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PROJECT SQUID

TECHNICAL REPORT ARAP-5-P

ENERGY AND MOMENTUM EXCHANGE BETWEEN NON-EQUIPARTITION GASES

By
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Technical Report ARAP-5-P

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A COOPERATIVE PROGRAM OF FUNDAMENTAL RESEARCH
AS RELATED TO JET PROPULSION
OFFICE OF NAVAL RESEARCH, DEPARTMENT OF THE NAVY

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ENERGY AND MOMENTUM EXCHANGE
BETWEEN NON-EQUIPARTITION GASES*

by

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Princeton, New Jersey

March 1963

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Abstract

The energy and momentum relaxation of the components of a non-equipartition gas mixture is considered. For the case where each component of the mixture has a Maxwellian distribution at a temperature T_i , with the peculiar velocity in the Maxwellian measured relative to the species diffusion velocity, $\underline{U}_i$, and a "diffusion" Mach number not too large, the results have a particularly simple form. The calculations were carried out for the hard sphere, Coulomb, and Maxwell force laws of interaction. It is also noted how these results may be used to construct approximate kinetic model equations for the case of hard sphere and Coulomb interaction, in a manner similar to that proposed by Sirovich.¹

Introduction

As Grad has previously noted,² when a gas mixture is far from equilibrium, under certain conditions, there may be three epochs, or time scales, of relaxation to thermodynamic equilibrium.³ First, the lighter species come into equilibrium with themselves, then the heavier species equilibrate, and finally, through cross collisions, the various components of the mixture come into equilibrium with one another. This final relaxation to thermodynamic equilibrium is characterized by an equipartition time, and it is chiefly the relaxation on this time scale that shall be discussed below. It should be noted that this description of epochal relaxation is only qualitative, in that the individual distribution functions will not exactly preserve a Maxwellian shape during the final relaxation to thermodynamic equilibrium. However, the fact that the individual distribution functions are not exactly Maxwellian should have but slight influence on the velocity and temperature moments, as is indicated by the Maxwell force law. In this case, the moments may be obtained without knowledge of the form of the distribution functions.¹ For the hard sphere and Coulomb force laws considered below, although Maxwellians are used to facilitate the integration of the Boltzmann cross collision integral, it is not expected, in the light of the results for the Maxwell law of force, that any non-pathological deviations from Maxwellian would produce significant differences in the moments of velocity and temperature.

Various physical situations may be imagined in which there is not equipartition of energy between the components of the gas mixture. Perhaps the simplest example would be in the mixing of two low density gas streams, initially at different temperatures and velocities. Another situation of non-equipartition and subsequent relaxation to thermodynamic equilibrium might occur as follows. If an arc jet is expanded through a hypersonic nozzle, space charge considerations dictate that the ion and electron velocities at the exit plane of the nozzle will be the same. However, to achieve this final velocity, the electrons, having a much smaller mass than the heavier particles present, will have to give up much less of their random translational energy, and hence their exit temperature will be higher than the ion exit temperature.^{4,5}

Non-equipartition in a gas mixture also occurs when an electric field is put upon an ionized gas, e.g., a noble gas seeded with an easily ionized substance. Since the electrons, due to their extremely small mass, will lose but a small fraction of the energy gained from the field upon collision with heavier particles, the electric field becomes a mechanism for preferentially putting energy into the electrons. This is the case when the mixture components possess no internal degrees of freedom, and inelastic collisions due to the presence of easily excited rotational degrees of freedom are absent. Most collisions in a range of parameters pertinent to MHD power

generation will be elastic for the situation described here. It has been shown, furthermore, that the electrons may be adequately represented by a Maxwellian distribution with a temperature significantly higher than the gas temperature.⁶ This accounts for the phenomenon of "non-equilibrium" ionization, important for a certain type of MHD generator under present consideration.^{7,8}

The exchange of energy between the non-equilibrium components of a gas mixture has been discussed in well known results of Spitzer,⁹ and Chandrasekhar¹⁰ for the case of Coulomb interaction, and Cravath,¹¹ for the case of hard spheres. From considerations of scattering probability in the limit of short range forces, Boulegue, et. al.,¹² T. Kihara and Y. Midzuno¹³ and E. Desloge¹⁴ have obtained a general expression for the exchange of energy between two gases that have Maxwellian distributions at different temperatures. These results are usefully given by an integral of a function containing the total momentum cross section, and such that the integrand depends only upon the magnitude of the relative velocity. The derivation from the Boltzmann equation directly has been done by T. Kihara¹⁵ and, using an individual moment approach, independently extended by this author to include momentum as well as energy differences. For one limiting condition, that of a small diffusion Mach number, which is discussed below, the energy and momentum relaxation equations

take on a particularly simple form with clear physical significance. Further, the relaxation coefficients permit the construction of approximate kinetic models for the situation when the distribution functions remain approximately Maxwellian during the approach to thermodynamic equilibrium.

In the following, it shall be assumed that the peculiar velocity in each Maxwellian shall be taken with reference to the macroscopic velocity of each component, thus providing a more flexible result than that presented by the lowest order evaluation of the energy exchange integral in Kolodner's NYU report.¹⁶ This report also contains the results of Boulegue, et. al.,¹² Desloge,¹⁴ and Kihara¹⁵. Everett,¹⁷ more recently, has used the 13 moment method of Grad¹⁸ with the Hermite polynomial expansion containing a peculiar velocity relative to the individual macroscopic component velocities rather than relative to the mass averaged velocity. This was done to obtain closed MHD equations for the case of the Coulomb interaction.

Energy and Momentum Transfer between Maxwellian Gases

Consider the final epoch of relaxation, assuming that each component of the gas mixture has a Maxwellian distribution at a temperature T_i , and that the peculiar velocity $\underline{c}_i$, in each Maxwellian is measured with respect to the macroscopic diffusion velocity $\underline{U}_i$, of the i th component. The i th distrib-

ution function is taken to be,

$$f_i = n_i \left(\frac{m_i}{2\pi k T_i} \right)^{3/2} e^{-m_i c_i^2 / 2k T_i} \quad (1)$$

$$V_i = C_i + U_i$$

It is assumed that the spatially homogeneous Boltzmann equation provides an adequate kinetic description of the relaxation of the i th distribution function to thermodynamic equilibrium.* By the above assumptions, only cross collisions appear. The following notation is standard and is taken from Chapman and Cowling.¹⁹

$$\frac{\partial f_i}{\partial t} = \sum_{j=2}^n \iint (f'_i f'_j - f_i f_j) K_{ij}(g, \underline{k} \cdot \underline{g}) d\underline{k} d\underline{V}_j \quad (2)$$

where n is the number of species in the mixture. It is assumed that the scattering function $K_{ij}(\underline{g}, \underline{k} \cdot \underline{g})$ depends only on the magnitude of the relative velocity g , and upon the scattering angle determined by $\underline{k} \cdot \underline{g}$, where $\underline{k}$ is the unit apsidal vector in the plane of scattering. This is naturally the case for a spherically symmetric potential. By considering the apsidal unit vector $\underline{k}$, it will be seen that the subsequent angular integrations may be completed more conveniently than by using the more conventional scattering angle.

