = \frac{1}{2\pi} \left| a(P - p(R)) \right|^2 \left| G(R - vt - \tfrac{1}{2} g t^2) \right|^2$$

Calling the initial time and coordinate t_o and r_o instead of 0 and 0 gives

$$f = \frac{1}{2\pi} \left| a G\left(R - v(t - t_0) - \tfrac{1}{2} g (t - t_0)^2 - r_0\right) \right|^2, \quad p(R) \to p(R - r_0)$$

and an ensemble average over r_o and v gives $\bar{f}$:

$$\bar{f} = F\left(R - \frac{P}{m}(t - t_0) - \tfrac{1}{2} g (t - t_0)^2, P - mg(t - t_0), t_0\right)$$

The absence of collisions implies, as in the classical argument, that the above is equal to F(R, P, t). The differential equation satisfied by F results for example from setting the two expressions for F equal to one another for $t - t_o = dt$, $dt \ll t$, and expanding the former about the latter to first order in dt and then letting $dt \to 0$:

$$F \cong F - \left[\frac{P}{m} \partial_R + mg \partial_P + \partial_t \right] F \, dt \, , \quad F = F(R, P, t)$$

so

$$0 = \frac{\partial F(R,P,t)}{\partial t} + \frac{P}{m} \partial_R F + mg \partial_P F$$

Recall the meaning of P, R, and g: P and g are the components of the momentum and acceleration along the trajectory and R is the curvillinear coordinate locating the particle on its trajectory. Thus the above is equivalent to the usual expression of the streaming terms:

$$0 = \frac{\partial F}{\partial t} + \underset{\sim}{v} \cdot \nabla_R F + m \underset{\sim}{g} \cdot \nabla_{\underset{\sim}{P}} \cdot F \, , \quad \underset{\sim}{v} = \frac{1}{m} \underset{\sim}{P}$$

Introducing nothing new, this same result follows from the procedure of averaging after rather than before derivatives are taken.

Doing things still another way as a check against an anomalous result, if one does not set $\Delta t = t$, then simply operating on $F(R - \frac{P}{m}(t-t_o) - \frac{1}{2} g (t-t_o)^2, P - mg(t-t_o), t_o)$ with $\partial/\partial t$ again yields the correct result if at one point $mg\Delta t/\underline{P}$ can be dropped with

respect to 1 which is the same thing as dropping terms of order Fx with respect to E.

5) The Wigner Function for Internal States

Originally, Wigner was motivated by the realization that there are two scales of distance, one appropriate for macroscopic events and one for microscopic events. The density matrix of von Neumann could be written in terms of these scales or coordinates as

$$\rho(\underset{\sim}{r},\underset{\sim}{r}') \longrightarrow \rho(\underset{\sim}{R},\underset{\sim}{x}) \equiv \psi(\underset{\sim}{R}+\underset{\sim}{x}/2)\,\psi^*(\underset{\sim}{R}-\underset{\sim}{x}/2), \qquad \begin{array}{l} \underset{\sim}{R} = \frac{1}{2}(\underset{\sim}{r}+\underset{\sim}{r}') \\ \underset{\sim}{x} = \underset{\sim}{r}-\underset{\sim}{r}' \end{array}$$

The density matrix contains all the theoretically available information about the system described by ψ. The "average" coordinate $\underset{\sim}{R}$ is associated with the center of mass of the system if the system can be considered localized with respect to its surroundings, the environment with which it interacts. Then the expectation value $\langle \underset{\sim}{R} \rangle(t)$ behaves classically - the center of mass can be regarded as a classical apparatus. Another way of stating this is to point out that interference effects due to the ψ-wave describing the center of mass are not observable over macroscopic distances. Non-local microscopic behaviour is associated with the "difference" coordinate $\underset{\sim}{x}$ which of course goes to zero for a truly classical object. The Wigner function is a particular fourier transform of ρ which replaces the two vectors $\underset{\sim}{r}$, $\underset{\sim}{r}'$ by $\underset{\sim}{R}$ and $\underset{\sim}{P}$, the center of mass coordinate and momenta. When the latter are sufficient to

describe a process, the Wigner function is more to the point than the density matrix.

In the case of internal states there are striking differences and parallels. For example, consider what is meant by the assertion that a molecule is in a particular rotational state JM. First of all, we know nothing about the polar angle of the molecular axis except that it is equally likely to be anywhere from 0 to 2π. The azimuthal coordinate, though not characterized by a flat distribution, can be localized only by a superposition of high J states. If we wanted to describe a classical rotator for example, we could imagine it rotating in the x-y plane, its center of mass at the origin. A wave packet of angular momentum states with $M \simeq J$ could describe its motion by predicting that, to within quantum mechanical uncertainties,

$$I \frac{d}{dt} \langle \varphi \rangle = L \quad , \quad L = \langle \hat{J} \rangle$$

$$\langle \vartheta \rangle = 0 \quad , \quad I = \text{mom. of inertia}$$

A two-parameter rotation of the coordinate axes transforms the packeted wave function into a description of a rotator rotating about some axis other than the z-axis.

For such a packeted state, one can talk about macro- and microscopic angular coordinates as in the case of the center of mass motion. But unless one ultimately wants a description of a gas of chemical rotators, loaded spheres, or what have you, there is no need to do this. Not that one is never interested in loaded spheres and the like. They enter model-based calculations of

transport properties through values of their moments of inertia and classical or semi-classical cross sections for example. And here is an important point - the limitations of such calculations whatever they may be, are not connected with the fact that one is ignorant of the internal coordinates. A knowledge of internal energy levels and how they are coupled with each other and with translational motion is all that is needed. Of course the coupling is not at all well understood and we have to rely on empirical quantities like viscosity and diffusion coefficients (which do not sensitively depend on internal states) in order to calculate quantities like thermal conductivity (which do). Highly successful calculations of this type have been carried out (5) and the errors are within experimental uncertainties and are due to an imprecise knowledge of certain empirically determined inputs rather than theoretically calculated ones. The starting point is the WCU equation which involves internal state labels, i.e., angular momenta, but not internal coordinates. As Uhlenbeck has pointed out, for a description of polyatomic gases in the classical regime, the WCU equation tells the whole story. (I think this has little to do with what the U in WCU stands for.) Of course the details are still missing from this story - the cross sections are unknown. But in principle, one cannot say that internal coordinates are lacking. They have simply been averaged out of the picture. Thus one is motivated to find a generalization of the Wigner function so that internal states may be described with the important proviso that internal coordinates will not be retained.

The generalization proves to be quite simple and straightforward.

The angular wave function is represented by the superposition

$$\Psi(\Omega) = \sum_{\mu\nu} C_{\mu\nu} Y_\mu^\nu(\Omega) \quad , \quad \Omega = (\theta, \varphi)$$

where Y_μ^ν is the spherical harmonic and $\sum_{\mu\nu} |C_{\mu\nu}|^2 = 1$. A tacit assumption is that internal and translational motions are decoupled. Furthermore, any internal vibrational motion is ignored. Such motion becomes significant only at temperatures much higher than those under consideration here. Instead of θ, $x = \cos\theta$ will be used. The density matrix is

$$\rho(x_1\varphi_1, x_2\varphi_2) = \sum_{\substack{\mu\nu \\ \rho\sigma}} C_{\mu\nu} C^*_{\rho\sigma} Y_\mu^\nu(x_1\varphi_1)\, Y_\rho^{*\sigma}(x_2\varphi_2)$$

and the difference and sum coordinates are

$$X = \tfrac{1}{2}(x_1 + x_2) \quad , \quad \Phi = \tfrac{1}{2}(\varphi_1 + \varphi_2)$$

$$x = x_1 - x_2 \quad , \quad \varphi = \varphi_1 - \varphi_2$$

We seek a kernel $K_{LM}(X\Phi|x\varphi)$ such that

$$f_{LM}(X, \Phi) = \int_x \int_\varphi K_{LM}\, \rho$$

has the properties

$$\int_X \int_\Phi f_{LM}(X, \Phi) = |C_{LM}|^2 , \quad \sum_{LM} f_{LM}(X, \Phi) = |\Psi(X, \Phi)|^2$$

Due to the orthogonality properties of the spherical harmonics, the correct kernel is

$$K_{LM} = Y_L^M(\Omega_1)^* \, Y_L^M(\Omega_2)$$

with

$$\sum_{LM} K_{LM} = \delta(x_1 - x_2)\,\delta(\varphi_1 - \varphi_2) = \delta(x)\,\delta(\varphi)$$

When expectation values of operators are calculated with this Wigner function according to the usual prescription, the operators are replaced by their classical analogs in a phase integral over internal coordinates and momenta. For calculating such quantities as the mean internal energy or polarization, the classical quantities are independent of coordinates and only an average over momentum states survives. For a given molecule in the state JM, the relevant part of the Wigner function is $\int_X \int_\Phi f_{\ell m} = \delta_{\ell m, JM}$ which, when averaged over an ensemble via $\sum_{JM} F_{JM}(\ldots)$ gives $F_{\ell m}$. In other words the procedure goes just as before only it is actually simpler in the present case. Of course, before we were guided by the fact that an F with all the right classical behaviour did in fact exist. For rotational states, such as F also exists, the distance between energy levels being very much smaller than kT, the mean transational energy and the rotation-translation coupling strong so that rotational levels are easily excited and distributed via collisions in the classical Boltzmann manner for all but the

lowest temperatures, i.e., everywhere except near the point of liquefaction. For vibrational states, the energies and their separations are large compared with kT and the vibration-translation coupling weak except for the exceptional case of end-on collisions between vibrating rotators. Relaxation of vibrational excitation is of the order of at least 100 times longer than rotational relaxation, which in turn is about 10 times longer than translational relaxation (18).

In the next section, the effect of collisions are derived, including a derivation of the optical theorem for wave packets and a lower limit for the mean time between collisions in order to justify the approach. We will not consider temperatures so high that excitation of vibrational levels is important. Thus it is sufficient to consider rotational states only. The generalized Wigner function is really just that - qute general. Instead of the Y_L^m'S, any orthonormalized set could be used to expand the internal wave function. The intergration over internal coordinates of the new f again will yield the square of the corresponding expansion coefficient.

6) Collisions Integral I - "Scattering In"

We will consider the problem of a molecule scattering from a static target rather than do a more general two-body collision. Generality is not lost however because this procedure amounts to going to the rest frame of the second particle. It will be easy to rewrite the final results valid in the more general case. For one interested in all the detailed calculation, some remarks on the wave packet picture of a two body collision are in appendices to this section.

In treating the terms involving the scattered wave, we ignore the effects of an external potential in the sense that for times prior to the collision, the molecule is represented by a free wave packet. Such neglect is standard procedure when deriving the collision integral by any means, the external potential being regarded as too small a perturbation to lead to any significant contribution.

What is envisaged here is a kind of experiment. We have a target sitting at the origin bombarded with a single molecule. Then we examine the effects related to the scattered portion of the wave and to the interference between the free and scattered parts, each making a contribution to the Wigner function. The experiment is considered to be repeated many times with the incoming molecule having a different momentum, internal state, and initial position each time. The dependence of the post-collision states on the initial conditions are removed by an ensemble average over such conditions which is slightly more involved than the previous averagings.

