

CONTRIBUTIONS TO THE THEORY OF DIFFUSION

IN GASES AND LIQUIDS.

Thesis

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Contribution to the Theory of Diffusion in Gases and Liquids.

I. Introduction.

The theory of diffusion in gases has been approached in two different ways in the past. The first is by means of the old free path theory initiated by Maxwell Boltzmann, improved by Tait, Meyer, Jeans and others which though unable to give exact quantitative results owing to the assumption that molecules after collision are distributed in the Maxwellian type in non-uniform gases, provides a simple vivid picture of the complex molecular transport phenomena in gases. The second one due to Chapman and Enskog is to find the deviation from the Maxwellian velocity distribution in a non-uniform gas by solving Maxwell and Boltzmann's Collision equation. This has been successful in most respects for gases at low density, but the generalization for the condensed phase leads to almost insurmountable difficulties. In part I of the present paper, the phenomenon of diffusion is examined in the light of the theory of Brownian motion. It is found that the coefficient of self-diffusion in gases can be rigorously calculated by treating the molecules as Brownian particles. The same method applied to mutual diffusion in mixtures reveals on the one hand the entirely different natures of self-diffusion and mutual diffusion, and on the other the inherently approximative nature of the free path theory and the necessity /

necessity of elaborating the rigorous theory in order to obtain exact quantitative results. In the theory of Brownian motion, the displacement of a Brownian particle in an interval Δt during which a large number of collisions is suffered by the particle with the surrounding molecules, is taken as a purely random process, i.e., there is assumed to be no correlation between the successive displacements in successive intervals Δt . The probability law governing the resultant displacement in a large number of such intervals Δt can be obtained from the probability laws governing each individual step by Markoff's Method. It is then shown that the ratio of the mean square displacement $\overline{(\Delta x)^2}$ to the corresponding time interval Δt is independent of the time interval chosen provided it is long enough to contain a large number of collisions. The constant ratio is obviously a physical property of the medium in which the particle moves. The relation of this constant to molecular data is not considered in the theory of Brownian motion; such a relation can be obtained only if we can follow the motion of the particle within the interval Δt in greater detail.

Following the spirit of the theory of Brownian motion we fix attention on a particular molecule and try to determine how the probability of finding such a molecule at a definite position becomes blurred with time, as the particle disperses and drifts in the /

the medium, which may consist of molecules of the same kind as well as other kinds. The "rate of dispersion" of this probability measured by $\overline{(\Delta x)^2}/\Delta t$ depends for any given molecule on the local physical parameters i.e., the number densities of the different kinds of molecules present, the temperature etc., while the "rate of drift" measured by $\overline{(\Delta x)}/\Delta t$ depends, in addition to the above mentioned parameters, also on their gradients. If the medium is in equilibrium, $\overline{(\Delta x)}/\Delta t$ alone represents the self-diffusion. In a non-equilibrium medium $\overline{(\Delta x)}/\Delta t$ contributes an additional part to the diffusion velocity. This consideration applies to liquids as well as to gases. In the gaseous region it is found that the calculation of the second part $\overline{(\Delta x)}/\Delta t$ requires the velocity distribution in a non-uniform state; the ordinary free path theory without finding the deviation from Maxwellian velocity distribution, has only taken the first part into account in a crude way, hence no exact results can be expected. This again suggests that in the liquid region a qualitative theory may be built on the first part $\overline{(\Delta x)}/\Delta t$ only, corresponding to the free path theory in the gas region. This is indicated in the last section in part I.

By taking advantage of the simplified features in a gas — low density, binary encounters and the hypothesis of molecular chaos, it has been found possible to follow statistically the future course of a given molecule /

molecule for as many successive free flights as one pleases. In a non-uniform gas Maxwell and Boltzmann's equation holds at each encounter between any two successive free flights. In the liquid region the mechanism of migration of molecules is very different, the molecules instead of travelling along free paths have to evade or overcome certain potential barriers before shifting to adjacent sites. It seems possible by considering the fluctuation of the potential barrier round a given molecule due to the nearest neighbours, to calculate the rate of escape of this molecule to adjacent sites.

The conclusion reached in the gas region in part I also indicates that in the liquid region the strict theory of diffusion will require finding the local velocity distribution in a non-uniform liquid, or the rate of drift $\overline{(\Delta x)}/\Delta t$ due to the presence of gradients of densities, temperature, etc. This is dealt with in Part II of the present paper where the method initiated by Born and Green is followed. Integro-differential equations for determining the velocity distribution in a non-uniform liquid mixture are derived corresponding to Maxwell and Boltzmann's collision equation in the gas theory. In the last section of part II formal expressions are given for the coefficients of viscosity and thermal conduction as well as the coefficients of ordinary and thermal diffusion /

diffusion from quite general considerations. A practical method of solution is proposed and discussed.

Part I. Diffusion and Brownian Motion.

I. - 1. Diffusion and transition probability.

The transport of molecular properties in a non-uniform fluid proceeds in two different ways. The first way is by means of the migration of molecules from one place to another carrying with them the local properties - the densities, the mass velocity and the temperature; this may be called the kinetic part of the transport process. The second way, called the potential part of the transport process is due to the action of the intermolecular forces. Diffusion is decidedly the simplest of all the transport processes, as it involves only the transfer of number densities. According to the nature of the process, one can further classify diffusion into the following two types. The first is self-diffusion, arising from the thermal agitation of the molecules. It is always in action whether the fluid is a simple one or a mixture, uniform or non-uniform. The second is diffusion arising from the non-homogeneity of the physical parameters inside the fluid such as the number densities (n_i) the temperature (T) the mass motion velocity (\underline{u}) and the potentials due to an external force field (E_i), the suffix i being used to denote a property pertaining to a particular component of the mixture considered. Though in a simple theory one can express diffusion of the second category in terms /

terms of self-diffusion as is the case with the free path theory in gases, the analysis of the present paper shows that such procedure can not give exact quantitative results.

In all cases the calculation of diffusion coefficients can be made from one probability function i.e., the transition probability $\psi_i(x, \Delta x, t, \Delta t)$ defined as the probability that a molecule of the i th kind at x at time t will suffer a displacement Δx in time Δt . ψ_i depends on x, t through the local parameters λ_i

($\lambda_i = \lambda_i(x, T, \mu, E_i)$) and their space gradients. The time interval Δt is supposed to be macroscopically small so that the mean square displacement suffered by the particle is also small by macroscopical standards, but at the same time it must be large compared to the intervals between individual collisions in the case of gaseous diffusion, and in liquid diffusion it can be identified in a rough way with the mean life of a molecule in one site. In both cases the velocity of the molecule at the end of the interval Δt is no longer correlated with that at the beginning of Δt . We are then justified in taking the displacements in successive intervals Δt to be independent of each other.