Multiplying equation 2 by $m_i c_i^2 / 2$ and integrating over all velocities yields,

* In a future note, the effect of recombination in slowing up the relaxation process shall be discussed.

$$\frac{\partial}{\partial t} \left(\frac{3}{2} n_i k T_i \right) = \sum_{i=2}^n \frac{m_i}{2} \iiint c_i^2 (f'_i f'_i - f_i f_i) K_{ii} d\mathbf{k} d\mathbf{c}_i d\mathbf{c}_i \quad (3)$$

which, by a standard transformation may be written as,

$$\frac{\partial}{\partial t} \left(\frac{3}{2} n_i k T_i \right) = \sum_{i=2}^n \frac{m_i}{2} \iiint (c_i'^2 - c_i^2) f_i f_i K_{ii} d\mathbf{k} d\mathbf{c}_i d\mathbf{c}_i \quad (4)$$

But, from momentum conservation, and from the dynamics of an elastic collision between particles of species 1 and species 1,

$$c_i'^2 - c_i^2 = \frac{4 m_i}{(m_i + m_i)} g [g m_i + c_i (m_i + m_i)] \cdot \mathbf{k} \quad (5)$$

Since the scattering function depends only upon the magnitude of the relative velocity g and the component of $\mathbf{k}$ parallel to the relative velocity, a transformation of integration variables from $d\mathbf{c}_1 d\mathbf{c}_1$ to $d\mathbf{c}_1 d\mathbf{g}$ is appropriate. Thus, equation 4 becomes,

$$\frac{\partial}{\partial t} \left(\frac{3}{2} n_i k T_i \right) = \sum_{i=2}^n \frac{2 (m_i m_i)^{5/2}}{(2\pi k)^{3/2} (m_i + m_i)^2 (T_i T_i)^{3/2}} \times \quad (6)$$

$$\iiint e^{-K(g - 4U)^2 - K_i \left[c_i + \frac{g - 4U}{\frac{m_i T_i}{m_i T_i} + 1} \right]^2} (g g m_i + g c_i (m_i + m_i)) \cdot \mathbf{k} K_{ii} d\mathbf{k} d\mathbf{c}_i d\mathbf{g}$$

where

$$K \equiv \frac{1}{\frac{2 k T_i}{m_i} + \frac{2 k T_i}{m_i}} \quad K_i \equiv \frac{m_i}{2 k T_i} + \frac{m_i}{2 k T_i}$$

$$4U \equiv \mathbf{U}_i - \mathbf{U}_i$$

Merely by completing the square, the $\underline{c}_1$ integral may be evaluated, leaving one odd term which vanishes by symmetry,

$$\text{and } \frac{\partial}{\partial \underline{c}} \left(\frac{3}{2} m_i k T_i \right) = \sum_{i=2}^n \frac{2 (m_i m_i)^{5/2} n_i n_i}{(2 \pi k)^{3/2} (m_i + m_i)^2 (m_i T_i + m_i T_i)^{5/2}} \times \quad (7)$$

$$\iiint e^{-K(\underline{g} - \Delta \underline{U})^2} [g g m_i m_i (T_i - T_i) + g \Delta U (m_i + m_i) m_i T_i] \cdot \underline{k} \underline{k} K_{ii} d\underline{k} dg$$

The $d\underline{k}$ integration may also be done, in principle, for a spherically symmetric scattering function, K_{11} . Consider the following laboratory reference system, in which $\underline{g}$ is fixed parallel to $\underline{e}_3$ during the $d\underline{k}$ integration. See figure 1. Thus $\underline{k} = \underline{k}_{||} + \underline{k}_{\perp}$. From the choice of coordinates in figure 1, $\underline{e}_3 \cdot \underline{g} = g$, $\underline{e}_2 \cdot \underline{g} = \underline{e}_1 \cdot \underline{g} = 0$, and

$$\int [g g m_i m_i (T_i - T_i) + g \Delta U (m_i + m_i) m_i T_i] \cdot \underline{k} \underline{k} K_{ii} d\underline{k} = \quad (8)$$

$$\int [g^2 k_{||}^2 m_i m_i (T_i - T_i) + g k_{||} \Delta U \cdot k (m_i + m_i) m_i T_i] K_{ii} d\underline{k}$$

$$\text{Now } \iint \underline{k} d\underline{k}_{\perp} d\underline{k}_{||} = \iint (\underline{k}_{\perp} + \underline{k}_{||}) d\underline{k}_{\perp} d\underline{k}_{||} = \int \underline{k}_{||} d\underline{k}$$

$$\text{and } \underline{k}_{||} = \frac{k_{||}}{g}$$

Thus the bracketed term and the $d\underline{k}$ integral of equation 7 become,

$$[g^2 m_i m_i (T_i - T_i) + g \Delta U (m_i + m_i) m_i T_i] \times \int k_{||}^2 K_{ii}(g, g \cdot \underline{k}) d\underline{k} \quad (9)$$

In order to establish contact with the more common angular form of the scattering function, consider the dynamics of a binary interaction as illustrated by figure 2. From figure 1, $\underline{k} = \underline{e}_3 \cos \theta'$, and $k^2 = \cos^2 \theta'$. In figure 2, it is seen that $\theta' = \frac{\pi + \theta}{2}$, and therefore, $\cos^2 \theta' = \sin^2 \theta/2 = \frac{1}{2}(1 - \cos \theta)$. It should also be noted that $K_{11}(\underline{g}, \underline{k} \cdot \underline{g}) d\underline{k} = g \sigma'_{11}(g, \theta) d\Omega$, where Ω is the solid angle of scattering. Thus,

$$\int k_{11}^2(\underline{g}, \underline{k} \cdot \underline{g}) d\underline{k} = \frac{1}{2} g \int (1 - \cos \theta) \sigma'_{11}(g, \theta) d\Omega \equiv \frac{1}{2} g \sigma_m(g) \quad (10)$$

where $\sigma_m(g)$ is the conventional total cross section for momentum transfer. Equation 7 may now be written as,

$$\frac{\partial}{\partial t} \left(\frac{3}{2} n_i T_i \right) = \sum_{i=2}^n \frac{(m_i m_j)^{5/2} n_i n_j}{(2\pi k)^{3/2} (m_i + m_j)^4 (m_i T_i + m_j T_j)^{5/2}} \times \int_{-\infty}^{\infty} e^{-\pi(g^2 - 4U)^2} \sigma_m g [g^2 m_i m_j (T_i - T_j) + g \cdot 4U (m_i + m_j) m_j T_j] dg \quad (11)$$

The vector integration dg may be reduced to a scalar integration over the magnitude of g , by again choosing an appropriate spherical coordinate system as shown in figure 3. It is perhaps most convenient to consider the two integrals of equation 11 separately.