The contribution to the Wigner function from the initial wave alone gives of course the streaming terms and these were considered in the previous sections. The pre-collision state is denoted by the plane wave $\chi = (2\pi)^{-3/2} e^{i\underset{\sim}{k}_0 \underset{\sim}{x}} Y_\ell^\mu$ (Y_ℓ^μ is the internal state function) and after scattering, the wave is

$$\psi = \chi + \sum_{JM} Y_J^M (2\pi)^{-3/2} \frac{e^{ikr}}{r} f$$

where the scattering is assumed for now to have taken place at the origin and the target is structureless. The scattering amplitude f is a matrix in angular momentum quantum numbers. The quantity k is some function of the kinematical variables and is the magnitude of the momentum associated with the outgoing spherical wave.

The initial state has mean momentum $\underset{\sim}{p}$ and internal energy ϵ_ℓ. When packeted, the scattered portion of the time dependent wave is

$$\frac{1}{(2\pi)^{3/2}} \sum_{JM} Y_J^M \frac{e^{ip_f r - iEt}}{r} f(\underset{\sim}{p}\ell\mu \to p_f \hat{r} JM)\, G_f$$

where

$$E = \frac{1}{2m} p^2 + \epsilon_\ell = \frac{1}{2m} p_f^2 + \epsilon_J \text{ defines } p_f$$

as

$$p_f = \left[p^2 + 2m(\epsilon_\ell - \epsilon_J)\right]^{1/2}$$

and

$$G_f \equiv G\left(\underset{\sim}{v}\left[\frac{r}{v_f} - t\right]\right) \quad , \quad \underset{\sim}{v} = \frac{1}{m}\underset{\sim}{p}, \quad v_f = \frac{1}{m} p_f$$

The quantity $r/v_f \equiv \Delta t$ is such that $\langle \Delta t \rangle = t$ = time elapsed since the scattering took place at $t = 0$. Putting in initial conditions, we shall instead say that at $t = 0$ the molecule was localized at $-\underset{\sim}{v}t_o + \underset{\sim}{b}$ and the collision occurred at $t = t_o$. The vector $\underset{\sim}{b}$ is the impact parameter. G_f becomes

$$G_f = G\left(\underset{\sim}{v}\left[\Delta t - (t - t_o)\right] - \underset{\sim}{b}\right)$$

so $\langle \Delta t \rangle = t - t_o$. The implicit understanding of $\underset{\sim}{b}$ is that it is small enough that G is non-zero somewhere for $t > t_o$, i.e., the impact parameter is sufficiently small that a collision did in fact take place. We include it here because it is explicitly averaged over later. Since $\underset{\sim}{b} \cdot \underset{\sim}{v} = o$, b must be $\lesssim$ w regardless of the rest of G's argument in order that G not always vanish. Also, even for such $\underset{\sim}{b}$, G vanishes unless $t = t_o + \Delta t$ to within w/v_f. For $t < t_o$ this cannot be unless Δt is of the order of w/v_f. But we consider the scattered wave to be in the asymptotic region where $\Delta t > w/v_f$ so the scattered wave is properly negligible prior to the mean time of collision t_o.

That part of the density matrix ρ due alone to the scattered portion of the wave is called ρ^+ (the notation is motivated by the knowledge that f^+ gives the "scattered-in"

collision integral)

$$\rho^{+} = \frac{1}{(2\pi)^3} \sum_{\substack{JM \\ J'M'}} \frac{e^{ip_f r - ip_{f'} r'}}{r r'} f(\text{initial} \to \hat{r} JM) f^{*\prime} Y_J^M Y_{J'}^{M'*} G_f G_f^{*\prime}$$

where $G_{f'}$, $P_{f'}$ are G_f and P_f evaluated for $J \to J'$. Going over to the variables $\underset{\sim}{R}$, $\underset{\sim}{x}$ we do the following:

In the phase we set

$$r = |\underset{\sim}{R} + \underset{\sim}{x}/2| = R + \hat{R} \cdot \underset{\sim}{x}/2$$

$$r' = R - \hat{R}\underset{\sim}{x}/2$$

and in the arguments of the G's we set

$$\Delta t = \overline{\Delta t} + \hat{R}\underset{\sim}{x}/2v_f \quad , \quad \overline{\Delta t} \equiv R/v_f$$

$$\Delta t' = \overline{\Delta t'} - \hat{R}\underset{\sim}{x}/2v_f$$

while f is assumed constant over the range of $\underset{\sim}{x}$, i.e., f is evaluated for $\hat{r}$, $\hat{r}'$ both equal to $\hat{R}$ and the macroscopic lengths r, r' are both replaced by R. The corresponding Wigner function f^+ is

$$f^{+} = (2\pi)^{-3} \int_{\underset{\sim}{x}} e^{-i\underset{\sim}{P}\underset{\sim}{x}} \int_{\text{angles}} K_{L_f M_f} \rho^{+}$$

The internal state kernel works so that we get the double sum $\sum_{JM, J'M'} (\cdot\cdot\cdot)$ collapsing via $\delta_{JM, L_f M_f} \delta_{J'M', L_f M_f}$ to give

$$f^{+} = \frac{1}{(2\pi)^3} \int_{\underset{\sim}{x}} e^{-i\underset{\sim}{P}\underset{\sim}{x}} \frac{1}{(2\pi)^3} \frac{e^{ip_f \hat{R}\underset{\sim}{x}}}{R^2} \left| f(\cdots \to \hat{R} L_f M_f) \right|^2 |G_f|^2$$

where p_f, G_f are evaluated with L_f.

The $\int_{\underset{\sim}{x}}$ gives $(2\pi)^3 \delta(\underset{\sim}{P} - p_f \hat{R})$ because we ignore $\underset{\sim}{x}$ in the arguments of the G's. The improved approximation is, as before, to replace $\delta(\underset{\sim}{P} - p_f \hat{R})$ by $|a(\underset{\sim}{P} - p_f \hat{R})|^2$ so that we have

$$f^{+} = \frac{1}{(2\pi)^3} |a(\underset{\sim}{P} - p_f \hat{R})|^2 \left| G\left(v\left[\frac{R}{v_f} - (t - t_0)\right] - b\right)\right|^2 \frac{|f(p\ell\mu \to p_f \hat{R} L_f M_f)|^2}{R^2}$$

with an obvious physical interpretation of the arguments. However, when evaluating the collision integral, all uncertainties due to the widths of $|a|^2$ and $|G|^2$ will be neglected consistent with dropping gradient terms in the collision integral. Thus the quantities $|a|^2$ and $|G|^2$ will be treated like δ-functions. The parameters $\underset{\sim}{p}$, $\underset{\sim}{b}$, and t_o are to be averaged over. Before we averaged over $\underset{\sim}{r}_o = -\underset{\sim}{v} t_o + \underset{\sim}{b}$, hence the two averagings are equivalent. The range of variation of the initial state parameters needs defining since there are definite physical limitations inherent in this hypothetical experiment. The two molecules are members of a gas of course and so, regardless of $\underset{\sim}{p}$, we expect a free flight time t_o from $\underset{\sim}{r}_o$ to the point of scattering to be weighted by the probability of such a free time, namely $\exp(-t_o/\tau)$ where τ is a mean free time. (This is not necessary mathematically however and other physical arguments suffice as will be seen below.) The volume over which

$\underset{\sim}{r}_o$ ranges is likewise characterized by the mean free path and $\underset{\sim}{R}$ is more or less central to this volume. The probability of the initial conditions is proportional to $F_{\ell\mu}(\underset{\sim}{p}, \underset{\sim}{r}_o, o) = F_{\ell\mu}(\underset{\sim}{p}, -\underset{\sim}{v}t_o + \underset{\sim}{b}, o) = F_{\ell\mu}(\underset{\sim}{p}, -\underset{\sim}{v}t_o, o)$ since $|G|^2$ restricts $\underset{\sim}{b}$ to the order of w and F is insensitive to such a microscopic length. The molecule moves freely, i.e., streams, from $t = o$ t_o $t = t_o$ so $F_{\ell\mu}(\underset{\sim}{p}, -\underset{\sim}{v}t_o, o) = F_{\ell\mu}(\underset{\sim}{p}, o, t_o)$. The naming of the origin is arbitrary and we will write $F_{\ell\mu}(\underset{\sim}{p}, x_1, t_o)$ because we want to average in general over the mass density of target molecules at $\underset{\sim}{x}_1$. For now we write the ensemble averaged f^+ as (dropping subscript f from L_f, M_f)

$$\overline{f^+_{LM}}(\underset{\sim}{p}, \underset{\sim}{R}, t) = \sum_{\ell\mu} \int_{\underset{\sim}{x}_1} \int_{\underset{\sim}{p}} \int d^2b \int v\,dt_o\, e^{-t_o/\tau} F_{\ell\mu}(\underset{\sim}{p}, \underset{\sim}{r}_o + \underset{\sim}{x}_1, o) f^+ n_1(\underset{\sim}{x}_1, 0)$$

where n_1 is the density function for the target at $t = o$. In f^+, the point $\underset{\sim}{R}$ is relabeled $\underset{\sim}{R} - \underset{\sim}{x}_1$, consistant with its meaning as the vector from the region of collision to the position where f^+ is being evaluated. Defining $\underset{\sim}{u} = \underset{\sim}{R} - \underset{\sim}{x}$, $d^3u = d^3x_1$, the $\int d\Omega_{x_1} \to \int d\Omega_{\hat{u}}$ is removed by the restriction due to $|a|^2$ that $\hat{u} = \hat{p}$ to within uncertainties over a wave packet. The point $\underset{\sim}{R}$ is considered the center of the volume over which $\underset{\sim}{u}$ is integrated. We also have $p^2dp = p^2dp_f \left|\frac{dp}{dp_f}\right| = p_f p dp_f$ and the rest of the restraint imposed by $|a|^2$ is to hold p_f to within $\hbar/w$ of P. So far this means

$$\overline{f^{+}_{LM}}(\underset{\sim}{P},\underset{\sim}{R},t) = \sum_{\ell\mu} \int du \int d\Omega_{\hat{p}} \int d^2b \int v\,dt_0\, e^{-t_0/\tau} \frac{\left|G\left(\underset{\sim}{v}\left[\frac{u}{P/m}(t-t_0)-\underset{\sim}{b}\right)\right|^2}{(2\pi)^3}$$

$$\times \left| f(p\ell\mu \to \underset{\sim}{P}LM)\right|^2 \frac{v}{P/m} F_{\ell\mu}(p, \underset{\sim}{r}_0 + \underset{\sim}{R} - u\hat{P}, 0)\, n_1(\underset{\sim}{R})$$

where p is fixed by kinematics in terms of $\underset{\sim}{P}$, L, and ℓ and $n_1(\underset{\sim}{x}_1)$ has been replaced by $n_1(\underset{\sim}{R})$, an approximation due originally to Boltzmann (and discussed further below). The operation

$$\int d^2b \int du \frac{|G|^2}{(2\pi)^3} = \frac{P/m}{v}$$

leaves an integral over t_o to be performed. What is left so far is

$$\overline{f^{+}_{LM}} = \sum_{\ell\mu} \int d\Omega_{\hat{p}} \int v\,dt_0\, e^{-t_0/\tau} F_{\ell\mu}\left(p, -vt_0 + \underset{\sim}{R} + \frac{\underset{\sim}{P}}{m}(t-t_0), 0\right) n_1(\underset{\sim}{R}) |f|^2$$

In the coordinate argument of $F_{\ell\mu}$, as t_o ranges from 0 to τ, the argument ranges from $\underset{\sim}{R} + \frac{1}{m}\underset{\sim}{P}t$ to $\underset{\sim}{R} + \frac{1}{m}\underset{\sim}{P}t - (\underset{\sim}{v} + \frac{\underset{\sim}{P}}{m}\tau)$. Now the time t is such that $t - t_o$ is of the order of a mean free time at most (and a collision duration at the least) since we seek the average change due to a single collision. Thus both $\frac{1}{m}\underset{\sim}{P}t$ and $-\underset{\sim}{v}t_o + \underset{\sim}{P}(t - t_o)/m$ are of the order of a mean free path. Thus approximating $F_{\ell\mu}$ simply by $F_{\ell\mu}(\underset{\sim}{R})$ is again equivalent to one of Boltzmann's original approximations leading to errors well investigated (14).