In fact for the purpose of calculating the coefficient of diffusion, we do not need the whole of the transition probability ψ_i , but only its first and second moments ($\overline{\Delta x}$, $\overline{(\Delta x)^2}$). We shall in the first /

first place consider the case of pure self-diffusion in a uniform fluid. The transition probability ψ can be a function of Δx and Δt only and it must be even in Δx for reasons of symmetry. Let $n^{(i)}(x, t)$ be the probability of finding any particular molecule at t in x, dx , then one can express the probability distribution of a given molecule at time $t + \Delta t$ in terms of that of the same molecule at time t and the transition probability $\psi(\Delta x, \Delta t)$.

$$n^{(i)}(x, t + \Delta t) = \int n^{(i)}(x - \Delta x, t) \psi(\Delta x, \Delta t) d(\Delta x) \quad (1-1)$$

the integration being extended over all values of Δx . Equation (1-1) can be expanded on account of our assumption that Δt is small.

$$\begin{aligned} n^{(i)}(x, t) + \Delta t \frac{\partial}{\partial t} n^{(i)}(x, t) + O(\Delta t)^2 \\ = \int \left\{ n^{(i)}(x, t) - \Delta x \frac{\partial}{\partial x} n^{(i)}(x, t) + \frac{1}{2} (\Delta x)^2 \frac{\partial^2}{\partial x^2} n^{(i)}(x, t) + O(\Delta x)^3 \right\} \psi(\Delta x, \Delta t) d(\Delta x) \\ = n^{(i)}(x, t) + \frac{1}{6} \frac{\partial^2}{\partial x^2} \frac{\partial}{\partial t} \left\{ n^{(i)}(x, t) \int \psi(\Delta x, \Delta t) (\Delta x)^2 d(\Delta x) \right\} + O(\Delta x)^4 \end{aligned}$$

knowing that ψ is normalized and even in (Δx) i.e.

$$\left. \begin{aligned} \int \psi(\Delta x, \Delta t) d(\Delta x) &= 1, \\ \int \psi(\Delta x, \Delta t) (\Delta x)^{\ell} d(\Delta x) &= 0, \quad (\ell \text{ odd}) \\ \int \psi(\Delta x, \Delta t) \Delta x^2 d(\Delta x) &= \frac{1}{3} \int \psi(\Delta x, \Delta t) (\Delta x)^2 d(\Delta x) = \frac{1}{3} \overline{(\Delta x)^2} \end{aligned} \right\} (1-2)$$

where the bars are used to denote averaging with the weight function ψ .

If $\overline{(\Delta x)^2}$ is taken to be of the same order as Δt , we can neglect $O(\Delta t)^2$ and $O(\overline{(\Delta x)^4})$ and obtain

$$\frac{\partial}{\partial t} n^{(i)}(x, t) = \frac{1}{6} \frac{\overline{(\Delta x)^2}}{\Delta t} \frac{\partial^2}{\partial x^2} n^{(i)}(x, t) \quad (1-3)$$

comparing with the standard form of the equation of diffusion we see that ^{the} coefficient of self-diffusion

D_s is

$$D_s = \frac{1}{6} \frac{\overline{(\Delta x)^2}}{\Delta t} \quad (1-4)$$

It is well known that this ratio is independent of $\Delta t/$

Δt provided that it fulfills the condition we imposed on it before. We notice further that this ratio is independent of the particular molecule we have chosen i.e. every molecule has the ^{same} tendency to disperse among the rest.

It may be parenthetically noted that the transition probability ψ can be found in this case to be

$$\psi(\Delta x, \Delta t) = \frac{1}{(4\pi D_s \Delta t)^{3/2}} \exp\left\{-\frac{(\Delta x)^2}{4 D_s \Delta t}\right\} \quad (1-5)$$

for sufficient large Δt by assuming the validity of the ordinary equation of diffusion

$$\frac{\partial}{\partial t} n(x, t) = D \frac{\partial^2}{\partial x^2} n(x, t). \quad (1-6)$$

The form of ψ in (1-5) is consistent with our assumption made about the order of magnitude of Δt and $(\Delta x)^2$. Thus under this assumption the ordinary equation of diffusion (1-6) and the transition probability ψ (1-5) can be obtained from each other.

We next consider diffusion in a non-uniform binary mixture in which the physical parameters λ_e ($\lambda_e = n_i, T, \mu, E_i$) vary smoothly in space. Fixing our attention first on a particular molecule, say the i th of the first kind, we examine the mechanism by which it migrates in a medium which consists of two different kinds of molecules and which itself changes in space and time.

ψ_i is here also a function of \underline{x} and t . As before we know from continuity considerations that the probability density $n_i^{(i)}(x, t)$ satisfies the relation.

$$n_i^{(i)}(x, t + \Delta t) = \int \psi_i(x - \Delta x, \Delta x, t, \Delta t) n_i^{(i)}(x - \Delta x, t) d(\Delta x), \quad (1-7)$$

where /

where the subscript 1 is used to indicate quantities pertaining to molecules of the first kind.

Expanding both sides of (1 - 7) as before, noticing ψ_1 should be expanded too, we obtain

$$\begin{aligned} \frac{\partial}{\partial t} n_1^{(1)}(x, t) \Delta t + O(\Delta t)^2 \\ = - \frac{\partial}{\partial x} \cdot [n_1^{(1)}(x, t) \overline{(\Delta x)}] + \frac{1}{2} \frac{\partial}{\partial x} \frac{\partial}{\partial x} \cdot [n_1^{(1)}(x, t) \overline{(\Delta x)^2}] + O(\overline{(\Delta x)^2 \Delta x}), \end{aligned} \quad (1 - 8)$$

If we neglect terms of higher order than Δt and let

$$\begin{aligned} \overline{(\Delta x)} &= \int \psi_1(x, \Delta x, t, \Delta t) \Delta x d(\Delta x) = \beta_1 \Delta t \\ \overline{(\Delta x)^2} &= \int \psi_1(x, \Delta x, t, \Delta t) \Delta x^2 d(\Delta x) = 2 \underline{\alpha}_1 \Delta t \end{aligned} \quad \left. \vphantom{\overline{(\Delta x)}} \right\} (1 - 9)$$

equation (1 - 8) becomes

$$\frac{\partial}{\partial t} n_1^{(1)}(x, t) = - \frac{\partial}{\partial x} \cdot (n_1^{(1)}(x, t) \beta_1) + \frac{\partial}{\partial x} \frac{\partial}{\partial x} \cdot [n_1^{(1)}(x, t) \underline{\alpha}_1] \quad (1 - 10)$$

Since ψ_1 depends on the space gradients at x, t the same holds for $\underline{\alpha}_1$; we may therefore expand $\underline{\alpha}_1$ with respect to the gradients, thus:

$$\underline{\alpha}_1 = \frac{1}{3} \alpha_1 \underline{\underline{1}} + O\left(\frac{\partial \alpha_1}{\partial x}\right), \quad \alpha_1 = \frac{1}{2} \frac{\overline{(\Delta x)^2}}{\Delta t} \quad (1 - 11)$$

As terms of higher order than the second in the gradients on the R.H.S. of (1 - 10) will be neglected, we require for β_1 terms involving at most the first order gradients and for $\underline{\alpha}_1$ only the first term in (1 - 11) $\frac{1}{3} \alpha_1 \underline{\underline{1}}$. Equation (1 - 10) can be rewritten in the form

$$\frac{\partial}{\partial t} n_1^{(1)}(x, t) = - \frac{\partial}{\partial x} \cdot (n_1^{(1)}(x, t) \beta_1) + \frac{1}{3} \frac{\partial}{\partial x} \frac{\partial}{\partial x} \cdot (n_1^{(1)}(x, t) \alpha_1) \quad (1 - 12)$$

Hence from the equation of continuity for $n_1^{(1)}$ we find the local flow $n_1^{(1)}(x, t) \underline{\underline{u}}_1^{(1)}(x, t)$ of the probability density $n_1^{(1)}(x, t)$ is

$$n_1^{(1)} \underline{\underline{u}}_1^{(1)} = n_1^{(1)}(x, t) \beta_1 - \frac{1}{3} \frac{\partial}{\partial x} (n_1^{(1)}(x, t) \alpha_1) \quad (1 - 13)$$