$$\int_{-\infty}^{\infty} e^{-\pi(g^2 - 4U)^2} \sigma_m g^3 dg = 2\pi \int_0^{\infty} e^{-\pi(g^2 + 4U^2)} \sigma_m g^5 dg \int_{-\pi/2}^{\pi/2} e^{\frac{\pi}{2} + 940 \cos \omega} d(\cos \omega) = \quad (12)$$

$$\frac{2\pi}{44U} \int_0^{\infty} e^{-\pi(g^2 + 4U^2)} \sigma_m g^4 \sinh(2\pi g 4U) dg$$

From figure 3, $\underline{e}_3 \cdot 4\underline{U} = U$, $\underline{g} = \underline{e}_1 \sin \omega \cos \psi + \underline{e}_2 \sin \omega \sin \psi + \underline{e}_3 \cos \omega$, and

$$\Delta U \cdot \int_{-\infty}^{\infty} g e^{-\kappa(g-\Delta U)^2} \sigma_m dg = \quad (13)$$

$$\frac{\pi(\Delta U \cdot \Delta U)}{\kappa^2 \Delta U^3} \int_0^{\infty} e^{-\kappa(g^2 + \Delta U^2)} \sigma_m g^2 [2\kappa g \Delta U \cosh(2g\kappa \Delta U) - \sinh(2g\kappa \Delta U)] dg$$

Substituting equations 12 and 13 into equation 11, one obtains,

$$\begin{aligned} \frac{\partial}{\partial t} \left(\frac{3}{2} m_i k T_i \right) = & \sum_{i=2}^n \frac{2\pi(m_i m_i)^{5/2} n_i n_i}{(2\pi k)^{3/2} (m_i + m_i)^{5/2} (m_i T_i + m_i T_i)^{5/2}} \times \\ & \left[\frac{m_i m_i (T_i - T_i)}{\kappa \Delta U} \int_0^{\infty} e^{-\kappa(g^2 + \Delta U^2)} \sigma_m g^4 \sinh(2g\kappa \Delta U) dg \right. \\ & \left. + \frac{m_i T_i (\Delta U \cdot \Delta U)}{2 \kappa^2 \Delta U^3} \int_0^{\infty} e^{-\kappa(g^2 + \Delta U^2)} \sigma_m g^2 [2g\kappa \Delta U \cosh(2g\kappa \Delta U) - \sinh(2g\kappa \Delta U)] dg \right] \end{aligned} \quad (14)$$

Taking the total energy moment of the Boltzmann equation, i.e., flow energy plus random translational energy, a similar calculation to the one above yields,

$$\begin{aligned} \frac{\partial}{\partial t} \left(\frac{3}{2} m_i k T_i + \frac{1}{2} m_i m_i U_i^2 \right) = & \sum_{i=2}^n \frac{2\pi(m_i m_i)^{5/2} n_i n_i}{(2\pi k)^{3/2} (m_i + m_i)^2 (m_i T_i + m_i T_i)^{5/2}} \times \\ & \left[\frac{m_i m_i (T_i - T_i)}{\kappa \Delta U} \int_0^{\infty} e^{-\kappa(g^2 + \Delta U^2)} \sigma_m g^4 \sinh(2g\kappa \Delta U) dg \right. \\ & \left. + \frac{(U_i m_i T_i + U_i m_i T_i) \cdot \Delta U}{\kappa^2 \Delta U^3} \int_0^{\infty} e^{-\kappa(g^2 + \Delta U^2)} \sigma_m g^2 [2g\kappa \Delta U \cosh(2g\kappa \Delta U) - \sinh(2g\kappa \Delta U)] dg \right] \end{aligned} \quad (15)$$

In the limit $\Delta U \rightarrow 0$, for a two component gas mixture, equations 14 and 15 reduce to,

$$\frac{\partial}{\partial t} \left(\frac{3}{2} m_i k T_i \right) = \frac{4\pi(m_i m_i)^{7/2} n_i n_i (T_i - T_i)}{(2\pi k)^{3/2} (m_i + m_i)^2 (m_i T_i + m_i T_i)^{5/2}} \int_0^{\infty} e^{-\kappa g^2} \sigma_m g^5 dg \quad (16)$$

This is the expression obtained by Boulegue, et. al.¹², Midzuno,¹³ Kihara,¹⁵ and Desloge.¹⁴ The calculation for the momentum transfer between the species of the mixture results in,

$$\frac{\partial}{\partial t}(m_i, m_j, U_i) = \sum_{i=2}^{\infty} \frac{\pi(m_i, m_j)^{5/2} m_i m_j \Delta U}{A^2 \Delta U^3 (2\pi k)^{3/2} (m_i + m_j) (m_i T_i + m_j T_j)^{3/2}} \times \int_0^{\infty} e^{-4(g^2 + \Delta U^2)} \sigma_m g^2 [24g\Delta U \cosh(24g\Delta U) - \sinh(24g\Delta U)] dg \quad (17)$$

Thus, equations 14 and 17 describe the energy and momentum relaxation of a gas mixture to thermodynamic equilibrium under the restriction that the individual distribution functions do not depart too far from a Maxwellian during the relaxation process. The conditions under which this is approximately correct are discussed below.

Energy and Momentum Relaxation for Specific Cross Sections

In order that the results of the preceding section be made useful, it is necessary to evaluate the integrals in equations 14 and 17, at least for certain cases of specific interest. This is done for Maxwell, Coulomb, and hard sphere interactions, and, for convenience, the results are restricted to a two component gas.

A. The Maxwell Force Law

For any inverse force law the cross section may be expressed as a product of a function of relative velocity and of certain parameters of the interaction.²⁰ Specifically, for the Maxwell law of force, the cross section is inversely

proportional to the relative velocity, and

$$\sigma_m = 2\pi(.422) \left[\frac{(m_1 + m_2) B_{12}}{m_1 m_2} \right]^{1/2} g^{-1} \quad (18)$$

where B_{12} is the constant of proportionality in the force law. Substituting the cross section as given above into equation 14, it is noted that both resulting integrands are even. Therefore, the integrals are equal to one half the same integral from $-\infty$ to $+\infty$. This permits a change of variables to symmetrize the Gaussian without effecting either limit, and the integration may be carried out directly to yield, after some manipulation,

$$\frac{\partial}{\partial t} \left(\frac{3}{2} m_1 k T_1 \right) = 4\pi \left[\frac{m_1 m_2 B_{21}}{m_1 + m_2} \right]^{1/2} (.422) m_1^{1/2} \left[\frac{3}{2} k (T_2 - T_1) + \frac{1}{2} m_2 \Delta U^2 \right] \quad (19)$$

The momentum relaxation is given by,

$$\frac{\partial}{\partial t} (m_1 m_2 \underline{U}_1) = 2\pi \left(\frac{m_1 m_2 B_{21}}{m_1 + m_2} \right)^{1/2} m_1 m_2 (.422) \Delta \underline{U} \quad (20)$$

As is well known, for the Maxwellian force law, the relaxation times are constant. The coefficients of $\Delta \underline{U}$ and ΔU^2 differ somewhat from those given by Sirovich¹, who obtained them from Kolodner,¹⁴ possible due to the fact that Kolodner's expansion was in a Maxwellian with reference to a mean velocity.