In the usual derivation of the Boltzmann equation, when constructing the collision integrals, one focusses attention on some small volume element d^3R within which everything is happening -- particles are being scattered in and out of some momentum all in this little volume element during a time dt. The distribution functions used to describe the mean occurrence of events are assumed constant over d^3R and during dt (although they are allowed to vary when constructing the streaming terms). In the above work one can simply consider the ranges of t_o, $\underset{\sim}{x}_1$, and $\underset{\sim}{r}_o$ small enough that these approximations are valid, the point $\underset{\sim}{R}$ being central to the volume that contributes. Further rewriting of $\overline{f^+_{LM}}$ comes by noticing that

$$\sum_{\ell\mu} |f(p\ell\mu \to \underset{\sim}{P}LM)|^2 = \sum_{\ell\mu} |f(\underset{\sim}{P}L,-M \to p\ell\mu)|^2$$

by parity and time reversal invariance, while

$$v|f|^2 = V\left(\frac{v}{V}|f|^2\right) \text{ where } V = P/m$$

so that

$$v\sum_{\ell\mu} |f(p\ell\mu \to \underset{\sim}{P}LM)|^2 = V\sum_{\ell\mu} \frac{v}{V} f(\underset{\sim}{P}L,-M \to p\ell\mu)|^2$$

$$= V\sum_{\ell\mu} \frac{d\sigma}{d\Omega_{\hat{p}}}(PL,-M \to p\ell\mu)$$

so

$$\overline{f^+_{LM}} = \sum_{\ell\mu} \int V d\sigma F_{\ell\mu}(\underset{\sim}{p}, \underset{\sim}{R}, 0)\, n_1(\underset{\sim}{R}, 0)\, \tau$$

With no preferred orientations, nothing is lost though much is simplified, by including a sum over M sending $\overline{f^+_{LM}} \rightarrow \overline{f^+_L}$ and allowing - M $\rightarrow$ M on the right hand side (M being a dummy index) We also drop the magnetic quantum number from F:

$$\overline{f^+_L} = \sum_{\substack{\ell\mu \\ M}} \int V d\sigma (\underset{\sim}{P} LM \rightarrow \underset{\sim}{p}\, \ell\mu)\, F_\ell(\underset{\sim}{p}, \underset{\sim}{R}, 0)\, n_1(\underset{\sim}{R}, 0)\, \tau$$

and again note that $\hat{p}$ is being integrated over while p is fixed by $p^2/2m + \epsilon_\ell = P^2/2m + \epsilon_L$.

If the target, remaining static, had structure represented by some initial internal state function $Y_{\ell_1}^{\mu_1}$, which could change as a result of the collision, then the scattered part of the wave would be

$$\sum_{\substack{JM \\ J_1M_1}} Y_J^M(\Omega)\, Y_{J_1}^{M_1}(\Omega_1) \frac{e^{ikr}}{(2\pi)^{3/2} r}\, f(\underset{\sim}{k_0}\ell\mu, \ell_1\mu_1 \rightarrow kJM, J_1M_1, \hat{r})$$

where $k^2/2m + \epsilon_J + \epsilon_{J_1} = k_0^2/2m + \epsilon_\ell + \epsilon_{\ell_1}$ fixes k.

The kernel for the internal part of the Wigner function would remain the same and $\overline{f^+_{LM}}$ would include a sum over J_1M_1 from above due to a trace over Ω_1 plus an additional average over $\ell_1\mu_1$. Moreover, if the second particle were allowed to have an

initial momentum $\underset{\sim}{p}$, certain obvious changes would occur in the final expression for $\overline{\mathcal{F}^{F}_{LM}}$. Firstly, we would have

$$\sum_{\substack{\ell\mu \\ M}} v \frac{d\sigma}{d\Omega_{\hat{p}}}(\underset{\sim}{P}LM \to \underset{\sim}{p}\ell\mu)\, d\Omega_{\hat{p}}\, F_{\ell\mu}(\underset{\sim}{p})\, n_1 \to$$

$$\sum_{\substack{\ell\mu \\ \ell_1\mu_1 \\ J_1M_1 \\ M}} v_r \frac{d\sigma}{d\Omega_{\hat{\kappa}_f}}(\underset{\sim}{P}LM, \underset{\sim}{p}_1' J_1 M_1 \to \underset{\sim}{p}\ell\mu, \underset{\sim}{p}_1 \ell_1\mu_1)\, d\Omega_{\hat{\kappa}_f}\, d^3p_1'\, F_{\ell\mu}(\underset{\sim}{p})\, F_{\ell_1\mu_1}(\underset{\sim}{p}_1)$$

$$= \sum_{\cdots} v_r\, d\sigma(\underset{\sim}{\kappa} LMJ_1M_1 \to \Omega\ell\mu\ell_1\mu_1)\, d^3p_1'\, F_{\ell\mu} F_{\ell_1\mu_1}$$

where $v_r = \frac{1}{m}|\underset{\sim}{P} - \underset{\sim}{p}_1'|$ and $\hat{\kappa}_f$ is the direction of the final relative momentum (tacitly defined with respect to the direction of the initial relative momentum)

$$\underset{\sim}{\kappa}_f = \frac{1}{2}(\underset{\sim}{p} - \underset{\sim}{p}_1)$$

The original integration variables were of the original initial state ($\hat{p}, \underset{\sim}{p}_1$), but well known kinematical arguments allowed the initial and final states to be interchanged in the argument of $d\sigma$ to give the transformation to the above.

The momentum arguments of $F_{\ell\mu}$, $F_{\ell_1\mu_1}$ originally were $\underset{\sim}{p}$ and $\underset{\sim}{p}_1$ but in the final form we would have

$$F_{\ell\mu}(\underset{\sim}{p}) F_{\ell_1\mu_1}(\underset{\sim}{p}_1) \to F_{\ell\mu}(\tfrac{1}{2}\underset{\sim}{G} + \underset{\sim}{\kappa}_f)\, F_{\ell_1\mu_1}(\tfrac{1}{2}\underset{\sim}{G} - \underset{\sim}{\kappa}_f)$$

where $\underset{\sim}{G} = \underset{\sim}{P} + \underset{\sim}{p}_1$ and

$$\kappa_f = \left[\kappa^2 + (\epsilon_L + \epsilon_{J_1} - \epsilon_\ell - \epsilon_{\ell_1})\, m\right]^{1/2}$$

with $\kappa = \frac{1}{2}\,|\underset{\sim}{P} - p_1'|$.

The final result is

$$\overline{f_L^+} = \tau \sum_{\substack{\ell\mu \\ \ell_1\mu_1 \\ J, M_1 \\ M}} \int d\Omega_{\hat{\kappa}_f} \int d^3p_1' v_r \frac{d\sigma}{d\Omega_{\hat{\kappa}_f}} F_{\ell\mu}\left(\tfrac{1}{2}(\underset{\sim}{P} + p_1') + \underset{\sim}{\kappa}_f\right) F_{\ell_1\mu_1}$$

The point $\underset{\sim}{R}$, as before, is considered the central point in the volume of integration over the collision point. If no orientations are preferred, the F's do not depend on the magnetic quantum number and we write F_ℓ instead of $F_{\ell\mu}$. This is always the case for homo-nuclear diatomic molecules, symmetry considerations ruling out electric or magnetic moments. In the absence of electric or magnetic fields there is no preferred orientation in any case.

Finally a word about the time arguments of the F's. Since $f_L^+ = 0$ for $t = 0$ because of the causal instructions from $|G|^2$ (no scattered wave packet prior to collision time), the procedure of obtaining $\overline{f_L^+}(t)$ knowing $F(0)$, $t \approx 0$ (mean free time), can be considered an iteration process like a repeated disorder assumption. Then one could regard

$$\frac{\overline{f_L^+}(t) - \overline{f_L^+}(0)}{\tau} = \overline{\frac{\partial}{\partial t} f_L^+(0)} \equiv J^+(0)$$

and since any initial time may be used, the empty time slot can be filled by t when J^+ (the usual symbol for the scattering-in part of the collision integral) is written in terms of an integral

over the F(0)'s.

Alternatively, since t is of the order of τ we could have used τ for t all along or have dropped the factor $e^{-t_o/\tau}$ with the understanding that for the usual reasons the variation in the F's due to changes in the coordinate argument dependent on t_o are ignored. In the latter case the physical restrictions on the range of integration over t_o are (1) that the minimum t_o is τ_c - something of the order of the duration of a collision because initially the molecules are out of each others range and (2) the maximum t_o is $t - \tau_c$ since t is an asymptotic time or $t - t_o$ must be at least great enough that again the molecules are free of each other. Then the t_o integration gives $t - 2\tau_c \approx t$ since $t \gg \tau_c$ so $\overline{f^{+}}$ is proportional to the time elapsed from the start. Classically the same result holds, t being analogous to the Δt or dt during which changes are occurring, the F's remaining constant during dt. Finally, taking ∂_t first and then performing the averages would have resulted in zero since, unlike the case of the streaming terms, gradients of the F's are dropped from the collision integral and it is only such terms that result from taking ∂_t .

Appendix 6A Wave Packets in Collision

The kinematics and close relation to a classical picture are brought out in the evaluation of a cross section for the scattering of two wave packets.

The starting point is the unpacketed wave generated by a collision beginning with the initial state

$$\chi = (2\pi)^{-3} e^{i\underset{\sim}{k}_1 \underset{\sim}{x}_1 + i\underset{\sim}{k}_2 \underset{\sim}{x}_2}$$

which, when packeted and time dependent, is

$$\chi = (2\pi)^{-3} e^{i\underset{\sim}{p}_1(\underset{\sim}{x}_1 - \underset{\sim}{x}_{10}) + i\underset{\sim}{p}_2(\underset{\sim}{x}_2 - \underset{\sim}{x}_{20}) - i(E_1+E_2)(t-t_0)} G_1 G_2$$

with

$$G_i = G_i(\underset{\sim}{x}_i - \underset{\sim}{v}_i(t-t_0) - \underset{\sim}{x}_{i0})$$

where the mean momenta are $\underset{\sim}{p}_1$, $\underset{\sim}{p}_2$ and the packets are localized at $\underset{\sim}{x}_{i0}$ at $t = t_0$.

The usual procedures lead to the unpacketed scattered wave

$$\psi_{sc} = (2\pi)^{-3} e^{i\underset{\sim}{G}\underset{\sim}{C} + i\kappa r} \frac{f}{r}$$

where $\underset{\sim}{G} = \underset{\sim}{k}_1 + \underset{\sim}{k}_2$

$$\kappa = \mu \left| \underset{\sim}{k}_1/m_1 - \underset{\sim}{k}_2/m_2 \right| , \quad \mu^{-1} = m_1^{-1} + m_2^{-1} , \quad M = m_1 + m_2$$

$$r = |\underset{\sim}{x}_1 - \underset{\sim}{x}_2|$$

$$f = -(2\pi)^2 \mu T$$

and T is the T-matrix element $T(E, \underset{\sim}{G}, \hat{\kappa} \cdot \hat{r})$, $E = E_1 + E_2$. Energy and momentum delta functions extracted from the T-matrix fix the final total momentum and final magnitude of the relative momentum in the asymptotic region at their original values (no changes in internal states being considered for simplicity here). The direction of the final relative momentum is not fixed of course, the relative probabilities for the different directions being proportional to the square of the appropriate scattering amplitude.