Up /

Up to the present, we have only considered the probability of finding a particular molecule at a given position. To relate it with the local partial density $n_1(x, t)$ of molecules of the first kind, we imagine that at some given instant when the mixture is already in its normal state, the λ_e 's are known throughout the fluid and in particular, the position of all the molecules are exactly known; the transition probability of each molecule is found by treating the rest as a medium, with λ_e 's known everywhere. At any later instant t , the probability of finding the volume element $\underline{x}, d\underline{x}$ to be occupied by any molecule of the first kind must be equal to the sum of the probability that it is occupied by each of the N_1 molecules of the first kind, i.e.

$$n_1(x, t) = \sum_{i=1}^{N_1} n_1^{(i)}(x, t). \quad (1-14)$$

Besides, α_1 and β_1 depends only on \underline{x}, t and are independent of which molecules of the first kind is chosen for consideration. The total local flow of molecules of the first kind is

$$n_1 \underline{u}_1 = \sum_{i=1}^{N_1} n_1^{(i)} \underline{u}_1^{(i)} = n_1 \beta_1 - \frac{1}{3} \frac{\partial}{\partial x} (n_1 \alpha_1), \quad (1-15)$$

of which a part is due to local mass velocity \underline{u} and the rest is the interdiffusion velocity \underline{u}' . Hence

$$\begin{aligned} \underline{u}' &= (\beta_1 - \underline{u}) - \frac{1}{3n_1} \frac{\partial}{\partial x} (n_1 \alpha_1) \\ &= \beta_1' - \frac{1}{3} \frac{\partial \alpha_1}{\partial x} - \frac{\alpha_1}{3n_1} \frac{\partial n_1}{\partial x}, \end{aligned} \quad (1-16)$$

where

$$\beta_1' = \beta_1 - \underline{u}. \quad (1-17)$$

Proceeding /

Proceeding in the same way, we obtain for molecules of the second kind

$$\bar{u}'_2 = \beta'_2 - \frac{1}{3} \frac{\partial \alpha_2}{\partial x} - \frac{\alpha_2}{3n_2} \frac{\partial n_2}{\partial x}, \quad (1-18)$$

where β'_2 , α_2 and n_2 have analogous meanings.

The mutual diffusion velocity ($\bar{u}'_1 - \bar{u}'_2$) follows from (1-16) and (1-18)

$$\bar{u}'_1 - \bar{u}'_2 = (\beta'_1 - \beta'_2) - \frac{1}{3} \frac{\partial (\alpha_1 - \alpha_2)}{\partial x} - \frac{1}{3} \left(\frac{\alpha_1}{n_1} \frac{\partial n_1}{\partial x} - \frac{\alpha_2}{n_2} \frac{\partial n_2}{\partial x} \right). \quad (1-19)$$

It is seen that the mutual diffusion velocity consists of three terms. Apart from the difference ($\beta'_1 - \beta'_2$) of the first moments of ψ_1 and ψ_2 divided by the time interval Δt which is characteristic of non-uniform fluids, there is the part due to the gradients of the difference of the second moments ($\alpha_1 - \alpha_2$) of ψ_1 and ψ_2 divided by the time interval and the part due to the presence of a density gradients. One can see at this point that without knowing the deviation from the Maxwellian velocity distribution in a non-uniform fluid one can at most approximate to the real diffusion velocity by the second and third term in (1-19), and this is what the old free path theory have intended to do, though the persistence of motion, i.e. the tendency of a molecule to continue its state of motion after collision has never been properly taken care of. In the next section α_1 and α_2 are calculated by following the molecule for a large number of successive flights; thus the correlation between the motions between successive encounters is rigorously taken into account.

The /

The second and third term in (1 - 19) with α_1 and α_2 thus calculated would represent the upper limit that one can expect for the diffusion velocity without finding the true velocity distribution in non-uniform gases. By making the same assumptions, a corresponding theory for diffusion in liquids is indicated in (1 - 5).

In the following we shall give the formal expression of the coefficient of ordinary diffusion (D_0) and of thermal diffusion (D_T) in terms of β'_1, β'_2 and α_2 . As β'_1 and β'_2 are linear in the gradients, so are $\frac{\partial \alpha_1}{\partial x}$, $\frac{\partial \alpha_2}{\partial x}$ and only the components in the direction of $\frac{\partial n_1}{\partial x}$, $\frac{\partial n_2}{\partial x}$ and $\frac{\partial T}{\partial x}$ are of interest in the present calculation; we write

$$\left. \begin{aligned} \beta'_1 &= \beta_1^{(1)} \frac{\partial n_1}{\partial x} + \beta_1^{(2)} \frac{\partial n_2}{\partial x} + \beta_1^{(3)} \frac{\partial T}{\partial x} \\ \frac{\partial \alpha_1}{\partial x} &= \frac{\partial n_1}{\partial x} \frac{\partial \alpha_1}{\partial n_1} + \frac{\partial n_2}{\partial x} \frac{\partial \alpha_1}{\partial n_2} + \frac{\partial T}{\partial x} \frac{\partial \alpha_1}{\partial T} \end{aligned} \right\} (1 - 20)$$

with similar expressions for β'_2 and $\frac{\partial \alpha_2}{\partial x}$.

In order to select the part of the diffusion due to the presence of a pressure gradient, we transform the gradients $\frac{\partial n_1}{\partial x}$, $\frac{\partial n_2}{\partial x}$ and $\frac{\partial T}{\partial x}$ to $\frac{\partial c_1}{\partial x}$, $\frac{\partial p}{\partial x}$ and $\frac{\partial T}{\partial x}$ where $c_1 = \frac{n_1}{n_1 + n_2}$ while $p = p_1 + p_2$ is the total pressure.

$$\left. \begin{aligned} \frac{\partial c_1}{\partial x} &= \frac{n_1 n_2}{n^2} \left(\frac{1}{n_1} \frac{\partial n_1}{\partial x} - \frac{1}{n_2} \frac{\partial n_2}{\partial x} \right), \quad n = n_1 + n_2 \\ \frac{\partial p}{\partial x} &= \frac{\partial n_1}{\partial x} \frac{\partial p}{\partial n_1} + \frac{\partial n_2}{\partial x} \frac{\partial p}{\partial n_2} + \frac{\partial T}{\partial x} \frac{\partial p}{\partial T} \end{aligned} \right\} (1 - 21)$$

Hence we can express $\frac{\partial n_1}{\partial x}$ and $\frac{\partial n_2}{\partial x}$ in terms of $\frac{\partial p}{\partial x}$, $\frac{\partial c_1}{\partial x}$ and $\frac{\partial T}{\partial x}$

$$\left. \begin{aligned} \frac{\partial n_1}{\partial x} &= \left\{ n^2 \frac{\partial p}{\partial n_2} \frac{\partial c_1}{\partial x} + n_1 \left(\frac{\partial p}{\partial x} - \frac{\partial p}{\partial T} \frac{\partial T}{\partial x} \right) \right\} / (n_1 \frac{\partial}{\partial n_1} + n_2 \frac{\partial}{\partial n_2}) p \\ \frac{\partial n_2}{\partial x} &= \left\{ -n^2 \frac{\partial p}{\partial n_1} \frac{\partial c_1}{\partial x} + n_2 \left(\frac{\partial p}{\partial x} - \frac{\partial p}{\partial T} \frac{\partial T}{\partial x} \right) \right\} / (n_1 \frac{\partial}{\partial n_1} + n_2 \frac{\partial}{\partial n_2}) p \end{aligned} \right\} (1 - 22)$$

In the experimental observation of diffusion in fluids the pressure is usually kept constant, thus one can take $\frac{\partial p}{\partial x} = 0$ in (1 - 22).