B. Hard Sphere Interaction

In the case of hard spheres, $\sigma_{ij} = \pi(r_1 + r_2)^2$ where r_1 and r_2 are the effective radii of particles involved in the collision. For this situation, it is no longer possible to complete the integrals of equations 14 and 17 in a simple form. By changing the variable to symmetrize the Gaussian, the lower limit of the integral becomes dependent upon ΔU , and the results can only be expressed in terms of the derivative of the error integral with respect to a parameter. A more useful, symmetric form for the case of the hard sphere, however, may be obtained by direct expansion of the sinh and cosh that appear in equations 14 and 17. Due to the factor $e^{-K\Delta U^2}$, convergence is assured. Thus, for the hard sphere interaction, the integrals of equation 14 are,

$$\begin{aligned} & \frac{m_1 m_2 (T_2 - T_1)}{K \Delta U} \int_0^\infty e^{-K(g^2 + \Delta U^2)} g^4 \sinh(2g\Delta U) dg + \frac{m_2 T_1 (m_1 + m_2) (\Delta U \cdot \Delta U)}{2K^2 \Delta U^3} \times \\ & \int_0^\infty e^{-K(g^2 + \Delta U^2)} g^2 [2K\Delta U \cosh(2g\Delta U) - \sinh(2K\Delta U)] dg = \quad (21) \\ & e^{-K\Delta U^2} \left[m_1 m_2 (T_2 - T_1) \left(\frac{2}{K^3} + \frac{4}{3} \frac{K\Delta U^2}{K^4} + \dots \right) + m_2 T_1 (m_1 + m_2) \Delta U^2 \left(\frac{8}{3} \frac{K}{K^3} + \dots \right) \right] = \\ & \frac{32}{3} e^{-K\Delta U^2} \frac{(m_1 T_2 + m_2 T_1)^3}{m_1 m_2} \left[\frac{1}{2} (T_2 - T_1) \left(\frac{3}{2} + 2K\Delta U^2 \right) + \frac{m_2}{2} \Delta U^2 + O(K^2 \Delta U^4) + \dots \right] \end{aligned}$$

Now let the dimensionless parameter $K\Delta U^2$ become small. This was not done in the evaluation of each integral separately, since the $K\Delta U^2$ contribution from the first integral combines with the second integral to yield a convenient form. For the

hard sphere interaction, in the limit of small $K\Delta U^2$, the energy relaxation is given by,

$$\frac{\partial}{\partial t} \left(\frac{3}{2} m_1 k T_1 \right) = \frac{16(2\pi k)^{1/2} (m_1 m_2)^{1/2} m_1 m_2 (r_1 + r_2)^4 (m_1 T_2 + m_2 T_1)^{1/2}}{3 (m_1 + m_2)^2} \times \left[\frac{3}{2} k (T_2 - T_1) + \frac{m_2}{2} \Delta U^2 \right] \quad (22)$$

and the momentum relaxation by,

$$\frac{\partial}{\partial t} (m_1 m_2 \underline{U}) = \frac{8(2\pi k)^{1/2} (m_1 m_2)^{1/2} m_1 m_2 (r_1 + r_2)^4 (m_1 T_2 + m_2 T_1)^{1/2}}{3 (m_1 + m_2)^2} \Delta \underline{U} \quad (23)$$

For the case $\Delta U \rightarrow 0$, equation 22 is the result previously obtained by Cravath.⁹

Equations 22 and 23 are not exact, although their forms are quite convenient. They hold only for $K\Delta U^2$ small, but

$$K\Delta U^2 = \frac{\gamma}{2} M_d^2, \quad M_d^2 \equiv \frac{\Delta U^2}{C_1^2 + C_2^2} \quad (24)$$

where C_1 and C_2 are the speeds of sound respectively in each mixture component. Thus, M_d is essentially a diffusion Mach number. In order that equations 22 and 23 be valid, the diffusion Mach number must not be larger than approximately .3, so that $M_d^2 \approx .1$. This will be true for many cases of interest. (In equation 24, γ is the ratio of specific heats.)

C. The Coulomb Interaction

Assuming the cross section σ_m to be that associated with the Coulomb interaction (cut off at the Debye length) for a singly ionized species, one obtains,²¹

$$\sigma_m \approx \frac{e^4 \ln \Lambda (m_1 + m_2)^2}{4\pi \epsilon_c^2 (m_1 m_2)^2} \quad (25)$$

where $\Lambda \equiv \frac{12\pi (\epsilon_c k T_e / e^2)^{3/2}}{n_e^{1/2}}$

With the cross section given by equation 25, the hyperbolic sines and cosines of equations 14 and 17 are expanded as in the hard sphere case, and only after regrouping the contributions from the first and second integrals is the parameter $K \Delta U^2$ allowed to become small. In this limit, the results are, for energy relaxation,

$$\frac{\partial}{\partial t} \left(\frac{3}{2} n_i k T_i \right) = \frac{2 (m_1 m_2)^{1/2} n_1 n_2 e^4 \ln \Lambda}{3 (2\pi k)^{3/2} \epsilon_c^2 (m_1 T_2 + m_2 T_1)^{3/2}} \times \quad (26)$$

$$\left[\frac{3}{2} k (T_2 - T_1) + \frac{m_2}{2} \Delta U^2 \right]$$

and for momentum relaxation,

$$\frac{\partial}{\partial t} (n_i m_i \underline{U}_i) = \frac{(m_2 m_i)^{1/2} n_i n_2 e^4 \ln \Lambda (m_1 + m_2) \Delta \underline{U}}{3 (2\pi k)^{3/2} (m_1 T_2 + m_2 T_1)^{3/2}} \quad (27)$$

It should be noted that, subject to the restrictions discussed above, the momentum and energy moments for all the cases here considered, acquire a particularly simple form. For energy,

$$\frac{\partial}{\partial t} \left(\frac{3}{2} k T_i \right) = \frac{1}{\tau_E} \left[\frac{3}{2} k (T_e - T_i) + \frac{m_e}{2} \Delta U^2 \right] \quad (28)$$

and for momentum,

$$\frac{\partial}{\partial t} (m_i U_i) = \frac{1}{\tau_M} m_i \Delta U \quad (29)$$

where τ_E and τ_M are the relaxation coefficients for energy and momentum, respectively, which correspond to the molecular force laws evaluated above. For all cases, the ratio of τ_M / τ_E is given by,

$$\tau_M / \tau_E = \frac{2}{1 + m_e / m_i} \quad (32)$$

If there is a great disparity between the masses of the two particles undergoing an interaction, as, for example, in the scattering of an electron by an ion, it is clear that the energy of the electron will relax more slowly than the momentum. This is merely due to the fact that the electrons exchange little energy in interacting with a heavy particle, but their momentum can be changed considerably in an encounter with a heavy particle.