When the scattered wave is packeted we write

$$\begin{aligned}
\underset{\sim}{G}\underset{\sim}{C} + \kappa r - \underset{\sim}{k}_1 \underset{\sim}{x}_{10} - \underset{\sim}{k}_2 \underset{\sim}{x}_{20} &= \underset{\sim}{k}_1 \underset{\sim}{x}_1 + \underset{\sim}{k}_2 \underset{\sim}{x}_2 - \underset{\sim}{\kappa}\, \underset{\sim}{r} + \kappa r - \underset{\sim}{k}_1 \underset{\sim}{x}_{10} - \underset{\sim}{k}_2 \underset{\sim}{x}_{20} \\
&= \underset{\sim}{p}_1 \underset{\sim}{x}_1 + \underset{\sim}{p}_2 \underset{\sim}{x}_2 - \bar{\underset{\sim}{\kappa}}\, \underset{\sim}{r} + \bar{\kappa} r - \underset{\sim}{p}_1 \underset{\sim}{x}_{10} - \underset{\sim}{p}_2 \underset{\sim}{x}_{20} \\
&\quad + (\underset{\sim}{k}_1 - \underset{\sim}{p}_1) \cdot \left(\underset{\sim}{x}_1 - \underset{\sim}{x}_{10} + \frac{r}{v_r} (\underset{\sim}{v}_1 - \underset{\sim}{v}_c) - \frac{m_2}{M} \underset{\sim}{r} \right) \\
&\quad + (\underset{\sim}{k}_2 - \underset{\sim}{p}_2) \cdot \left(\underset{\sim}{x}_2 - \underset{\sim}{x}_{20} + \frac{r}{v_r} (\underset{\sim}{v}_2 - \underset{\sim}{v}_c) + \frac{m_1}{M} \underset{\sim}{r} \right)
\end{aligned}$$

to first order in $\underset{\sim}{p}_i = \underset{\sim}{k}_i - \underset{\sim}{p}_i$ with barred quantities evaluated for $\underset{\sim}{k}_i \to \underset{\sim}{p}_i$

since

$$\kappa = \mu \left| \underset{\sim}{v}_1 - \underset{\sim}{v}_2 + p_1/m_1 - p_2/m_2 \right|$$

$$= \mu \bar{v}_r + \mu \hat{v}_r \left(p_1/m_1 - p_2/m_2 \right)$$

to first order in p_i and

$$\underset{\sim}{\bar{\kappa}} = p_1 - \frac{m_1}{M} \underset{\sim}{\bar{G}} \quad \text{or} \quad \underset{\sim}{\bar{\kappa}} = -p_2 + \frac{m_2}{M} \underset{\sim}{\bar{G}}$$

so

$$\underset{\sim}{\bar{\kappa}}/m_1 = \underset{\sim}{v}_1 - \underset{\sim}{v}_c \quad , \quad \underset{\sim}{\bar{\kappa}}/m_2 = -\underset{\sim}{v}_2 + \underset{\sim}{v}_c$$

where

$$\underset{\sim}{v}_c = \underset{\sim}{\bar{G}}/M$$

Extracted from the packeting integral is

$$\exp\left[i p_1 (\underset{\sim}{x}_1 - \underset{\sim}{x}_{10}) + i p_2 (\underset{\sim}{x}_2 - \underset{\sim}{x}_{20}) - i \underset{\sim}{\bar{\kappa}} \underset{\sim}{r} + i \bar{\kappa} r \right]$$

which equals

$$\exp\left[i \underset{\sim}{\bar{G}} (\underset{\sim}{c} - \underset{\sim}{c}_0) + i \bar{\kappa} r - i \underset{\sim}{\bar{\kappa}} \underset{\sim}{r}_0 \right]$$

where

$$\underset{\sim}{c}_0 = \underset{\sim}{c} (\underset{\sim}{x}_{10}, \underset{\sim}{x}_{20}) \quad , \quad \underset{\sim}{r}_0 = \underset{\sim}{x}_{10} - \underset{\sim}{x}_{20}$$

Including the time dependence in the usual way, the integration over $\underset{\sim}{p}_1, \underset{\sim}{p}_2$ gives the factors (dropping bars)

$$G_1 \left(\underset{\sim}{x}_1 + \underset{\sim}{v}_1 \left(\frac{r}{v_r} - (t - t_0) \right) - \frac{m_2}{M} \underset{\sim}{r} - \frac{r}{v_r} \underset{\sim}{v}_c - \underset{\sim}{x}_{10} \right)$$

and

$$G_2\left(\underset{\sim}{x}_2 + \underset{\sim}{v}_2\left(\frac{r}{v_r} - (t-t_0)\right) + \frac{m_1}{M}\underset{\sim}{r} - \frac{r}{v_r}\underset{\sim}{v}_c - \underset{\sim}{x}_{20}\right)$$

But since

$$\underset{\sim}{c} + \frac{m_2}{M}\underset{\sim}{r} = \underset{\sim}{x}_1$$

$$\underset{\sim}{c} - \frac{m_1}{M}\underset{\sim}{r} = \underset{\sim}{x}_2$$

the arguments become

$$G_1\left(\underset{\sim}{c} - \underset{\sim}{v}_c\frac{r}{v_r} + \underset{\sim}{v}_1\left(\frac{r}{v_r} - (t-t_0)\right) - \underset{\sim}{x}_{10}\right)$$

and

$$G_2\left(\underset{\sim}{c} - \underset{\sim}{v}_c\frac{r}{v_r} + \underset{\sim}{v}_2\left(\frac{r}{v_r} - (t-t_0)\right) - \underset{\sim}{x}_{20}\right)$$

and in terms of the classical point of collision $\underset{\sim}{z}_0$:

$$\underset{\sim}{z}_0 = \underset{\sim}{c} - \underset{\sim}{v}_c\frac{r}{v_r} = \underset{\sim}{c} - \underset{\sim}{v}_c\,\Delta t\,, \quad \Delta t = \frac{r}{v_r}\,, \langle\Delta t\rangle = t - t_0$$

we get

$$G_1\left(\underset{\sim}{v}_1\left[\Delta t - (t-t_0)\right] + \underset{\sim}{z}_0 - \underset{\sim}{x}_{10}\right)$$

and

$$G_2\left(\underset{\sim}{v}_2\left[\Delta t + (t_0 - t)\right] + \underset{\sim}{z}_0 - \underset{\sim}{x}_{20}\right)$$

The scattering amplitude f is considered constant across the width of the packets so the scattered wave packet is

$$\psi_{sc} = \frac{(2\pi)^{-3}}{r} \exp i\left[\underset{\sim}{G}(\underset{\sim}{C}-\underset{\sim}{C}_0) + \kappa r - \underset{\sim}{\kappa}\,\underset{\sim}{r}_0 - E(t-t_0)\right] f\, G_1 G_2$$

Specifying the direction of the final relative momentum fixes the final state. In other words the final momenta can be defined in terms of the numbers ($\underset{\sim}{x}_1$, $\underset{\sim}{x}_2$). It goes this way:

$$\kappa\hat{r} = \underset{\sim}{\kappa}_f = \frac{m_2}{M}\underset{\sim}{p}_{1f} - \frac{m_1}{M}(\underset{\sim}{G} - \underset{\sim}{p}_{1f}) \quad , \quad \underset{\sim}{p}_{2f} = \underset{\sim}{G} - \underset{\sim}{p}_{1f}$$

The first equation defines $\underset{\sim}{p}_{1f}$, the second $\underset{\sim}{p}_{2f}$ and, by construction, momentum and energy are conserved. We find $\underset{\sim}{p}_{1f}$ to be

$$\underset{\sim}{p}_{1f} = m_1(\underset{\sim}{x}_1 - \underset{\sim}{z}_0)/\Delta t = m_1 \underset{\sim}{v}_{1f}$$

and

$$\underset{\sim}{p}_{2f} = m_2(\underset{\sim}{x}_2 - \underset{\sim}{z}_0)/\Delta t = m_2 \underset{\sim}{v}_{2f}$$

further illustrating the role of $\underset{\sim}{z}_0$ as the classical point of collision. Now $\underset{\sim}{x}_1$ and $\underset{\sim}{x}_2$ are arbitrary so $\underset{\sim}{z}_0$ is not necessarily the mean point of collision. However the G_1G_2 factor is significant only for those values of $\underset{\sim}{x}_1$ and $\underset{\sim}{x}_2$ such that $\langle \underset{\sim}{z}_0 \rangle = \underset{\sim}{x}_{10}$ or $\underset{\sim}{x}_{20}$. Since all expectation values are uncertain due to the finite size of the packets, $\langle \underset{\sim}{z}_0 \rangle$ can be either $\underset{\sim}{x}_{10}$ or $\underset{\sim}{x}_{20}$ because, for a collision to have occurred (a tacit assumption), $|\underset{\sim}{x}_{10} - \underset{\sim}{x}_{20}|$ must be $\lesssim w_0$.

The final momenta can be introduced into the phase of ψ_{sc} by the following manipulations:

$$\begin{aligned}
\underset{\sim}{G}(\underset{\sim}{C}-\underset{\sim}{C}_0)+Kr-\underset{\sim}{K}\underset{\sim}{r}_0 &= \underset{\sim}{G}\underset{\sim}{C}+\underset{\sim}{K}_f\underset{\sim}{r}-\underset{\sim}{G}\underset{\sim}{C}_0-\underset{\sim}{K}\underset{\sim}{r}_0 \\
&= \underset{\sim}{G}(\underset{\sim}{C}-\underset{\sim}{z}_0)+\underset{\sim}{K}_f\underset{\sim}{r}-\left[\underset{\sim}{G}(\underset{\sim}{C}-\underset{\sim}{z}_0)+\underset{\sim}{K}\underset{\sim}{r}_0\right] \\
&= (\underset{\sim}{p}_{1f}+\underset{\sim}{p}_{2f})(\underset{\sim}{C}-\underset{\sim}{z}_0)+(\mu\underset{\sim}{v}_r)\underset{\sim}{r}-[\quad] \\
&= \underset{\sim}{p}_{1f}\left(\underset{\sim}{C}-\underset{\sim}{z}_0+\frac{m_2}{M}\underset{\sim}{r}\right)+\underset{\sim}{p}_{2f}\left(\underset{\sim}{C}-\underset{\sim}{z}_0-\frac{m_1}{M}\underset{\sim}{r}\right)-[\quad] \\
&= \underset{\sim}{p}_{1f}(\underset{\sim}{x}_1-\underset{\sim}{z}_0)+\underset{\sim}{p}_{2f}(\underset{\sim}{x}_2-\underset{\sim}{z}_0)-[\quad]
\end{aligned}$$

The first two terms give the increase in phase from the initial point $\underset{\sim}{z}_0$ to $\underset{\sim}{x}_1$, $\underset{\sim}{x}_2$ while the last term including the minus sign is the initial phase at $\underset{\sim}{z}_0$, i.e., for $\underset{\sim}{x}_1$, $\underset{\sim}{x}_2 \rightarrow \underset{\sim}{x}_{10}, \underset{\sim}{x}_{20}$. The time dependent part of the initial phase is defined as zero so the last term is the total phase for $\underset{\sim}{x}_1$, $\underset{\sim}{x}_2$, $t \rightarrow \underset{\sim}{x}_{10}, \underset{\sim}{x}_{20}, t_0$.