Substituting /

Substituting (1 - 22) in (1 - 20) we have

$$\left. \begin{aligned} \beta_1' &= \frac{n^2 \left(\frac{\partial p}{\partial n_2} \beta_1^{(1)} - \frac{\partial p}{\partial n_1} \beta_1^{(2)} \right)}{\Delta p} \frac{\partial c_1}{\partial x} + \left\{ \beta_1^{(2)} - \left(\frac{n_1 \beta_1^{(1)} + n_2 \beta_1^{(2)}}{\Delta p} \right) \frac{\partial p}{\partial T} \right\} \frac{\partial T}{\partial x} \\ \frac{\partial \alpha_1}{\partial x} &= \frac{n^2 \frac{\partial(\alpha_1 p)}{\partial(n_1 n_2)}}{\Delta p} \frac{\partial c_1}{\partial x} + \left[\frac{\partial \alpha_1}{\partial T} - \frac{\Delta d_1}{\Delta p} \frac{\partial p}{\partial T} \right] \frac{\partial T}{\partial x} \end{aligned} \right\} \quad (1 - 23)$$

where

$$\Delta = n_1 \frac{\partial}{\partial n_1} + n_2 \frac{\partial}{\partial n_2} \quad (1 - 24)$$

with similar expressions for β_2' and $\frac{\partial \alpha_2}{\partial x}$.

Equation (1 - 19) becomes after inserting the formal expressions of β_1' , β_2' , $\frac{\partial \alpha_1}{\partial x}$ and $\frac{\partial \alpha_2}{\partial x}$

$$\begin{aligned} u_1' - u_2' &= \frac{n^2}{\Delta p} \left\{ \left(\beta_1^{(1)} - \beta_2^{(1)} \right) \frac{\partial p}{\partial n_2} - \left(\beta_1^{(2)} - \beta_2^{(2)} \right) \frac{\partial p}{\partial n_1} - \frac{1}{3} \frac{\partial(d_1 - d_2)p}{\partial(n_1 n_2)} - \frac{1}{3} \left(\frac{\alpha_1}{n_1} \frac{\partial p}{\partial n_2} + \frac{\alpha_2}{n_2} \frac{\partial p}{\partial n_1} \right) \frac{\partial c_1}{\partial x} \right. \\ &\quad \left. + \left\{ \left(\beta_1^{(2)} - \beta_2^{(2)} \right) - \left[n_1 \left(\beta_1^{(1)} - \beta_2^{(1)} \right) + n_2 \left(\beta_1^{(2)} - \beta_2^{(2)} \right) \right] \frac{\partial p}{\Delta p} - \frac{1}{3} \left[\frac{\partial}{\partial T} (d_1 - d_2) - \frac{\partial p}{\Delta p} (1 + \Delta) (d_1 - d_2) \right] \right\} \frac{\partial T}{\partial x} \right\} \end{aligned} \quad (1 - 25)$$

Comparing with the usual definition of the coeff.

of ordinary diffusion D_0 and thermal diffusion D_T

$$u_1' - u_2' = - \frac{n^2}{n_1 n_2} \left(D_0 \frac{\partial c_1}{\partial x} - \frac{D_T}{T} \frac{\partial T}{\partial x} \right) \quad (1 - 26)$$

we obtain finally

$$D_0 = \frac{n_1 n_2}{\Delta p} \left\{ \frac{1}{3} \frac{\partial(d_1 - d_2)p}{\partial(n_1 n_2)} + \frac{1}{3} \left(\frac{\alpha_1}{n_1} \frac{\partial p}{\partial n_2} + \frac{\alpha_2}{n_2} \frac{\partial p}{\partial n_1} \right) - \left[\left(\beta_1^{(1)} - \beta_2^{(1)} \right) \frac{\partial p}{\partial n_2} - \left(\beta_1^{(2)} - \beta_2^{(2)} \right) \frac{\partial p}{\partial n_1} \right] \right\} \quad (1 - 27)$$

$$D_T = \frac{n_1 n_2}{n^2} \left\{ \frac{1}{3} \left[\frac{T \frac{\partial p}{\partial T}}{\Delta p} (1 + \Delta) - T \frac{\partial}{\partial T} \right] (d_1 - d_2) - \left[n_1 \left(\beta_1^{(1)} - \beta_2^{(1)} \right) + n_2 \left(\beta_1^{(2)} - \beta_2^{(2)} \right) \right] \frac{T \frac{\partial p}{\partial T}}{\Delta p} + T \left(\beta_1^{(2)} - \beta_2^{(2)} \right) \right\} \quad (1 - 28)$$

In a dilute gas $p = nkT = (n_1 + n_2)kT$, we have

$$D_0 = \frac{n_1 n_2}{n} \left\{ \frac{1}{3} \left(\frac{\partial}{\partial n_1} - \frac{\partial}{\partial n_2} \right) (d_1 - d_2) + \frac{1}{3} \left(\frac{\alpha_1}{n_1} + \frac{\alpha_2}{n_2} \right) - \left(\beta_1^{(1)} + \beta_2^{(2)} \right) + \left(\beta_2^{(1)} + \beta_1^{(2)} \right) \right\} \quad (1 - 29)$$

$$D_T = \frac{n_1 n_2}{n^2} \left\{ \frac{1}{3} \left(1 + \Delta - T \frac{\partial}{\partial T} \right) (d_1 - d_2) - \left[n_1 \left(\beta_1^{(1)} - \beta_2^{(1)} \right) + n_2 \left(\beta_1^{(2)} - \beta_2^{(2)} \right) \right] + T \left(\beta_1^{(2)} - \beta_2^{(2)} \right) \right\} \quad (1 - 30)$$

I. - 2. Statistics of motion of gas molecules.

In the present section it will be shown that one can actually follow the path of a single molecule statistically, assuming the real velocity distribution of the medium as a function of \underline{x} and t to be known. We shall take advantage of the particularly simple feature in gases of low or moderate density by virtue of which the molecules spend most of their time almost free from the influence of the rest so that a fairly well defined straight free path is possible; in fact at N.T.P the mean free path is usually about several hundred times as long as the diameters of the molecules. Thereby the assumption of molecular chaos and binary encounters are justified.

Strictly speaking one can define rigorously the free path only for rigid spheres. In any general force law the total cross section calculated classically is always infinite due to the weak interaction of the distant molecules while in quantum theory it is finite. For the present purpose we may cut off the interaction beyond a reasonable distance with negligible error and it can then be shown that the final results α_1, α_2 etc., are practically independent of the range of interaction which we have chosen at the beginning so long as it is not too short.

Two basic probability functions used in the present section will be defined first.

(1) /

(1) $\mu(\underline{x}, \underline{\xi}^{(i)}, t) dt =$ probability that a molecule at \underline{x} of velocity $\underline{\xi}^{(i)}$ at time t will have suffered a collision in t, dt .

(2) $\chi(\underline{\xi}^{(i)}, \underline{\xi}^{(j)}, \underline{x}, t) d\underline{\xi}^{(j)} dt =$ probability that a molecule at \underline{x} of velocity $\underline{\xi}^{(i)}$ at time t will have been deflected into $\underline{\xi}^{(j)}, d\underline{\xi}^{(j)}$ in t, dt .

It will be shown in the appendix that both μ and χ can be calculated for any force law with finite range.