Equipartition Relaxation Times

Perhaps the most appropriate measure of the time required for the system to approach thermodynamic equilibrium is the equipartition time. This is the time required for both diffusion velocity and temperature differences to become negligible. The equations for the relaxation of temperature and velocity differences, for a two component mixture, may be written in a convenient form as follows,

$$\frac{\partial}{\partial t} (T_2 - T_1) = -\alpha_E \left[(T_2 - T_1) \left(\frac{1}{m_2} + \frac{1}{m_1} \right) + \frac{(\underline{U}_2 - \underline{U}_1)^2}{3k} \left(\frac{m_2}{m_1} - \frac{m_1}{m_2} \right) \right] \quad (33)$$

$$\frac{\partial}{\partial t} (\underline{U}_2 - \underline{U}_1) = -\alpha_E \left(\frac{1}{m_2 m_2} + \frac{1}{m_1 m_1} \right) \left(\frac{m_1 + m_2}{2} \right) (\underline{U}_2 - \underline{U}_1) \quad (34)$$

where α_E is the coefficient of $\left[\frac{3}{2} k (T_2 - T_1) + \frac{m_2}{2} (\underline{U}_2 - \underline{U}_1)^2 \right]$ in equations 19, 22, and 26, for the Maxwell, hard sphere, and Coulomb force laws, respectively. To an order of magnitude, the temperature equilibration time is given by

$$1/\tau_T = \alpha_E \left(\frac{1}{m_2} + \frac{1}{m_1} \right) \quad (35)$$

and the velocity equilibration time by,

$$1/\tau_v = \alpha_E \left(\frac{1}{m_2 m_2} + \frac{1}{m_1 m_1} \right) \left(\frac{m_2 + m_1}{2} \right) \quad (36)$$

It should be noted that these times, for the situation where α_E depends upon temperature, are not e-folding times of

the relaxation of temperature and velocity differences. Thus, they can, at best, give an order of magnitude estimate of the times required to reach thermodynamic equilibrium. The ratio of these two times is given by,

$$\frac{\tau_T}{\tau_v} = \frac{(1 + \frac{m_2}{m_1})(1 + \frac{m_1 m_2}{m_2 m_2})}{2(1 + \frac{m_1}{m_2})} \quad (37)$$

For the case where $n_1 = n_2$, this ratio becomes,

$$\frac{\tau_T}{\tau_v} = \frac{(1 + \frac{m_2}{m_1})(1 + \frac{m_1}{m_2})}{4} \quad (38)$$

which illustrates once more how the mass effect tends to lengthen the time required for temperature differences to become small as compared with the time required for velocity differences to become small.

Separability of Time Scales in the Relaxation Process

In order that the energy and momentum relaxation processes be described by equations 14 and 17, it is necessary for the individual Maxwellians only approximately to retain their shapes during the approach to thermodynamic equilibrium. (This is perhaps indicated by the Maxwell molecule, where the momentum and energy moments are independent of the shape of the distribution function.) Even though the distribution functions might become somewhat non-Maxwellian during the relaxation process, as, for example, cross collisions causing the tail of the distribution function of the lower temperature

component to be overpopulated with higher energy particles, this should have but slight effect upon the moment equations themselves.

It should be noted that the mathematical criteria have not yet been given for those conditions under which one component of a gas mixture, initially having a Maxwell distribution, but not in equilibrium with the other components of the mixture, will relax to thermal equilibrium while retaining its Maxwell shape. D.I. Osipov²² has recently shown that for a slightly ionized gas, with the heavy particles at one fixed temperature, if a Fokker-Plank type equation describes the neutral-electron interaction with a Maxwell force law, then, if the electron distribution function is initially Maxwellian, it will remain so during the relaxation process. Acting as reviewer for this paper, Schuler has pointed out that it is not clear if a Fokker-Plank equation is applicable in describing the relaxation of a light gas in a sea of constant temperature heavy particles, since the average momentum transfer to the electrons is certainly not small.

The question of whether an initial Maxwellian will remain such during relaxation, is intimately connected with the validity of the epochal description of relaxation. Although the deeper mathematical aspects of this question remain unknown, it would seem that a useful order of magnitude criterion in determining the range of validity of a qualitative epochal relaxation is to be found in the ratio of the self relaxation time to the equipartition time. The self relaxation time measures

the effect of self collisions in bringing the individual distribution functions toward a local Maxwellian, and if this time is much smaller than the equipartition time, the distribution functions will remain essentially Maxwellian during the third phase of relaxation. This is schematically shown in figure 4.

To obtain an estimate of a self-collision time, consider once more the Boltzmann collision integral. This contains two parts, of which one represents the particles leaving an elemental volume of phase space, and the other represents the particles that enter this volume element in phase space.

Thus,

$$\frac{\partial f}{\partial t} = \iint f' f' g \sigma d\mathbf{c}_1 d\mathbf{c}_2 - f \iint f_1 g \sigma d\mathbf{c}_1 d\mathbf{c}_2 \quad (39)$$

For conditions where the individual distribution functions are not far removed from a Maxwellian distribution, it is convenient to assume that the complicated emission term of the Boltzmann equation may be replaced by a Maxwellian divided by some appropriate relaxation time. Thus, the self collisions are approximated by the BGK model,²³

$$\frac{\partial f}{\partial t} = \frac{M - f}{\tau} \quad (40)$$

where,

$$\frac{1}{\tau} = \iint f_1 g \sigma d\mathbf{c}_1 d\mathbf{c}_2 \quad (41)$$

and τ may be velocity dependent. A general integral expression for τ is developed below and evaluated for the hard sphere and Maxwell molecule.

For a central force interaction, it may be shown that

$$\int \sigma(g) d\Omega \equiv A g^{\delta-1} \quad (42)$$

where A depends upon the integrated angular part of the cross section. Moreover, $\delta = 1$ for hard spheres, and $\delta = 0$ for the Maxwell molecule. Since the BGK model is strictly appropriate only for departures from equilibrium that are not too great, the self collision time will be essentially given by allowing f_1 in equation 41 to be Maxwellian, and the collision time becomes,

$$\frac{1}{\tau(c)} = n \left(\frac{m}{2\pi kT} \right)^{3/2} A \int_{-\infty}^{\infty} e^{-\frac{m_1 c_1^2}{2kT}} |c_1 - c|^{\delta} d\mathbf{c}_1 \quad (43)$$

Asuitable change of variables is indicated,

$$\begin{aligned} Z &\equiv \left(\frac{m}{2kT} \right)^{1/2} |c_1 - c| \\ \underline{c} &\equiv \left(\frac{m}{2kT} \right)^{1/2} c \end{aligned} \quad (44)$$

With these simple transformations and a change to spherical coordinates, the angular integrations may be done, and equation 43 becomes,

$$\frac{1}{\tau(c)} = \frac{1}{\sqrt{\pi}} \left(\frac{2kT}{m} \right)^{\frac{\gamma+1}{2}} \frac{mH}{c} \quad (45)$$

$$\left[\int_0^\infty e^{-z^2} [(z+\xi)^{\gamma+1} - (z-\xi)^{\gamma+1}] dz + \int_0^\xi e^{-z^2} [(\xi-z)^{\gamma+1} + (z-\xi)^{\gamma+1}] dz \right]$$

When $\gamma+1$ is odd, the second integrand vanishes and the collision time may be most conveniently obtained. This is the case of the Maxwell molecule, when $\gamma=0$. Evaluating equation 45 for $\gamma=0$, and taking the value of A from equation 18, one obtains,

$$\frac{1}{\tau_1} = 2\pi(1.422) \left[\frac{2B_{11}}{m_1} \right]^{1/2} \quad (46)$$

where B_{11} is the proportionality constant of the Maxwell force law. The Maxwell self collision time is also independent of velocity.