For later use, note the kinematical relations

$$\frac{v_r}{r}=\frac{v_{if}}{|\underset{\sim}{x}_i-\underset{\sim}{z}_0|}=\frac{v_{if}}{R} \qquad \text{so} \quad \frac{1}{r}=\frac{v_{if}}{v_r}\frac{1}{R}$$

We now proceed to get the cross-section from ψ_{sc}. We have

$$\psi_{sc}=(2\pi)^{-3}\exp i\left[p_{1f}|\underset{\sim}{x}_1-\underset{\sim}{z}_0|+p_{2f}|\underset{\sim}{x}_2-\underset{\sim}{z}_0|-E(t-t_0)\right]\frac{v_{if}f\psi_0}{Rv_r}$$

where

$$\psi_0 \equiv \exp i\left[\underset{\sim}{G}(\underset{\sim}{z}_0 - \underset{\sim}{C}_0) - \underset{\sim}{\kappa}\underset{\sim}{r}_0\right] G_1 G_2$$
$$= \exp i\left[\underset{\sim}{p}_1(\underset{\sim}{z}_0 - \underset{\sim}{x}_{10}) + \underset{\sim}{p}_2(\underset{\sim}{z}_0 - \underset{\sim}{x}_{20})\right] G_1 G_2$$

If when packeting we had changed the integration variables from $\underset{\sim}{k}_1$, $\underset{\sim}{k}_2$ to $\underset{\sim}{G}$, $\underset{\sim}{\kappa}$, the argument of the G's would be

$$\underset{\sim}{C} - \underset{\sim}{C}_0 - \underset{\sim}{v}_c (t - t_0)$$

and

$$\hat{\bar{\kappa}} r - \underset{\sim}{r}_0 - \underset{\sim}{\bar{v}}_r (t - t_0)$$

for the center of mass and relative packets respectively. Since $\hat{\bar{\kappa}} = \hat{\bar{v}}_r$, the argument of the latter is

$$\underset{\sim}{v}_r \left[\Delta t - (t - t_0)\right] - \underset{\sim}{r}_0$$

so ψ_{sc} vanishes unless $r_0 \lesssim w$, i.e., unless the packets do actually overlap at $t = t_0$ - something only tacitly assumed before. For $t < t_0$, ψ_{sc} always vanishes. The argument of G_c simply requires

$$\langle \underset{\sim}{C} \rangle = \underset{\sim}{C}_0 + \underset{\sim}{v}_c (t - t_0)$$

and tells us nothing about the initial conditions. Actually everything has been preordained in the arguments of G_1 and G_2 appearing in the initial state packet X. There, it is generally required that

$$|\underset{\sim}{x}_1 - \underset{\sim}{v}_1 (t-t_0) - \underset{\sim}{x}_{10}| \lesssim O(w)$$

$$|\underset{\sim}{x}_2 - \underset{\sim}{v}_2 (t-t_0) - \underset{\sim}{x}_{20}| \lesssim O(w)$$

for X to be appreciably different from zero.

If at $t = t_o$ we require a collision, then $\langle r \rangle \lesssim R$, the range of the intermolecular force. Now $R \underset{\sim}{<} w$ by construction so we want

$$|\underset{\sim}{r} - \underset{\sim}{r}_0| \lesssim O(w)$$

which implies $r_0 \lesssim O(w)$.

To return, the density of m_1 at $\underset{\sim}{x}_1$ is

$$\rho_1(\underset{\sim}{x}_1) = \int_{\underset{\sim}{x}_2} |\psi_{sc}|^2 = \frac{(2\pi)^{-6}}{|\underset{\sim}{x}_1 - \langle \underset{\sim}{z}_0 \rangle|^2} \left(\frac{v_{1f}}{v_r}\right)^2 |f|^2 \int_{\underset{\sim}{x}_2} |G_1 G_2|^2$$

where $\underset{\sim}{z}_0 \to \langle \underset{\sim}{z}_0 \rangle$ in the denominator and was brought out of the integral. The integration can be more simply carried out in terms of $\underset{\sim}{z}_o$ rather than $\underset{\sim}{x}_2$. We have

$$\int_{\underset{\sim}{x}_2} |G_1 G_2|^2 = \int_{\underset{\sim}{z}_0} J \, |G_1 G_2|^2$$

where $J = |\partial \underset{\sim}{x}_2 / \partial \underset{\sim}{z}_0|$ is found by solving for $\underset{\sim}{z}_o$ in terms of $\underset{\sim}{x}_2$, forming $|\partial \underset{\sim}{z}_0 / \partial \underset{\sim}{x}_2|$ and inverting. The result is

$$J = \left(\frac{M}{m_2}\right)^3 \left(1 + \hat{r} \, \underset{\sim}{G} \, \frac{m_1}{\kappa M}\right)^{-1}$$

The initial flux at $t = t_o$ is

$$\phi_o = (2\pi)^{-6} v_r \int |G_1 G_2|^2 d^3 z_o = (2\pi)^{-6} v_r \int_{\underset{\sim}{z}_o} |G_1(\underset{\sim}{z}_o - \langle \underset{\sim}{z}_o \rangle) G_2(\underset{\sim}{z}_o - \langle \underset{\sim}{z}_o \rangle)|^2$$

a generalization correctly reducing to the more usual case where the beam packet is much broader than the target packet. The final flux of m_1 at $\underset{\sim}{x}_1$ is $v_{1f} \rho_1(\underset{\sim}{x}_1)$ and the number of particles per second through $R^2 d\Omega_{1f}$ at $\underset{\sim}{x}_1$ is

$$N = \rho_1 \underset{\sim}{v}_{1f} \cdot \hat{R}\, d\Omega_{1f}\, R^2 ,$$

then

$$\frac{N}{\phi_o} = \left(\frac{v_{1f}}{v_r}\right)^3 |f|^2 J\, d\Omega_{\hat{R}} = d\sigma$$

or

$$\frac{d\sigma}{d\Omega_{\hat{R}}} = |f|^2 \left(\frac{p_{1f}}{\kappa}\right)^3 \left(1 + \hat{r} \cdot \underset{\sim}{G} \frac{m_1}{M \kappa}\right)^{-1}$$

which is the usual non-realistivistic cross section in the lab system. This result depended on the cancellation of

$$\frac{\int_{\underset{\sim}{z}_o} |G_1(\underset{\sim}{v}_1[\Delta t - (t - t_o)] + \underset{\sim}{z}_o - \langle \underset{\sim}{z}_o \rangle) G_2|^2}{\int_{\underset{\sim}{z}_o} |G_1(\underset{\sim}{z}_o - \langle \underset{\sim}{z}_o \rangle) G_2(\underset{\sim}{z}_o - \langle \underset{\sim}{z}_o \rangle)|^2}$$

with $0/0 \rightarrow 1$ not allowed, i.e., the outgoing and incoming fluxes are non-zero by hypothesis. When $\underset{\sim}{x}_1$, $\underset{\sim}{x}_2$ are such that the classical kinematical expectation values are realized, i.e., when $\Delta t = \langle \Delta t \rangle$ for instance, we also have $\underset{\sim}{z}_o = \langle \underset{\sim}{z}_o \rangle$ as well, all equal signs correct to within quantum mechanical uncertainties.

Appendix 6B <u>Handling a non-static target</u>

The part of the phase of the scattered wave packet dependent on $\underset{\sim}{x}_1$, $\underset{\sim}{x}_2$ is

$$\underset{\sim}{G}\,\underset{\sim}{C} + \kappa_f r = \underset{\sim}{p}_1 \underset{\sim}{x}_1 + \underset{\sim}{p}_2 \underset{\sim}{x}_2 - \underset{\sim}{\kappa}\,(\underset{\sim}{x}_1 - \underset{\sim}{x}_2) + \kappa_f\,|\underset{\sim}{x}_1 - \underset{\sim}{x}_2|$$

When the Wigner function is formed, the part of the phase proportional to $\underset{\sim}{x} \equiv \underset{\sim}{x}_1 - \underset{\sim}{x}_1'$ is

$$\left(\underset{\sim}{p}_1 - \underset{\sim}{\kappa} + \kappa_f\,(\widehat{R - x_2})\right)\underset{\sim}{x} - \underset{\sim}{P}\,\underset{\sim}{x}$$

But $\underset{\sim}{p}_1 = \frac{m_1}{M}\underset{\sim}{G} + \underset{\sim}{\kappa}$ so we have as the coefficient of $\underset{\sim}{x}$

$$\left(\frac{m_1}{M}\underset{\sim}{G} + \underset{\sim}{\kappa}_f\right) - \underset{\sim}{P}$$

where

$$\underset{\sim}{\kappa}_f = \kappa_f\,(\widehat{R - x_2})$$

$$\kappa_f = \left[\kappa^2 + (\epsilon_{\ell_1} + \epsilon_{\ell_2} - \epsilon_{\ell_{1f}} - \epsilon_{\ell_{2f}})\,2\mu\right]^{1/2}$$

and

$$\underset{\sim}{p}_{1f} = \frac{m_1}{M}\underset{\sim}{G} + \underset{\sim}{\kappa}_f$$

and the ϵ_i's are the initial and final internal state energies. The internal state functions and internal Wigner function were handled in the case of the static target with internal structure. Only where the kinematics are affected by internal states will their presence be made explicit. The point of this appendix is

to present the method needed to handle the algebraic complications arising from doing the problem in the lab frame rather than the rest frame of the target particle. In the spirit of neglecting terms proportional to gradients of the F's in the collision integral, the expressions $|a(\underset{\sim}{g})|^2$ and $|G(\underset{\sim}{x})|^2$ will be handled as if they were $\delta(\underset{\sim}{g})$ and $(2\pi)^3\delta(\underset{\sim}{x})$.

The unaveraged Wigner function for "scattering in" is

$$f^+ = (2\pi)^{-3}\int_{\underset{\sim}{x}} e^{-i\underset{\sim}{P}\underset{\sim}{x}} \int_{\underset{\sim}{x}_2} \rho^{(2)}(\underset{\sim}{R}+\underset{\sim}{x}/2, \underset{\sim}{x}_2 | \underset{\sim}{R}-\underset{\sim}{x}/2, \underset{\sim}{x}_2)$$

$$= (2\pi)^{-3}\int_{\underset{\sim}{x}} e^{-i\underset{\sim}{P}\underset{\sim}{x}} \int_{\underset{\sim}{x}_2} e^{i\underset{\sim}{P}_{1f}\underset{\sim}{x}} (2\pi)^{-6} \frac{|G_1 G_2|^2 |f|^2}{|\underset{\sim}{R}-\underset{\sim}{x}_2|^2}$$

where

$$G_1 = G_1(\underset{\sim}{R} - \underset{\sim}{v}_{1f}\Delta t + \underset{\sim}{v}_1[\Delta t - \langle\Delta t\rangle] + \underset{\sim}{z}_0 - \underset{\sim}{x}_{10})$$

$$G_2 = G_2(\underset{\sim}{x}_2 - \underset{\sim}{v}_{2f}\Delta t + \underset{\sim}{v}_2[\Delta t - \langle\Delta t\rangle] + \underset{\sim}{z}_0 - \underset{\sim}{x}_{20})$$

$$f = f(\kappa l_1 l_2 \to l_{1f} l_{2f}\ \hat{\kappa}\cdot(\widehat{R-x_2}))$$

$$\Delta t = |\underset{\sim}{R} - \underset{\sim}{x}_2| / v_{r_f}$$

$$\underset{\sim}{z}_0 = \underset{\sim}{R} - \underset{\sim}{v}_{1f}\Delta t$$

$\underset{\sim}{x}_{10}$ and $\underset{\sim}{x}_{20}$ are the localizations of m_1 and m_2 at $t = t_o$ and

by postulating a collision, $\underset{\sim}{x}_{10} - \underset{\sim}{x}_{20} = \underset{\sim}{b}$ - an impact parameter whose magnitude is at most of the order of the range of the intermolecular potential. For larger b, ψ_{sc} vanishes since then there is no way for $|G_1|^2$ and $|G_2|^2$ to be simultaneously appreciable. Eventually $\underset{\sim}{b}$ is averaged over and the factor $|G_1G_2|^2$ restricts b to a magnitude too small to affect the averaging functions F_1F_2.