It is obvious from the definition that μ is obtainable from χ i.e.

$$\mu(\underline{\xi}^{(i)}, \underline{x}, t) = \int \chi(\underline{\xi}^{(i)}, \underline{\xi}^{(j)}, \underline{x}, t) d\underline{\xi}^{(j)} \quad (1 - 31)$$

Both μ and χ depend only on the instantaneous velocity $\underline{\xi}^{(i)}$ of the selected molecule at time t and not on its history; it does not matter how long the molecule has travelled with that velocity $\underline{\xi}^{(i)}$ before reaching \underline{x} at t . In a gas in equilibrium μ and χ are independent of \underline{x} and t ; μ is a function of $|\underline{\xi}^{(i)}|$ only and χ of $|\underline{\xi}^{(i)}|, |\underline{\xi}^{(j)}|$ and θ only, θ being the angle between $\underline{\xi}^{(i)}$ and $\underline{\xi}^{(j)}$.

In dealing with a series of successive flights i.e. motions between encounters, we shall denote by $t_i, \underline{x}^{(i)}$ and $\underline{\xi}^{(i)}$ the time, position and velocity vector at the beginning of the i th flight and by $\tau_{ij} = |t_i - t_j|$ the time interval between the i th and j th encounter where the i th encounter occurs at the beginning of the i th flight. In particular $\tau_{i, i+1}$ is the time of the i th flight.

We /

We first find the probability that a molecule at x'' with velocity ξ'' at time t_1 will travel freely for τ_{12} and suffer a collision in $\tau_{12}, d\tau_{12}$. Denote this probability by $\overline{w}(\xi'', x'', t_1, \tau_{12}) d\tau_{12}$, we have

$$\overline{w}(\xi'', x'', t_1, \tau_{12}) d\tau_{12} = \left\{ 1 - \int_0^{\tau_{12}} \overline{w}(\xi'', x'', t_1, \tau) d\tau \right\} \mu(\xi'', x'', t_2) d\tau_{12}, \quad (1 - 32)$$

where the first factor on the R.H.S. gives the probability that it will not collide before $t_2 = t_1 + \tau_{12}$ and the second factor the probability that it will collide in $\tau_{12}, d\tau_{12}$.

Dividing both sides of the above equation by $\mu(\xi'', x'', t_2)$ and differentiating with respect to τ_{12} , we obtain

$$\frac{d}{d\tau_{12}} \left(\frac{\overline{w}(\xi'', x'', t_1, \tau_{12})}{\mu(\xi'', x'', t_2)} \right) = -\overline{w}(\xi'', x'', t_1, \tau_{12}).$$

Hence after integration we have

$$\overline{w}(\xi'', x'', t_1, \tau_{12}) = \mu(\xi'', x'', t_2) e^{-\int_0^{\tau_{12}} \mu(\xi'', x'' + \xi'' \tau, t_1 + \tau) d\tau} \quad (1 - 33)$$

using the initial condition

$$\overline{w}(\xi'', x'', t_1, 0) = \mu(\xi'', x'', t_1).$$

We notice here that the probability that a molecule of velocity ξ'' at x'' , t_1 will travel freely for an interval not less than τ_{12} without collision is according to (1 - 32)

$$\left\{ 1 - \int_0^{\tau_{12}} \overline{w}(\xi'', x'', t_1, \tau) d\tau \right\} = e^{-\int_0^{\tau_{12}} \mu(\xi'', x'' + \xi'' \tau, t_1 + \tau) d\tau} \quad (1 - 34)$$

We now proceed to consider the statistics of a complete flight. (By a complete flight is meant the flight of /

of a molecule between two successive collisions. The correct definition of free path should be based on this concept. One sees clearly at this point the difference between Maxwell's free path which is in accord with the present definition and Tait's free path which is not).

Let $\overline{w}_1(\xi''', x''', t_1, \tau_{12}) d\xi''' dx''' d\tau_{12}$ be the probability of finding a molecule at x''', dx''' at time t with its velocity in $\xi''', d\xi'''$ which travels freely for τ_{12} and suffers a collision in $\tau_{12}, d\tau_{12}$. We have simply

$$\overline{w}_1(\xi''', x''', t_1, \tau_{12}) d\xi''' dx''' d\tau_{12} = f_1(x''', \xi''', t_1) w(\xi''', x''', t_1, \tau_{12}) d\xi''' dx''' d\tau_{12} \quad (1 - 35)$$

where $f_1(x''', \xi''', t_1)$ is the density in phase space for a single molecule at x''', ξ''' at time t_1 .

We notice here that among the molecules to be found in x''', dx''' at t_1 with velocity in $\xi''', d\xi'''$ some are just being deflected into $\xi''', d\xi'''$ but by far the large majority of them have already acquired a velocity in $\xi''', d\xi'''$ before t_1 passing merely through x''', dx''' at t_1 . It would be incorrect to identify the average flight of the above set of molecules after t_1 with the free path of a single molecule and this is just Tait's free path l_T in the direction of ξ'''

$$l_T = \frac{\int \overline{w}_1(\xi''', x''', t_1, \tau_{12}) \xi''' \tau_{12} \xi''' d\xi''' d\tau_{12}}{\int \overline{w}_1(\xi''', x''', t_1, \tau_{12}) \xi''' d\xi''' d\tau_{12}}$$

which for equilibrium state becomes

$$l_T = \overline{\left(\frac{\xi'''}{\mu(\xi''')} \right)}$$

where the bar denotes the average with respect to the Maxwellian velocity distribution.

In/

In order to determine the real mean free path one has to select from the above set of molecules those which are just starting their new free path at t, dt . This can be done by making use of the function χ .

The probability of finding at t , a molecule in x'', dx'' with velocity in $\underline{v}'', d\underline{v}''$ which is deflected into $\underline{v}', d\underline{v}'$ in t, dt , is $f_1(x'', \underline{v}'', t) d\underline{v}'' dx'' \chi(\underline{v}', \underline{v}'', x'', t) d\underline{v}' dt$.

Hence the probability that a molecule with any velocity in x'', dx'' at t , is deflected into $\underline{v}', d\underline{v}'$ in t, dt , is

$$dx'' d\underline{v}' dt, \int f_1(x'', \underline{v}'', t) \chi(\underline{v}', \underline{v}'', x'', t) d\underline{v}''.$$

It can be shown that in gases in equilibrium the above probability reduces to $f_1(x'', \underline{v}'', t) \mu(\underline{v}', x'', t) d\underline{v}' dx'' dt$,

and in gases which are not in equilibrium it reduces

to $(\mu(\underline{v}', x'', t) + \frac{\partial}{\partial t} + \underline{v}' \cdot \frac{\partial}{\partial x''}) f_1(x'', \underline{v}'', t) d\underline{v}' dx'' dt$.

That this is correct in the equilibrium state can be inferred from the principle of detailed balancing.

For according to this principle, to every type of collision there exists the inverse type occurring with equal frequency exactly undoing the effect of the first.

We therefore conclude that the probability of finding a molecule of any velocity at t , in x'', dx'' which is deflected into $\underline{v}', d\underline{v}'$ in t, dt , is equal to the probability of finding a molecule in x'', dx'' at t , with velocity in $\underline{v}', d\underline{v}'$ which is deflected into a motion with any velocity in t, dt . i.e.,

$$\begin{aligned} dx'' d\underline{v}' dt, \int f_1(x'', \underline{v}'', t) \chi(\underline{v}', \underline{v}'', x'', t) d\underline{v}'' \\ = f_1(x'', \underline{v}'', t) \mu(\underline{v}', x'', t) d\underline{v}' dx'' dt. \end{aligned} \quad (1 - 36)$$

For /

For the non-equilibrium state the distribution function f , changes with time so that the set of molecules in $x''; dx''$ with velocity in $\xi''; d\xi''$ increases in time dt , by the amount $(\frac{\partial}{\partial t} + \xi'' \frac{\partial}{\partial x''}) f_1(\xi''; x''; t) d\xi'' dx'' dt$, which is just the extra term given above.