For the hard sphere interaction, $\gamma=1$, and the second integral of equation 45 introduces error functions. In this case, $A=\pi(2r)^2$, and

$$\begin{aligned} \frac{1}{\tau(c)} = & \left(\frac{2kT}{m} \right)^{1/2} \frac{\pi n (2r)^2}{c} \left[2\xi (2e^{-\xi^2} - 1) \right. \\ & \left. + \xi^2/\sqrt{\pi} P(\xi) + \frac{\sqrt{\pi}}{2} P(\xi) - \frac{\xi}{2} e^{-\xi^2} \right] \end{aligned} \quad (47)$$

where,

$$P(\xi) = \frac{2}{\sqrt{\pi}} \int_0^\xi e^{-y^2} dy$$

Since an average collision time shall be taken as the measure of self relaxation, the average particle speed shall be used in equation 47, i.e., $\xi = \left(\frac{3}{2} \right)^{1/2}$ and the mean collision time

for hard spheres is given by,

$$\frac{1}{\tau} \approx 4.3 \sqrt{\frac{\pi}{3}} \left(\frac{kT}{m} \right)^{1/2} n (2r)^2 \quad (48)$$

In the case of the Coulomb interaction, the self relaxation time may best be obtained by an impulse approximation that takes into account the high probability of many small successive deflections. Using this criterion, Spitzer⁹ has given the estimate of the time required for self collisions to bring the ion and electron distribution functions to their own Maxwellians. This is, for a particle of average speed,

$$\frac{1}{\tau} = \frac{5.7 \pi n e^7 \ln \Lambda}{m^{1/2} (3kT)^{3/2}} \quad (49)$$

Summary of Relaxation Results

Table 1 summarizes the energy, and momentum equipartition times, and the self-collisional relaxation times for a two component gas, subject to the restriction that the diffusion Mach number be small. In order that Grad's hypothesis concerning the three basic epochs of relaxation be approximately valid, it should be sufficient that each self relaxation time be smaller than the appropriate equipartition time. As can be seen, not only the mass ratio is of significance in describing the criteria for epochal relaxation. Even for the Maxwell molecule, the density plays an important role. For example, if the number of particles of species 1 were much larger than that of species 2, self collisions among species 2 would be rare,

and it is not evident that the distribution function of species 2 would remain even approximately Maxwellian during the relaxation to thermodynamic equilibrium. This comment on the density ratio is equally applicable for the Coulomb and hard sphere force laws. Furthermore, for the Coulomb and hard sphere interactions, the temperature ratio of the interacting gases also has the effect, at least initially, of introducing a separation of time scales into the problem. Also, for a steady state two temperature situation, the temperature ratio as well as the mass ratio might prove useful in determining the expansion parameters of the system. A semi-quantitative estimate of the effects of temperature, density, and mass ratio on the scheme of relaxation to thermodynamic equilibrium may be obtained from table 1.

Molecular Models

For the situation in which the individual distribution functions are not too far from Maxwellian, the effect of cross collisions, to zeroth order, may be represented as occurring between two gases that have Maxwellian distributions. That is, for a smaller self collision than equipartition time, the non-Maxwellian contribution to the relaxation of the distribution function will be zeroth order for self collisions, but higher order in the moments that describe cross collisions, i.e., the exchange of energy and momentum that leads to thermodynamic equilibrium. Thus, in the spirit of the kinetic models proposed by Sirovich,¹ one may write approximate kinetic

whose main virtue is in the fact that the correct conservation equations are obtained upon taking moments. The model equations may be written as,

$$\frac{Df_1}{Dt} = \frac{M_1 - f_1}{\tau_1} + \alpha_E M_1 \left[\left\{ \frac{\frac{3}{2} k(T_2 - T_1) + \frac{m_2}{2} (\underline{U}_2 - \underline{U}_1)^2}{m_1 k T_1} \right\} \left(\frac{m_1 \underline{U}_1^2}{3 k T_1} - 1 \right) + \frac{(1 + \frac{m_2}{m_1})(\underline{U}_2 - \underline{U}_1) \cdot \underline{C}_1}{3 m_1 k T_1} \right] \quad (50)$$

with a similar equation for the evolution of the distribution function for particles of species 2. It is also evident in comparing the magnitude of self to cross collisions, that the self collisional time might be characterized, for example, by a hard sphere interaction, while the cross collision terms could be appropriate to a Maxwell force law. This might be the situation for neutral-neutral collisions for self-relaxation, and neutral-ion collisions for cross collisions. It should also be noted, that even though α_E may be appropriate to the Coulomb or hard sphere force laws, the phenomenon of thermal diffusion will not appear in this form of a model equation.

Conclusions

By taking moments of the Boltzmann equation for a mixture of gases, in the situation where the individual distribution functions are Maxwellian at different temperatures in the frame of reference of the individual species diffusion velocities, general equations for the relaxation of energy and momentum have been obtained for an arbitrary cross section. The

integrals in these equations have been evaluated for the Maxwell, Coulomb, and hard sphere force laws, and, in the limit of a small diffusion Mach number, the energy and momentum relaxation equations take on a particularly simple form, which might have been predicted from phenomenological considerations. The fact that, in actuality, the true form of the individual distribution functions become somewhat non-Maxwellian during the relaxation process should have little effect upon the moment equations. This is indicated by the Maxwell law of force, where the temperature and velocity moments can be obtained for an arbitrary distribution function. It is not expected that the Coulomb and hard sphere force laws should yield qualitatively different results.

In order for an approximate epochal relaxation to occur, the effect of self collisions must drive any large departures from Maxwellian back toward a Maxwellian distribution on a faster time scale than the time required to establish equipartition of energy. Thus, it was necessary to obtain an estimate of the self collision times, which for the Maxwell and hard sphere force laws, was found from the absorption term of the Boltzmann collision integral. These results are presented in table 1, with the relaxation times for equipartition of energy and momentum. These coefficients should be of use in determining the expansion parameters appropriate to obtaining transport coefficients for the steady state, non-equipartition situation found in the two temperature, non-equilibrium MHD

generator. This problem is under current investigation.

Further, the calculation of relaxation coefficients for the hard sphere and Coulomb force laws allows the detailed construction of approximate kinetic models. The use of these models, as has been mentioned elsewhere¹, greatly simplifies the Chapman-Enskog procedure for a gas mixture.