At t = 0, the packets are localized at $\underset{\sim}{r}$ and $\underset{\sim}{r}$ respectively with

$$\underset{\sim}{r}_{10} = \underset{\sim}{x}_{10} - \underset{\sim}{v}_1 t_0$$

$$\underset{\sim}{r}_{20} = \underset{\sim}{x}_{20} - \underset{\sim}{v}_2 t_0 = \underset{\sim}{x}_{10} - \underset{\sim}{v}_2 t_0 - \underset{\sim}{b} = \underset{\sim}{r}_{10} - \underset{\sim}{b} + \underset{\sim}{v}_r t_0$$

$$\underset{\sim}{b} \cdot (\underset{\sim}{v}_1 - \underset{\sim}{v}_2) = \underset{\sim}{b} \cdot \underset{\sim}{v}_r = 0$$

the last condition by the definition of an impact parameter. The averaging functions are

$$F_1(\underset{\sim}{p}_1, \underset{\sim}{r}_{10}, 0) \quad \text{and} \quad F_2(\underset{\sim}{p}_2, \underset{\sim}{r}_{20}, 0)$$

and $\overline{f^+}$ is given by

$$\overline{f^+} = \int_{\underset{\sim}{p}_1} \int_{\underset{\sim}{p}_2} \int_{\underset{\sim}{r}_{10}} \int_{\underset{\sim}{r}_{20}} F_1 F_2 \int_{\underset{\sim}{x}_2} \delta(\underset{\sim}{P} - \underset{\sim}{p}_{1f}) \frac{|f|^2}{|\underset{\sim}{R} - \underset{\sim}{x}_2|^2} \left| \frac{G_1 G_2}{(2\pi)^3} \right|^2$$

First of all we have $\int_{\underset{\sim}{p}_1} \int_{\underset{\sim}{p}_2} \cdots = \int_{\underset{\sim}{G}} \int_{\underset{\sim}{K}} \cdots$ and the integration over $\underset{\sim}{G}$ removes $\delta(\underset{\sim}{P} - \frac{m_1}{M}\underset{\sim}{G} - \underset{\sim}{K}_f)$ leaving

$$\overline{f^+} = \iiiint_{\underset{\sim}{\kappa}\, \underset{\sim}{r}_{10}\, \underset{\sim}{r}_{20}\, \underset{\sim}{x}_2} \left(\frac{M}{m_1}\right)^3 F_1\left(\frac{m_1}{M}(\underset{\sim}{P}+\underset{\sim}{p}_{2f})+\underset{\sim}{\kappa}\right) F_2\left(\frac{m_2}{M}(\underset{\sim}{P}+\underset{\sim}{p}_{2f})-\underset{\sim}{\kappa}\right) \frac{|f|^2 |G_1 G_2|^2}{\left[(2\pi)^3 |\underset{\sim}{R}-\underset{\sim}{x}_2|\right]^2}$$

Now define $\underset{\sim}{u} \equiv \underset{\sim}{R} - \underset{\sim}{x}_2$ with $d^3u = d^3x_2$ and make the transformation

$$d^3u\, d^3\kappa = u^2 du\, d\Omega_u\, \kappa^2 d\kappa\, d\Omega_\kappa$$
$$= u^2 du\, d\Omega_\kappa \left(\frac{\kappa}{\kappa_f}\right)\left[\kappa_f^2\, d\kappa_f\, d\Omega_u\right]$$

and

$$\kappa_f^2\, d\kappa_f\, d\Omega_u \equiv d^3\kappa_f$$

so

$$d^3u\, d^3\kappa = u^2 du\, d\Omega_\kappa \left(\frac{v_r}{v_{r_f}}\right) d^3\kappa_f$$

where κ is written as a function of κ_f and the internal states. Next, since

$$\underset{\sim}{p}_{2f} = \frac{m_2}{M}\underset{\sim}{G} - \underset{\sim}{\kappa}_f = \frac{m_2}{M}(\underset{\sim}{P} + \underset{\sim}{p}_{2f}) - \underset{\sim}{\kappa}_f$$

or

$$\underset{\sim}{p}_{2f} = \frac{m_2}{m_1}\underset{\sim}{P} - \frac{M}{m_1}\underset{\sim}{\kappa}_f$$

we have $d^3\kappa_f = \left(\frac{m_1}{M}\right)^3 d^3p_{2f}$ so $\overline{f^+}$ becomes

$$\overline{f^{+}} = \int_{\underset{\sim}{r}_{10}} \int_{\underset{\sim}{r}_{20}} \int du \int d\Omega_{\kappa} \int d^3 p_{2f} \, F_1 F_2 \, |f|^2 \left| \frac{G_1 G_2}{(2\pi)^3} \right|^2 \left(\frac{v_r}{v_{r_f}} \right)$$

and, wherever it appears, $\underset{\sim}{\kappa} \to \kappa \hat{\kappa} = \kappa(\kappa_f, \Delta\epsilon)\hat{\kappa}$ and κ_f is given in terms of $\underset{\sim}{P}$ and $\underset{\sim}{p}_{2f}$. The arguments of the G's may be written

$$\frac{|G_1 G_2|^2}{(2\pi)^6} = \frac{|G_1(\underset{\sim}{z}_0 - \underset{\sim}{r}_{10} - \underset{\sim}{v}_1 t_0)|^2}{(2\pi)^3} \cdot \frac{\left|G_2\left(\underset{\sim}{b} - \underset{\sim}{v}_r \left[\frac{u}{v_{r_f}} - (t - t_0)\right]\right)\right|^2}{(2\pi)^3}$$

since the only appreciable contributions from their product come when both arguments are simultaneously zero to within w, the width of the packets.

Holding $\underset{\sim}{r}_{10}$ and κ fixed during the integration over $\underset{\sim}{r}_{20}$ the following transformation helps remove $|G_2|^2$:

From $\underset{\sim}{r}_{20} = \underset{\sim}{r}_{10} - \underset{\sim}{b} + \underset{\sim}{v}_r t_0$ and $\underset{\sim}{b} \cdot \underset{\sim}{v}_r = 0$, the three independent components of $\underset{\sim}{b}$ and $\underset{\sim}{v}_r$ can be used instead of $\underset{\sim}{r}_{20}$. We define the new variable y:

$$\underset{\sim}{y} \equiv \underset{\sim}{b} - \underset{\sim}{v}_r \frac{u}{v_{r_f}} \quad , \quad d^3 y = d^2 b \, du \left(\frac{v_r}{v_{r_f}} \right)$$

and with

$$du \, d^3 r_0 = du \, d^2 b \, v_r \, dt_0 = \left(d^2 b \, du \frac{v_r}{v_{r_f}} \right) v_{r_f} dt_0 = d^3 y \, v_{r_f} dt_0$$

we have

$$\overline{f^+} = \int_{\underset{\sim}{r}_{10}} \int d\Omega_\kappa \int_{p_{2f}} \int dt_0 \int_{y} F_1 F_2 |f|^2 v_r \frac{|G_1|^2}{(2\pi)^3} \cdot \frac{|G_2(\underset{\sim}{y} + \underset{\sim}{v}_r(t-t_0))|^2}{(2\pi)^3}$$

$$= \int_{\underset{\sim}{r}_{10}} \int d\Omega_\kappa \int_{p_{2f}} \int dt_0 \, F_1 F_2 |f|^2 v_r \frac{|G_1(\underset{\sim}{R} - \underset{\sim}{v}(t-t_0) - \underset{\sim}{r}_{10} - \underset{\sim}{v}_1 t_0)|^2}{(2\pi)^3}$$

where $\underset{\sim}{z}_0$ has gone over to $\underset{\sim}{R} - \underset{\sim}{v}(t - t_0)$, $\underset{\sim}{v} = \underset{\sim}{P}/m$, and $\underset{\sim}{b} \to 0$ from arg $G_2 = 0$. The integral over $\underset{\sim}{r}_{10}$ goes out with $|G_1|^2$ leaving an integral over t_0 which has been discussed before along with the meaning of $\overline{\frac{\partial f^+}{\partial t}}$ or J^+ so we can write

$$J^+(t=0) = \int d\Omega_\kappa \int d^3 p_{2f} \, v_r \frac{d\sigma}{d\Omega_\kappa} F_1\left(\frac{m_1}{M}(\underset{\sim}{P} + p_{2f}) + \kappa_f \hat{\kappa}, \underset{\sim}{R} - \underset{\sim}{v}(t-t_0) + \right.$$
$$\left. - v_1 t_0, 0\right) F_2$$

where $\underset{\sim}{v}_1$, $\underset{\sim}{v}_2$ are expressed in terms of $\underset{\sim}{P}$, p_{2f}, and κ and the coordinate arguments are $\underset{\sim}{r}_{10}$ and $\underset{\sim}{r}_{20}$ respectively. Again as is well discussed elsewhere (14), the coordinate arguments are each set equal to $\underset{\sim}{R}$ since, for situations not far removed from equilibrium, the left hand side of the Boltzmann equation is linear in $\nabla_{\underset{\sim}{R}}$ and the collision integral with $F = F^{(0)}(\underset{\sim}{R})(1 + \varphi(\underset{\sim}{R})\epsilon)$ substituted as the solution (F^0 is the equilibrium distribution, ϵ the perturbation parameter) is also linear in $\nabla_{\underset{\sim}{R}}$.

Thus expanding the product $F_1(\underset{\sim}{r}_{10})\ F_2(\underset{\sim}{r}_{20})$ about $F_1(\underset{\sim}{R})\ F_2(\underset{\sim}{R})$ beyond the leading term gives an inconsistent result, i.e., terms non-linear in $\nabla_{\underset{\sim}{R}}$.

Relabeling variables and using $v_r\, d\sigma(\kappa \epsilon_{int} \to \epsilon_f\ \hat{\kappa}\cdot\hat{\kappa}_f) =$ $= v_{r_f}\, d\sigma(\kappa_f \epsilon_f \to \epsilon\ \hat{\kappa}\cdot\hat{\kappa}_f)$ and reversing the labels of initial and final states, we have

$$J^+(t) = \int d\Omega_\kappa \int d^3p_2\, v_r\, d\sigma\ F_1\ F_2$$

with κ_f written in terms of κ, and $\Delta\epsilon$ and $v_r = \left|\frac{1}{m_1}\underset{\sim}{P} - \frac{1}{m_2}p_2\right|$.
The momenta $\underset{\sim}{P}$ and $\underset{\sim}{p}_2$ define via $\underset{\sim}{\kappa}$ the direction of the axis with respect to which Ω_κ is defined in $d\sigma$ and the F's.

7) Collision Integral II - "Scattering Out"

The remainder of the work will be carried out in the rest frame of the target particle. The generalization to the lab or rest frame of the entire gas will, as before, be obvious.