An alternative proof which may clarify the situation still further is as follows:

Let $P_1(\xi''; x''; t_1; \tau_{12}) dt_1 d\xi'' dx'' d\tau_{12}$ be the probability of finding a molecule with any velocity at $x''; dx''$ at t_1 , which is deflected into $\xi''; d\xi''$ in $t_1; dt_1$, travels freely for τ_{12} and collides in $\tau_{12}; d\tau_{12}$. Then it is seen that the number of the set of molecules

$\overline{w}_1(\xi''; x''; t_1; \tau_{12}) dx'' d\xi'' d\tau_{12}$ must be equal to the integrated sum for all values of $t_0 < t_1$ of the number of molecules starting at $x^{(0)}; dx^{(0)}$ ($x^{(0)} = x'' - \xi'' \tau$) with velocity in $\xi''; d\xi''$, passing through $x''; dx''$ at $t_1; dt_1$ and arriving at $x^{(0)}; dx^{(0)}$ at $t_0; dt_0$. (The subscript 0 is used to indicate events prior to the instant t_1). Therefore

$$dx^{(0)} d\xi^{(0)} d\tau_{02} \int P_1(\xi''; x''; t_0; \tau_{02}) dt_0 = \overline{w}_1(\xi''; x''; t_1; \tau_{12}) d\tau_{12} dx'' d\xi'',$$

the integration is to be carried out over all $t_0 < t_1$. If the time intervals are counted from t_2 we can replace $dt_0; d\tau_{02}$ and $d\tau_{12}$ by $d\tau_{02}; dt_2$ and dt_2 respectively.

Thus

$$dx'' d\xi'' dt_2 \int_{\tau_{12}}^{\infty} P_1(\xi''; x'' - \xi'' \tau_{02}; t_2 - \tau_{02}; \tau_{02}) d\tau_{02} = \overline{w}_1(\xi''; x''; \xi'' \tau_{12}; t_2 - \tau_{12}; \tau_{12}) d\xi'' dx'' dt_2.$$

The volume elements $dx^{(0)}$ and $d\xi^{(0)}$ can be chosen equal.

After differentiating both sides with respect to τ_{12}

we obtain

$$-P_1(\xi''; x'' - \xi'' \tau_{12}; t_2 - \tau_{12}; \tau_{12}) = \frac{d}{d\tau_{12}} \overline{w}_1(\xi''; x'' - \xi'' \tau_{12}; t_2 - \tau_{12}; \tau_{12}) - \int_0^{\tau_{12}} \left\{ f_1(\xi''; x'' - \xi'' \tau; t_2 - \tau) \mu(\xi''; x''; t_2) e^{-\int_0^{\tau} \mu(\xi''; x'' - \xi'' \tau', t_2 - \tau') d\tau'} \right\} d\tau.$$

Hence /

Hence

$$P_1(\underline{x}''', \underline{x}''', t_1, \tau_2) = \left\{ \mu(\underline{x}''', \underline{x}''', t_1) + \frac{\partial}{\partial t_1} + \underline{x}''', \frac{\partial}{\partial \underline{x}'''} \right\} f_1(\underline{x}''', \underline{x}''', t_1) \int_0^{\tau_2} \mu(\underline{x}''', \underline{x}''', t_1 + \tau) e^{-\int_0^{\tau} (\frac{\partial}{\partial t_1} + \underline{x}''', \frac{\partial}{\partial \underline{x}'''})} dt \quad (1 - 37)$$

By definition and (1 - 37) we have

$$\begin{aligned} d\underline{x}'''' d\underline{x}'''' dt_1 \int f_1(\underline{x}''', \underline{x}''', t_1) \chi(\underline{x}''', \underline{x}''', \underline{x}''', t_1) d\underline{x}'''' \\ = d\underline{x}'''' d\underline{x}'''' dt_1 \int P_1(\underline{x}''', \underline{x}''', t_1, \tau_2) d\underline{x}'''' \quad (1 - 38) \\ = d\underline{x}'''' d\underline{x}'''' dt_1 \left(\mu(\underline{x}''', \underline{x}''', t_1) + \frac{\partial}{\partial t_1} + \underline{x}''', \frac{\partial}{\partial \underline{x}'''} \right) f_1(\underline{x}''', \underline{x}''', t_1) \end{aligned}$$

which is the relation to be proved.

It should be added that equation (1 - 38) is merely another form of the Maxwell & Boltzmann's equation.

For using (1 - 31) we have

$$\begin{aligned} \left(\frac{\partial}{\partial t_1} + \underline{x}''', \frac{\partial}{\partial \underline{x}'''} \right) f_1(\underline{x}''', \underline{x}''', t_1) \\ = \int \left\{ f_1(\underline{x}''', \underline{x}''', t_1) \chi(\underline{x}''', \underline{x}''', \underline{x}''', t_1) - f_1(\underline{x}''', \underline{x}''', t_1) \chi(\underline{x}''', \underline{x}''', \underline{x}''', t_1) \right\} d\underline{x}'''' \quad (1 - 39) \end{aligned}$$

Having obtained $P_1(\underline{x}''', \underline{x}''', t_1, \tau_2)$ in (1 - 37) we can define the real free path l_M for the direction \underline{x}'''' as

$$l_M = \frac{\int P_1(\underline{x}''', \underline{x}''', t_1, \tau_2) \underline{x}'''' \tau_2 \underline{x}''''^2 d\underline{x}'''' d\underline{x}''''}{\int P_1(\underline{x}''', \underline{x}''', t_1, \tau_2) \underline{x}''''^2 d\underline{x}'''' d\underline{x}''''}$$

For the equilibrium state it becomes the usual

Maxwellian free path l_M

$$l_M = \frac{\bar{\underline{x}''''}}{\mu(\underline{x}'''')}$$

where the bars denote the average with respect to the Maxwellian velocity distribution.

The extension from a single flight to a series of successive flights is immediate. For two steps we define $P_2(\underline{x}''', \underline{x}''', t_1, \tau_2; \underline{x}''', \underline{x}''', t_2, \tau_3) d\underline{x}'''' d\underline{x}'''' dt_1 d\underline{x}'''' dt_2 d\underline{x}'''' d\underline{x}''''$ as the probability of finding at t_1 in $\underline{x}''', d\underline{x}'''$ with any velocity which is deflected into $\underline{x}''', d\underline{x}'''$ in t_1, dt_1 , travels freely for an interval τ_2 , is deflected again into $\underline{x}''', d\underline{x}'''$ in t_2, dt_2 , travels freely for another interval τ_3 and /

and finally collides in $\tau_3, d\tau_3$. Then we can write

$$\begin{aligned}
 & P_2(\xi^0, z^0, t_1, \tau_2; \xi^1, z^1, t_2, \tau_3) d\xi^0 d\xi^1 dt_1 d\xi^2 dt_2 d\tau_3 \\
 &= \left\{ \left(\mu(\xi^0, z^0, t_1) + \frac{\partial}{\partial t_1} + \xi^0 \frac{\partial}{\partial x^0} \right) f_1(\xi^0, z^0, t_1) d\xi^0 d\xi^1 dt_1 \right\} \\
 & \left\{ e^{-\int_0^{\tau_2} \mu(\xi^0, z^0, \xi^1, t_1 + \tau) d\tau} \chi(\xi^0, \xi^1, z^0, t_1) d\xi^2 dt_2 \right\} \\
 & \left\{ e^{-\int_0^{\tau_3} \mu(\xi^0, z^0, \xi^2, t_2 + \tau) d\tau} \mu(\xi^0, z^0, t_3) d\tau_3 \right\}, \quad (1-40)
 \end{aligned}$$

where the first factor gives the probability of finding a molecule at x^0, dx^0 with velocity in $\xi^0, d\xi^0$ starting its free path in t_1, dt_1 , the second factor gives the probability that it will travel freely for τ_2 , be deflected into $\xi^1, d\xi^1$ in t_2, dt_2 and the last factor gives the probability that it will travel again for τ_3 and suffer a collision in $\tau_3, d\tau_3$.