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References

1. L. Sirovich, Phys. Fluids 5, 917, (1962).
2. H. Grad, "Theory of Rarefied Gases" in Rarefied Gas Dynamics, F. Devienne, editor, (Pergamon Press, London, 1960).
3. This concept of "time scales" has recently been employed to derive the hydrodynamic equations from the Boltzmann equation. See J. McCune, T. F. Morse, and G. Sandri, "On the Relaxation of Gases Toward Continuum Flow", Proceedings of the Third International Symposium on Rarefied Gases", Paris, 1962, to be published.
4. I. R. McNab and B. C. Lindley, "Electron Temperature in the Rapid Expansion of a Plasma Flow", C. A. Parsons and Co., Ltd. Research Report, NRC 61-122, May 1962. Fossway, Newcastle upon Tyne.
5. K. N. C. Bray and J. A. Wilson, "A Preliminary Study of Ionic Recombination of Argon in Wind Tunnel Nozzles", Ministry of Aviation, Aeronautical Research Council, 22, 326, London, 1961.
6. D. J. Ben Daniel and S. Tamor, "Nonequilibrium Ionization in Magnetohydrodynamic Generators", General Electric Research Laboratory Report No. 62-RL-(2922E), January 1962.
7. J. Kerrebrock, "Conduction in Gases with Elevated Electron Temperatures", Second Symposium on Engineering Aspects of Magnetohydrodynamics, (Columbia University Press, New York, pp. 327-346, 1962).
8. H. Hurwitz, Jr., G. W. Sutton, and S. Tamor, ARS Journal, August 1962.
9. L. Spitzer, Jr., Physics of Fully Ionized Gases (Interscience Publishers, Inc., New York, 1956).
10. S. Chandrasekhar, Principles of Stellar Dynamics, (Univ. of Chicago Press, Chicago, Ill., 1942).
11. A. M. Cravath, Phys. Rev. 35, 248 (1930).
12. G. Boulegue, et. al., in Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy (United Nations, Geneva, 1958) Vol. 31, p. 242.
13. T. Kihara, and Y. Midzuno, Rev. Mod. Phys. 32, 722, (1960). The author wishes to thank H. Grad for calling this reference to his attention.
14. Edward A. Desloge, Physics Fluids 5, 1223 (1962).

15. T. Kihara, J. Phys. Soc. Japan 14, 402 (1959).
16. I. Kolodner, "Moment Description of Gas Mixtures, I", NYU 7980, Courant Institute of Mathematical Sciences, NYU (1957).
17. Willis L. Everett, "Generalized Magnetohydrodynamic Equations for Non-Equilibrium Plasma Systems", Proceedings of Third International Symposium on Rarefied Gas Dynamics, Paris, 1962, to be published.
18. H. Grad, "Comm. Pure and Applied Math., II, 33, (1949).
19. S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases (Cambridge Univ. Press, New York, 1952).
20. *ibid*, p. 171.
21. D. J. Rose and M. Clark, Jr., Plasmas and Controlled Fusion, (John Wiley and Sons, Inc., New York, 1961) p. 163.
22. D. I. Osipov, AIAA Journal, Russian Supplement, I, 261 (1963).
23. P. L. Bhatnager, E. P. Gross, and M. Krook, Phys. Rev. 94, 511 (1954).

	$1/\tau_1$	$1/\tau_2$	$\propto E$
Maxwell	$2\pi(.422)(\frac{2\theta_{11}}{m_1})^{1/2} n_1$	$2\pi(.422)(\frac{2\theta_{22}}{m_2})^{1/2} n_2$	$\frac{4\pi n_1 n_2 (.422)(\theta_{21})^{1/2}}{m_1^{1/2} (1 + \frac{m_2}{m_1})^{3/2}} (\frac{m_2}{m_1})^{1/2}$
Hard Sphere	$4.3\sqrt{\frac{\pi}{3}} (\frac{kT_1}{m_1})^{1/2} (2r_1)^2 n_1$	$4.3\sqrt{\frac{\pi}{3}} (\frac{kT_2}{m_2})^{1/2} (2r_2)^2 n_2$	$\frac{\frac{16}{3} (2\pi k)^{1/2} n_1 n_2 (r_1 + r_2)^2 (\frac{m_2}{m_1})^{1/2} (\frac{T_2}{T_1 + \frac{m_2}{m_1}})^{1/2} T_1^{1/2}}{m_1^{1/2} (1 + \frac{m_2}{m_1})^2}$
Coulomb	$\frac{5.7\pi n_1 e^4 \ln \Lambda}{m_1^{1/2} \epsilon_0^2 (3kT_1)^{3/2}}$	$\frac{5.7\pi n_2 e^4 \ln \Lambda}{m_2^{1/2} \epsilon_0^2 (3kT_2)^{3/2}}$	$\frac{2e^4 n_1 n_2 (\frac{m_2}{m_1})^{1/2}}{3(2\pi k)^{3/2} \epsilon_0^2} \frac{1}{(m_1 T_1)^{1/2}} \ln \Lambda (\frac{T_2}{T_1 + \frac{m_2}{m_1}})^{3/2}$
	$1/\tau_T = \alpha_E (\frac{1}{n_2} + \frac{1}{n_1})$		
	$1/\tau_V = \alpha_E (\frac{1}{n_2 m_2} + \frac{1}{n_1 m_1}) (\frac{m_1 + m_2}{2})$		