We work with

$$\psi^{+} = \chi + \psi_{sc}$$

where χ is a free packet moving off in the forward direction and ψ_{sc} is a spherical shell of a packet propagating outward from the target center. These two packets overlap in the forward direction only and then only for times subsequent to the collision. The part of the density matrix or Wigner function arising from cross terms or interference between χ and ψ_{sc} vanishes prior to the collision so the previous notion of a time derivative of the Wigner function holds: $[f_w(t) - f_w(0)]/t$ with t of the order of a mean free time and $f_w(0) = 0$. Since only ψ_{sc} in the forward direction comes into the calculation (and hence f(o) i.e., scattering amplitude in forward direction) one anticipates that the optical theorem will play a role. For there are two interference terms, one the complex conjugate of the other, and thus one proportional to the scattering amplitude f(o) and one to $f^*(o)$. At first glance however, one thing is lacking - a sign difference. One needs $f(o) - f^*(o)$ to invoke the optical theorem but the two interference terms come in with the same sign. It all comes out in the wash of course and then one is left with the correct sign change which gives the imaginary part

of f(o) which then is eliminated in favor of the total cross section and this is precisely what appears in J^- - the scattering-out part of the collision integral. The demonstration follows:

The packeted ψ^+ is

$$\psi^+ = (2\pi)^{-3/2} e^{i\underset{\sim}{p}(\underset{\sim}{r}-\underset{\sim}{b}) - iE(t-t_0)} G_i(\underset{\sim}{r}-\underset{\sim}{v}(t-t_0)-\underset{\sim}{b}) Y_{l_1}^{\mu_1} Y_{l_2}^{\mu_2} +$$

$$+ (2\pi)^{-3/2} \sum_{\substack{l_{1f}\mu_{1f} \\ l_{2f}\mu_{2f}}} f \exp i\left[p_f r - E(t-t_0) - \underset{\sim}{p}\underset{\sim}{b}\right] \frac{G_f(\underset{\sim}{v}[\Delta t - \langle\Delta t\rangle] - \underset{\sim}{b})}{r} Y_{1f} Y_{2f}$$

where

$$\underset{\sim}{b} \cdot \underset{\sim}{v} = 0$$

$$p_f = [p^2 + 2m\Delta\epsilon_{int.}]^{1/2}, \quad \underset{\sim}{p}_f = p_f \hat{r}, \quad \Delta\epsilon_{int} = \epsilon_{l_1} + \epsilon_{l_2} - \epsilon_{l_{1f}} - \epsilon_{l_{2f}}$$

$$f = f(p, \hat{r}\cdot\hat{p}, l_1\mu_1 l_2\mu_2 \to l_{1f}\mu_{1f}, l_{2f}\mu_{2f})$$

$$E = p^2/2m + \epsilon_{l_1} + \epsilon_{l_2}$$

$$\Delta t = r/v_f, \quad t_0 = \text{time of collision}$$

From $\psi^+(\underset{\sim}{r})\psi^+(\underset{\sim}{r}')^* = \psi^+(\underset{\sim}{R}+\frac{\underset{\sim}{r}}{2})\psi^+(\underset{\sim}{R}-\frac{\underset{\sim}{r}}{2})^*$ we pick out the so-called interference terms:

$$(2\pi)^{-3} \sum_{\substack{l_{1f}\mu_{1f} \\ l_{2f}\mu_{2f}}} \frac{f^*(\hat{R}\hat{p})}{R} \exp i\left[\underset{\sim}{p}(\underset{\sim}{R}+\frac{\underset{\sim}{x}}{2}) - p_f(R - \hat{R}\frac{\underset{\sim}{x}}{2})\right] Y_1 Y_2 Y_{1f}^* Y_{2f}^* \cdot$$

$$G_i(\underset{\sim}{R}-\underset{\sim}{v}(t-t_0)-\underset{\sim}{b})\, G_f^*(\underset{\sim}{v}[\frac{R}{v_f} - (t-t_0)] - \underset{\sim}{b}) +$$

$$+(2\pi)^{-3}\sum \frac{f^*}{R}\exp i\left[-p\left(\underset{\sim}{R}-\frac{\underset{\sim}{x}}{2}\right)+p_f\left(R+\hat{R}\frac{\underset{\sim}{x}}{2}\right)\right]Y_1^*Y_2^*Y_{1f}Y_{2f}G_i^*G_f$$

where $\underset{\sim}{r}$ and $\underset{\sim}{r}'$ have been set equal to $\underset{\sim}{R}$ in the denominator and arguments of the f and G's while in the phase, r and r' $\rightarrow R \pm \hat{R}\frac{\underset{\sim}{x}}{2}$ respectively. The effect of the operation $(2\pi)^{-3}\int_{\underset{\sim}{x}} e^{-i\underset{\sim}{P}\underset{\sim}{x}}\int_{\Omega_2}\rho$ on these terms gives the usual Wigner function due to the interference or f^-. In addition we operate with the internal state kernal on f^-

$$\int_{\Omega_1}\int_{\Omega_{1f}} Y_L^M(\Omega_1)^* Y_L^M(\Omega_{1f})\, f^- = f^-_{LM}$$

to get the generalized Wigner function

$$f^-_{LM} = (2\pi)^{-3}\sum_{\substack{l_{1f}\mu_{1f}\\ l_{2f}\mu_{2f}}} \frac{f^*}{R}\delta\left(\underset{\sim}{P}-\tfrac{1}{2}(p+p_f)\right)e^{i(p-p_f)\underset{\sim}{R}}\, G_i G_f^*\, \delta^{l_2\mu_2}_{l_{2f}\mu_{2f}}\,\delta^{LM}_{l_{1f}\mu_{1f}} + c.c.$$

where $p_f, f, \Delta t$ i.e., everything that depends on final internal angular momenta is evaluated with the initial momenta instead and we set the initial values $l_1\mu_1 \rightarrow LM$ as well. The arguments of the G's are simultaneously small when

$$\Delta t = t - t_0, \qquad \hat{R} = \hat{v}$$

By hypothesis $b \approx 0$ so $(2\pi)^{-3}G_i G_f^*$ has the effect of a delta function with respect to F's as before. Furthermore, the momentum delta function requires $\underset{\sim}{P} = \underset{\sim}{p}$ once the ~~with~~ G's imply $\hat{p} = \hat{R}$

since we already have $p = p_f$ from $\Delta\epsilon_{int} = 0$. However with respect to phases or rapidly oscillating terms, the factor $G_i G_f^*$ and even $\delta(\underset{\sim}{P} - \frac{1}{2}(\underset{\sim}{p} + \underset{\sim}{p}_f))$ is considered broad (recall that the latter approximates $|a|^2$).

Next, f_{LM}^- is averaged over $\ell_1\mu_1$, $\underset{\sim}{p}$, $\underset{\sim}{r}_o = -\underset{\sim}{v}t_o + \underset{\sim}{b}$, $\ell_2\mu_2$ and the density of targets:

$$\overline{f_{LM}^-} = \sum_{\substack{\ell_1\mu_1 \\ \ell_2\mu_2}} \int_{\underset{\sim}{p}} \int_{\underset{\sim}{r}_o} \int_{\underset{\sim}{u}} F_{\ell_1\mu_1}(\underset{\sim}{p}, \underset{\sim}{r}_o, 0)\, n_{\ell_2\mu_2}(\underset{\sim}{R} - \underset{\sim}{u})\, f_{LM}^-$$

where $n_{\ell_2\mu_2}(\underset{\sim}{x})$ is the density of targets at the point $\underset{\sim}{x}$ with internal wave function $Y_{\ell_2}^{\mu_2}$ and $\underset{\sim}{u} = \underset{\sim}{R} - \underset{\sim}{x}$ as before, i.e., consider the target to have been at $\underset{\sim}{x}$ - the meaning of $\underset{\sim}{R}$ in the former case was the vector from the static target and in the latter case, $\underset{\sim}{u}$ replaces $\underset{\sim}{R}$. We have

$$\overline{f_{LM}^-} = \sum_{\ell_2\mu_2} \int_{\underset{\sim}{p}} \int_{\underset{\sim}{r}_o} \int_{\underset{\sim}{u}} F_{LM}\, n_{\ell_2\mu_2}\, \delta(\underset{\sim}{P} - \tfrac{1}{2}(\underset{\sim}{p} + \underset{\sim}{p}_f))\, \delta(\underset{\sim}{u} - \underset{\sim}{v}(t - t_o) - \underset{\sim}{b}) \cdot \frac{1}{u}\left[e^{i(\underset{\sim}{p}\underset{\sim}{u} - pu)} f^* + c.c.\right]$$

We cannot set $\underset{\sim}{p}\underset{\sim}{u} = pu$ in the phase since the $G_i G_f^*$ acts like a delta function only with respect to F_{LM}. The integration over $\underset{\sim}{p}$ eventually sends $\underset{\sim}{p} \rightarrow \underset{\sim}{P}$ in F_{LM} and removes the momentum delta function. But first the integration over $\hat{u}$ will be carefully handled. As far as the bracket expression goes, $\hat{u}$ is limited to a small finite region in the forward direction, i.e., to $\Delta\Omega = 2\pi(\delta\theta)^2$. With $x = \cos(\hat{p}, \hat{u})$ we consider

$$\int u^2 du \int d\Omega_u \frac{1}{u}\left[e^{ipu(x-1)} f^* - e^{-ipu(x-1)} f\right]$$

But

$$\int d\Omega_u = 2\pi \int_{1-(\delta\theta)^2/2}^{1} dx \quad \text{and} \quad \int d\Omega_u e^{ipu(x-1)} = \frac{1-e^{-ipu(\delta\theta)^2/2}}{ipu}$$

The exponential factor oscillates rapidly as u varies since $pu(\delta\theta)^2 \ll 1$ (the only physically reasonable circumstance) whereas none of the other u-dependent terms behave this way so we can drop the exponentials from $\overline{f_{LM}}$. Looked at in another way, this factor will be averaged over p and in actuality the momentum delta function is only an approximation, $|a(\underset{\sim}{P} - \frac{1}{2}(\underset{\sim}{p} + \underset{\sim}{p}_{f}))|^2$ being a better one when averaging rapidly varying quantities such as $\exp[ipu(\delta\theta)^2/2]$. The broadness of $|a|^2$ insures that the exponential does not survive an average in p-space. Thus we have, with this understanding,

$$\left[1-e^{-ipu(\delta\theta)^2/2}\right]\frac{f^*}{ipu} \rightarrow \left[1-e^{ipu(\delta\theta)^2/2}\right]\frac{f}{ipu} \rightarrow \frac{f^*-f}{ipu}$$

and now we can set $\underset{\sim}{p} = \underset{\sim}{P}$ everywhere else and remove the momentum delta function or $|a|^2$ to give

$$\overline{f_{LM}} = \sum_{l_2\mu_2} \int_{\underset{\sim}{r}_0} \int_{u} \frac{2\pi}{iP}\left[f^*(0) - f(0)\right] F_{LM}\, n_{l_2\mu_2}\, \delta(\underset{\sim}{u} - \underset{\sim}{v}(t-t_0) - \underset{\sim}{b})$$