By making use of the properties of χ (1-31), (1-38) it can be shown that

$$\iint P_2(1,2) d\xi^2 d\tau_3 = P_1(1),$$

$$\iint P_2(1,2) d\xi^1 dt_1 = P_1(2),$$

where $P_2(1,2)$ and $P_2(1,2)$ are used to denote $P_1(\xi^1, z^1, t_2, \tau_3)$ and $P_2(\xi^0, z^0, t_1, \tau_2; \xi^1, z^1, t_2, \tau_3)$ respectively.

Similarly the probability function for N successive flights can be written down as

$$\begin{aligned}
 & P_N(\xi^0, z^0, t_1, \tau_{1,2}; \dots; \xi^{N-1}, z^{N-1}, t_N, \tau_{N,N+1}) d\xi^0 d\xi^1 dt_1 \dots d\xi^{N-1} dt_N d\tau_{N,N+1} \\
 &= P_N(1,2 \dots N) d\xi^0 d\xi^1 dt_1 \dots d\xi^{N-1} dt_N d\tau_{N,N+1} \\
 &= \left\{ \left(\mu(\xi^0, z^0, t_1) + \frac{\partial}{\partial t_1} + \xi^0 \frac{\partial}{\partial x^0} \right) f_1(\xi^0, z^0, t_1) d\xi^0 d\xi^1 dt_1 \right\} \\
 & \prod_{i=1}^{N-1} \left\{ e^{-\int_0^{\tau_{i,i+1}} \mu(\xi^i, z^i, \xi^{i+1}, t_i + \tau) d\tau} \chi(\xi^i, \xi^{i+1}, z^i, t_i) d\xi^{i+1} dt_{i+1} \right\} \\
 & \frac{d}{d\tau_{N,N+1}} \left\{ e^{-\int_0^{\tau_{N,N+1}} \mu(\xi^{N-1}, z^{N-1}, \xi^N, t_N + \tau) d\tau} \right\} d\tau_{N,N+1} \quad (1-41)
 \end{aligned}$$

As expected the following relations are automatically satisfied by $P_N(1,2 \dots N)$

$$\iint P_N(1,2 \dots N) d\xi^N d\tau_{N,N+1} = P_{N-1}(1,2 \dots, N-1)$$

$$\iint P_N(1,2 \dots N) d\xi^0 dt_1 = P_{N-1}(2,3 \dots N),$$

or /

or more generally

$$\int \dots \int P_N(1,2,\dots,N) dt_1 d\xi^{(1)} \dots dt_r d\xi^{(r)} d\xi^{(s)} d\tau_{s,s+1} \dots d\xi^{(N)} d\tau_{N,N+1}$$

$$= P_{s-r-1}(r+1, \dots, s-1), \quad (s-r \geq 2)$$

For the equilibrium state P_N reduces to

$$P_N(1,2,\dots,N) d\xi^{(1)} d\xi^{(2)} dt_1 \dots d\xi^{(N)} dt_N d\tau_{N,N+1}$$

$$= \left\{ \mu(\xi^{(1)}) f(\xi^{(1)}) d\xi^{(1)} dt_1 \right\} \prod_{i=1}^{N-1} \left\{ e^{-\mu(\xi^{(i)}) \tau_{i,i+1}} \chi(\xi^{(i)}, \xi^{(i+1)}) d\xi^{(i+1)} dt_{i+1} \right\} \quad (1-42)$$

$$\frac{d}{d\tau_{N,N+1}} \left\{ e^{-\mu(\xi^{(N)}) \tau_{N,N+1}} \right\} d\tau_{N,N+1}$$

I. - 3. Self diffusion in gases

Having found $P_N(1,2,\dots,N)$ in (1-42) for a gas in equilibrium, we can calculate the mean time of flight Δt and mean square displacement $\overline{(\Delta x)^2}$ for any number N of successive flights. To conform with the condition imposed on Δt in I. - 1, we choose a large number of flights so that $\overline{(\Delta x)^2} / \Delta t$ approaches a plateau value.

It can be shown that

$$\Delta t = \left\langle \sum_{i=1}^N \tau_{i,i+1} \right\rangle = N \langle \tau_{12} \rangle = N / \mu^{(1)} \quad (1-43)$$

where

$$\mu^{(1)} = \int \frac{f^{(1)}}{n} \mu^{(1)} d\xi^{(1)}, \quad \mu^{(1)} = \mu(\xi^{(1)}), \quad f^{(1)} = f(\xi^{(1)}) \quad \text{and}$$

n is the number density, the square bracket $\langle \rangle$ is used to denote the average with respect to P_N .

To prove (1-43) we have to calculate $\langle \tau_{i,i+1} \rangle$,

$$\langle \tau_{i,i+1} \rangle = \frac{\int \dots \int P_i(1,2,\dots,i) \tau_{i,i+1} d\xi^{(1)} d\tau_{12} \dots d\xi^{(i)} d\tau_{i,i+1}}{\int \dots \int P_i(1,2,\dots,i) d\xi^{(1)} d\tau_{12} \dots d\xi^{(i)} d\tau_{i,i+1}}$$

$$= \int \dots \int f^{(1)} \frac{\chi^{(1,2)} \dots \chi^{(i-1,i)}}{\mu^{(2)} \dots \mu^{(i)}} d\xi^{(2)} \dots d\xi^{(i)} / (n \mu^{(1)})$$

$$= 1 / \mu^{(1)}$$

using (1-42) and (1-36), and $\chi^{(1,2)} = \chi(\xi^{(1)}, \xi^{(2)})$.

The mean displacement $\left\langle \sum_{i=1}^N \xi^{(i)} \tau_{i,i+1} \right\rangle$ obviously vanishes by /

by symmetry. The mean square displacement $\langle (\sum_{i=1}^N \xi^{(i)} \tau_{i,i+1})^2 \rangle$ will next be shown to be

$$\overline{(\Delta x)^2} = \langle (\sum_{i=1}^N \xi^{(i)} \tau_{i,i+1})^2 \rangle = \frac{2}{n} \left\{ N \int \frac{f(v)}{\mu(v)} \frac{\xi^{(1)2}}{v} d\xi^{(1)} + (N-1) \int \int \frac{f(v)}{n} \frac{\chi(1,2)}{\mu(v)\mu(v)} \xi^{(1)} \xi^{(2)} d\xi^{(1)} d\xi^{(2)} \right. \\ \left. + (N-2) \int \int \int \frac{f(v)}{n} \frac{\chi(1,2)\chi(2,3)}{\mu(v)\mu(v)\mu(v)} \xi^{(1)} \xi^{(2)} \xi^{(3)} d\xi^{(1)} d\xi^{(2)} d\xi^{(3)} + \dots \right\}, \quad (1-44)$$

where the first term inside the bracket represents the main contribution from each individual step, the second term represents the contribution from the correlation between two successive steps, the third term from the correlation between two steps separated by one flight, etc.. Physically it is clear that such correlation decreases rapidly for each step, and the above series is therefore a rapidly convergent one.