Table 1. Summary of Self and Equipartition Relaxation Times

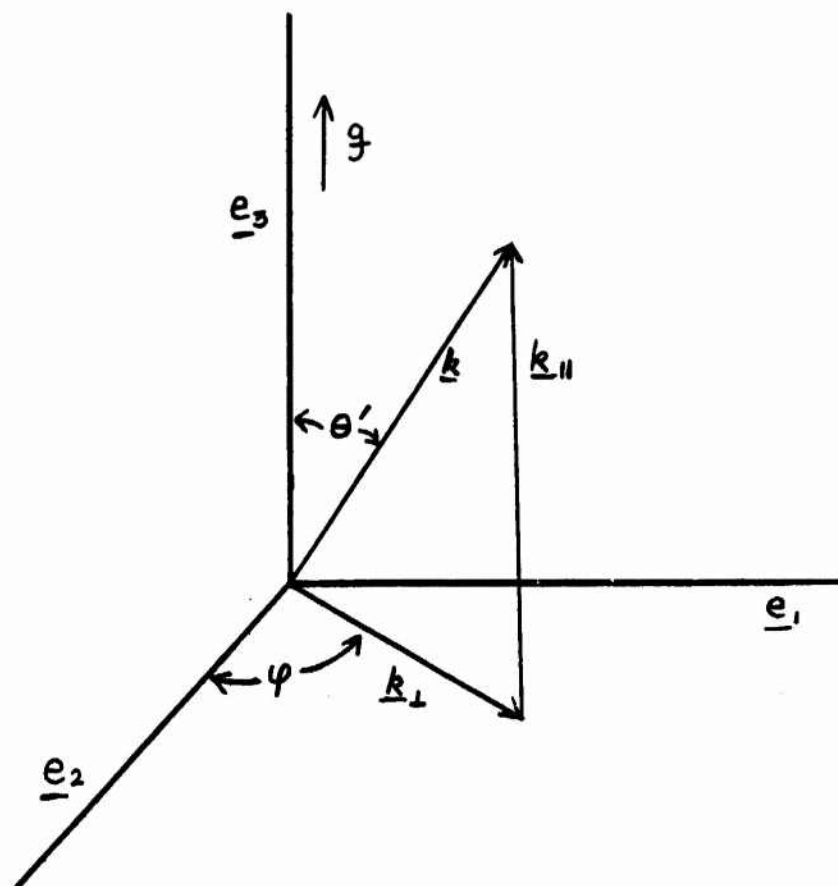


Figure 1. Vector Orientation for $d\underline{k}$ Integration

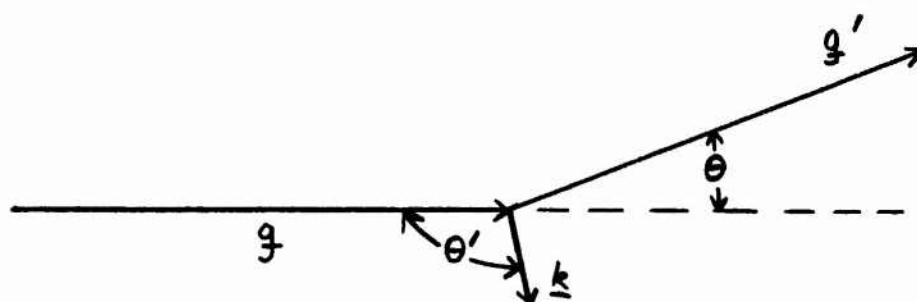


Figure 2. Initial and Final Relative Velocity Vectors in Plane of Scattering

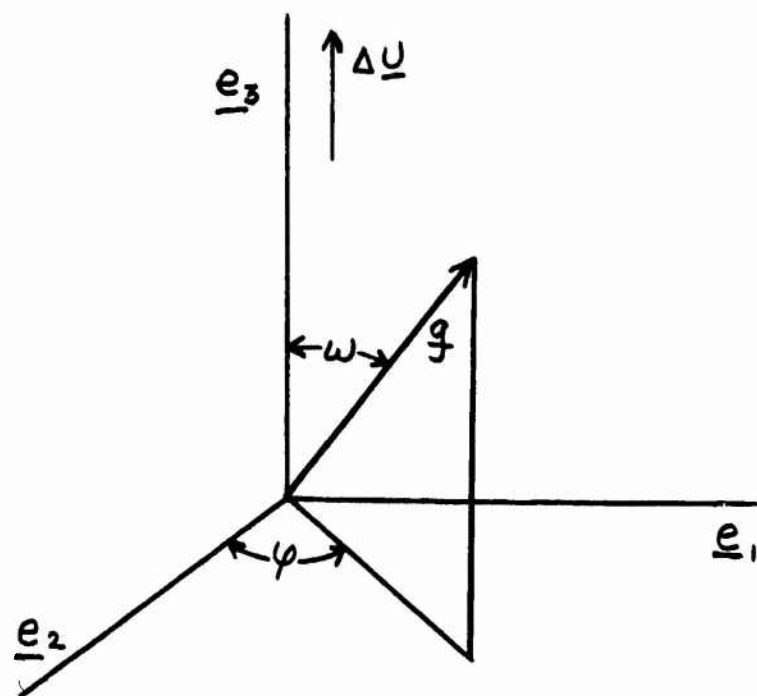


Figure 3. Vector Orientation for $d\underline{g}$ Integration

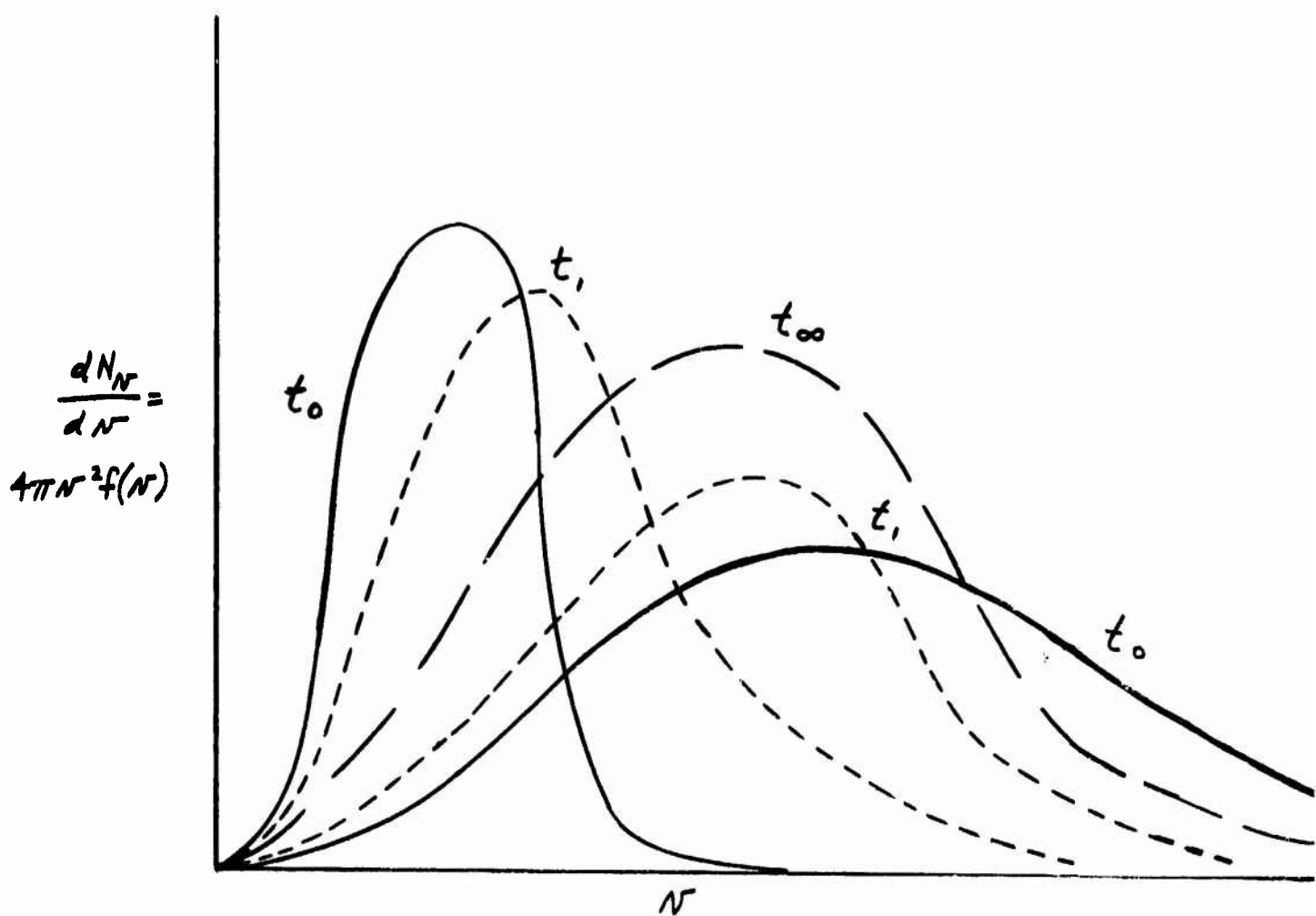


Figure 4. Schematic Relaxation of a Two Component Non-Equipartition Gas Mixture