But $f^* - f = -2i\,\mathrm{Im}\, f$

and $\frac{4\pi}{P}\,\mathrm{Im}\,f(0)=\sigma_T$ by the optical thorem where σ_T is the total cross section for scattering from the initial state $\underset{\sim}{P}$, LM, $\ell_2\mu_2$ to all possible final states. This means

$$\overline{f^-_{LM}} = -\sum_{\ell_2\mu_2}\int d^2b\int_{\tau_c}^{\tau}\frac{1}{m}P\,dt_0\int du\,F_{LM}\,n_{\ell_2\mu_2}\sigma_T\,\delta(\underset{\sim}{u}-\underset{\sim}{v}(t-t_0)-\underset{\sim}{b})$$

$$= -\tau\sum_{\ell_2\mu_2} V\sigma_T F_{LM}(\underset{\sim}{P},\underset{\sim}{R},0)\,n_{\ell_2\mu_2}(\underset{\sim}{R}),\quad V=P/m$$

where again, in the collision integral one makes the approximation

$$F_{LM}(\underset{\sim}{R}-\underset{\sim}{v}t)\,n_{\ell_2\mu_2}(\underset{\sim}{R}-\underset{\sim}{v}(t-t_0)) = F_{LM}(\underset{\sim}{R})\,n_{\ell_2\mu_2}(\underset{\sim}{R})$$

and the

$$\int d^3r_0 \to \int d^2b\int v\,dt_0 \to \int d^2b\int_{\tau_c}^{\tau} V\,dt_0 = \int d^2b\,V\tau \qquad \tau \gg \tau_c$$

Writing

$$\sigma_T = \int\frac{d\sigma}{d\Omega}d\Omega = \sum_{\ell_2'\mu_2'}\int d\sigma(\underset{\sim}{P}LM\,\ell_2\mu_2\to\hat{P}\cdot\hat{\Omega}\,L'M'\ell_2'\mu_2')$$

we have with $J^- = -\frac{\overline{f^-_{LM}}}{\tau}$, and calling the initial time t instead of 0,

$$J^-(t) = \sum_{\substack{\ell_2\mu_2\\ \ell_2'\mu_2'\\ L'M'}}\int V\,d\sigma\,F_{LM}(\underset{\sim}{P},\underset{\sim}{R},t)\,n_{\ell_2\mu_2}(\underset{\sim}{R},t)$$

The generalization to a non-static target is straightforward. V is a relative velocity and if the target has momentum $\underset{\sim}{p}_2$ then V becomes $v_r = \left| \frac{\underset{\sim}{P}}{m_1} - \frac{p_2}{m_2} \right|$. Moreover, $n(\underset{\sim}{R},t) \to F(p_2, \underset{\sim}{R}, t)$ so

$$J^- = \sum_{\substack{l_2\mu_2 \\ l_2'\mu_2' \\ L'M'}} \int_{\underset{\sim}{p}_2} \int_{\Omega} v_r \frac{d\sigma}{d\Omega} F_{LM} P_{l_2\mu_2}$$

If there are no preferred orientations as before, we sum on M and the resulting right hand side for the Boltzmann equation is then

$$J^+ - J^- = \sum_{\substack{l_2\mu_2 \\ l_2'\mu_2', l_1'\mu_1' \\ \mu_1}} \int d\Omega_{k_f} \int_{p_2} v_r \frac{d\sigma}{d\Omega_{k_f}} (p_1 p_2 l_1\mu_1 l_2\mu_2 \to \;') \left[F_{l_1'\mu_1'} F_{l_2'\mu_2'} - F_{l_1\mu_1}(p_1) F_{l_2\mu_2}(p_2) \right]$$

where some of the variables have been changed to conform with common usage. For example, the momentum of the beam particle m_1, is p_1, and $\underset{\sim}{P}$ now becomes $p_1 + p_2$.

The right hand side without the summation over μ_1 is the result given by Watson (13). Summing over μ_1 allowed the cross-section in J^+ to be written in the same form as in J^- so a factoring could be effected. In this form we have the WCU equation.

8) Afterthoughts and Conclusions

Some side questions have not been answered or even brought up. This is partly for the reason that they in no way affect the main thrust of this work, and partly because to have treated them in detail would have involved a great deal of additional paperwork which in the end would have been no more revealing or of interest than a brief physical discussion of the ideas. So these questions will now be raised in the form of afterthoughts and discussed in a simple, direct manner.

First there is the question of quantum statistics. There was no mention of when or how to symmetrize the wave function. Any text on quantum mechanics can tell you how. Just when it should be done is a question best answered by experience for many end results of a calculation are left unaffected by the decision of whether or not to symmetrize. When constructing a kinetic equation, the cross section is considered an imput datum -- someone else's problem to solve theoretically or empirically. In practice the cross section itself is not always used. If it can be related to a measured quantity then it is often eliminated in favor of that quantity. This has always been the practice when handling internal transitions. The cross-section has been eliminated in favor of an empirically determined relaxation time for the transfer of internal rotational or vibrational energy to translational motion (19). In this sense the gas itself has handled the question of symmetrization. But for the purposes of this work, the question must be decided at the outset. If one symmetrizes the scattered

wave function then one does roughly twice as much paperwork as before to find that in the end one has a correspondingly symmetrized cross section instead of an unsymmetrized one. That is all.

Another problem arises when one considers the initial internal state of a molecule to be superposition $\sum_m c_m Y_{\ell m}$ instead of just $Y_{\ell m}$. What happens here is just that the form of the cross section is changed in the usual way for a beam mixture of internal states. For example in J^-, the relevant part becomes

$$F_L \sum_n (\rho_{Mn} f^*_{nM} - f_{Mn} \rho_{nM})$$

where $\rho_{Mn} = c_M c_n^* = \rho_{nM}^*$ and $f_{nM} = f(M \to n)$, all other variables supressed. But in the forward scattering amplitude we can set $f_{Mn}(0) = f(0)\delta_{Mn}$ so we get

$$F_L |c_M|^2 (f^*(0) - f(0)) = F_L |c_M|^2 (-2i \operatorname{Im} f(0))$$

(An ensemble average would send $F_L |c_M|^2 \to F_{LM}$) and a $\sum_M$ removes the $|c_M|^2$ or the M subscript leaving the same final result as before.

For J^+ things look a little different and what appears is $\sum_\ell F_\ell \sum_{nn'} \rho_{nn'} f(\ell n \to LM) f^\dagger(\ell n' \to LM) \frac{v_{rf}}{v_r}$

the coefficient of F_ℓ is $\mathrm{Tr}(\rho ff^+)\ v_{rf}/v_r$ which is $\frac{d\sigma}{d\Omega}$ averaged over initial spin states. When $\sum_M$ is included, one again can invoke conservation of parity and time reversal invariance to be able to rewrite the differential cross section with initial and final scattering states interchanged.

There is also the question of the connections between these results and the work of Snider and Waldmann. They also used an approach based on scattering theory to give the density matrix as a function of time. Their physical assumptions are the same as those used here except they (and everyone else for that matter who has approached this problem) made no attempt to treat the internal states classically in the sense of finding an internal state Wigner function. Had the derivation here been carried through with the internal state information deposited in a density matrix, the results would have been identical to theirs. Such results are however not useful being written in terms of presently unknown scattering amplitudes rather than cross sections. To assert that the integrated form of the internal state Wigner function, i.e., $\int_\Omega f_{LM}(\Omega)$ is the whole story, one must have faith in one's intuition. It has not been proved although the calculations of Mason have given strong support to this supposition. Mason foresees no experimental conditions where it may be disproved (private communication) and Uhlenbeck concurs -- the WCU equation is, in his opinion, the last word (also private communication).

For a spin system such as gaseous He^3 rather than a gas of polyatomic molecules one is not faced with a multitude of possible rotational states, all easily excited. The density matrix is particularly simple but there are no internal coordinates to deal with -- at least none with classical characteristics. There is of course no classical analogy to be exploited, no Wigner function from spin wave functions and no hope for a high temperature, high quantum number passage to a classical limit. Here one must use the full density matrix for lack of an alternative approach if for no other reason. Still, in the end, calculations have been performed in this case only after the rough approximation of throwing away off -diagonal contributions (10).

Thus the WCU equation for polyatomic molecules is a well justified ansatz. In the limit of continuous rather than quantized internal angular momenta, the WCU equation and its results pass over to the purely classical work of Taxman.

Finally there is the possibility that the approach presented here could be pushed further. For example, density corrections and multiple collisions might be handled along these lines. Consider then a hypothetical situation in which a molecule (beam) is impinging upon a volume element in which there are two other molecules (targets). The initial beam wave function is and the scattering matrices from the two targets are t_1 and t_2. The Schrodinger equation for the scattered beam is

$$\Psi^+ = \chi + \frac{1}{d} V \Psi^+$$

where $d = E - K$

K = free Hamiltonian for beam and total target Hamiltonian

V = sum of interactions between beam and target particles

Then a solution for ψ^+ is (16)

$$\psi^+ = \chi + \frac{1}{d}\left(t_1\psi_1 + t_2\psi_2\right)$$

where

$$\psi_i = \chi + \frac{1}{d} t_j \psi_j \qquad i \neq j$$

so

$$\psi_1 = \chi + \frac{1}{d}\left[t_2 + t_2\frac{1}{d}t_1 + t_2\frac{1}{d}t_1\frac{1}{d}t_2 + \cdots\right]\chi$$

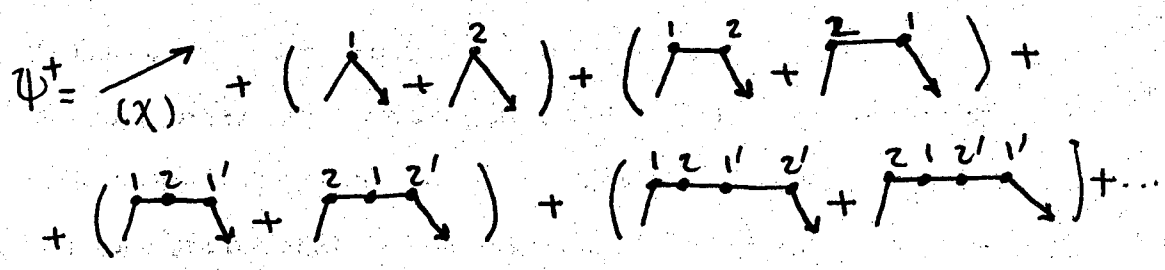
i.e., the wave incident on target 1 is the sum "free wave plus once scattered wave plus twice scattered wave plus . . ." and ψ^+ becomes

$$\psi^+ = \chi + \frac{1}{d}(t_1 + t_2)\chi + \frac{1}{d}\left(t_1 d^{-1} t_2 + t_2\frac{1}{d}t_1\right)\chi +$$

$$\frac{1}{d}\left(t_1\frac{1}{d}t_2\frac{1}{d}t_1 + 1 \leftrightarrow 2\right)\chi + \frac{1}{d}\left(t_1\frac{1}{d}t_2\frac{1}{d}t_1\frac{1}{d}t_2 + 1 \leftrightarrow 2\right)\chi + \cdots$$

Now ψ^+ was carried out to only 4 collisions for a definite reason. For hard spheres, kinemetical arguments forbid more than 4 collisions so corrections to the Boltzmann equation

due to multiple collisions have not been carried beyond this point. Quantum mechanically, more than four collisions are allowed but to begin with, one might limit an attempt to just producing at most the four body corrections since other attempts have not gone beyond this point while experiments have not yet even reached it. Graphically one could represent ψ^+ as



where 1' means target 1 once scattered. The first term gives the streaming contribution, the second gives the usual collision integral, the third allows for the density corrections considered by Enskog (2), the fourth gives the so-called 3-body terms and the last gives the 4-body terms. The classical kinematics have been worked out (3) and the wave packets will have to build in the appropriate initial conditions. Since for the case of the normal or binary collision Boltzmann equation, this method proved to be far simpler than previous methods, perhaps one can hope it will remain the most physical, direct, and shortest approach.

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