To prove (1-44) we write

$$\langle (\sum_{i=1}^N \xi^{(i)} \tau_{i,i+1})^2 \rangle = \sum_{i=1}^N \langle (\xi^{(i)} \tau_{i,i+1})^2 \rangle + 2 \sum_{i=1}^{N-1} \langle \xi^{(i)} \xi^{(i+1)} \tau_{i,i+1} \tau_{i+1,i+2} \rangle \\ + 2 \sum_{i=1}^{N-2} \langle \xi^{(i)} \xi^{(i+2)} \tau_{i,i+1} \tau_{i+1,i+2} \tau_{i+2,i+3} \rangle + \dots \quad (1-45)$$

So using (1-42) and (1-36) we have

$$\langle (\xi^{(i)} \tau_{i,i+1})^2 \rangle = \frac{\int \dots \int P_i(1,2,\dots,i) (\xi^{(i)} \tau_{i,i+1})^2 d\xi^{(1)} d\tau_{1,2} \dots d\xi^{(i)} d\tau_{i,i+1}}{\int \dots \int P_i(1,2,\dots,i) d\xi^{(1)} d\tau_{1,2} \dots d\xi^{(i)} d\tau_{i,i+1}} \\ = \frac{2}{n\mu(v)} \int \frac{f(v)}{v} \frac{\xi^{(1)2}}{\mu(v)} d\xi^{(1)} \\ \langle \xi^{(i)} \xi^{(i+k)} \tau_{i,i+1} \tau_{i+1,i+2} \dots \tau_{i+k,i+k+1} \rangle = \frac{\int \dots \int P_{i+k}(1,2,\dots,i+k) \xi^{(i)} \xi^{(i+k)} \tau_{i,i+1} \tau_{i+1,i+2} \dots \tau_{i+k,i+k+1} d\xi^{(1)} d\tau_{1,2} \dots d\xi^{(i+k)} d\tau_{i+k,i+k+1}}{\int \dots \int P_{i+k}(1,2,\dots,i+k) d\xi^{(1)} d\tau_{1,2} \dots d\xi^{(i+k)} d\tau_{i+k,i+k+1}} \\ = \frac{1}{n\mu(v)} \int \dots \int f(v) \frac{\chi(i,i+1) \dots \chi(i+k-1, i+k)}{\mu(v) \dots \mu(i+k)} \xi^{(i)} \xi^{(i+k)} d\xi^{(1)} \dots d\xi^{(i+k)} \\ = \frac{1}{n\mu(v)} \int \dots \int \frac{f(v)}{v} \frac{\chi(1,2) \dots \chi(k, k+1)}{\mu(v) \dots \mu(k+1)} \xi^{(1)} \xi^{(k+1)} d\xi^{(1)} \dots d\xi^{(k+1)}$$

The above expression will give for $k=1, 2, \dots$ the second, third, ... term in (1-45). Equation (1-44) follows therefore from (1-45). For large N the ratio of the mean square displacement to the mean time of travel is therefore

$$\overline{(\Delta x)^2} / \Delta t = 2 \left\{ \int \frac{f(v)}{n} \frac{\xi^{(1)2}}{\mu(v)} d\xi^{(1)} + \int \int \frac{f(v)}{n} \frac{\chi(1,2)}{\mu(v)\mu(v)} \xi^{(1)} \xi^{(2)} d\xi^{(1)} d\xi^{(2)} \right. \\ \left. + \int \int \int \frac{f(v)}{n} \frac{\chi(1,2)\chi(2,3)}{\mu(v)\mu(v)\mu(v)} \xi^{(1)} \xi^{(2)} \xi^{(3)} d\xi^{(1)} d\xi^{(2)} d\xi^{(3)} + \dots \right\}. \quad (1-46)$$

Hence /

Hence the coeff. of self diffusion is

$$D_s = \frac{1}{6} \frac{d\langle x^2 \rangle}{dt} = \frac{1}{3} \left\{ \int \frac{f(v)}{n} \frac{\xi^{(v)2}}{\mu(v)} d\xi^{(v)} + \left(\left(\frac{f(v)}{n} \frac{x(12)}{\mu(v)\mu(2)} \xi^{(v)} \xi^{(2)} d\xi^{(v)} d\xi^{(2)} \right. \right. \right. \\ \left. \left. \left. + \left(\left(\frac{f(v)}{n} \frac{x(12)x(23)}{\mu(v)\mu(2)\mu(3)} \xi^{(v)} \xi^{(2)} \xi^{(3)} d\xi^{(v)} d\xi^{(2)} d\xi^{(3)} + \dots \right) \right) \right\} \quad (1-47)$$

The above calculation refers to pure self-diffusion in an equilibrium gas consisting of only one kind of molecules. The extension to an equilibrium gas mixture is immediate. Consider a binary gas mixture in equilibrium. Let n_1 and n_2 be the number densities of the two kinds of molecules, $f_1(v) (= f_1(\xi_1^{(v)}))$ and $f_2(v) (= f_2(\xi_2^{(v)}))$ be the densities in their molecular phase spaces, $\mu_1(v) (= \mu_1(\xi_1^{(v)}))$ and $\mu_2(v) (= \mu_2(\xi_2^{(v)}))$ be the total collision frequencies of a molecule of the first kind with velocity $\xi_1^{(v)}$ and of a molecule of the second kind with velocity $\xi_2^{(v)}$ respectively. We shall have

$$\mu_1(v) = \mu_{11}(v) + \mu_{12}(v) \quad (1-48)$$

where $\mu_{11}(v)$ represents collision between molecules of the first kind and $\mu_{12}(v)$ between molecules of the first kind and second kind.

Using the same type of subscript, we have for the deflection probability χ

$$\chi_1(v, v+1) = \chi_{11}(v, v+1) + \chi_{12}(v, v+1) \quad (1-49)$$

We can then write for the coeff. of self-diffusion of the first kind of molecules among the rest D_{1s} as

$$D_{1s} = \frac{1}{3} \left\{ \int \frac{f_1(v)}{n_1} \frac{\xi_1^{(v)2}}{\mu_1(v)} d\xi_1^{(v)} + \left(\left(\frac{f_1(v)}{n_1} \frac{x_1(12)}{\mu_1(v)\mu_1(2)} \xi_1^{(v)} \xi_1^{(2)} d\xi_1^{(v)} d\xi_1^{(2)} \right. \right. \right. \\ \left. \left. \left. + \left(\left(\frac{f_1(v)}{n_1} \frac{x_1(12)x_1(23)}{\mu_1(v)\mu_1(2)\mu_1(3)} \xi_1^{(v)} \xi_1^{(2)} \xi_1^{(3)} d\xi_1^{(v)} d\xi_1^{(2)} d\xi_1^{(3)} + \dots \right) \right) \right\} \quad (1-50)$$

In /

In order to see the meaning of the various terms in (1 - 47) more clearly, we shall rewrite it as follows. Let $\sum^{(i)} \tau_{c,i+1} = \underline{e}^{(i)}$, equation (1 - 45) becomes

$$\begin{aligned} \overline{(\Delta x)^2} &= \left\langle \left(\sum_{i=1}^N \underline{e}^{(i)} \right)^2 \right\rangle = \sum_{i=1}^N \langle \underline{e}^{(i)^2} \rangle + \sum_{i=1}^{N-1} \langle 2 \underline{e}^{(i)} \cdot \underline{e}^{(i+1)} \rangle + \sum_{i=1}^{N-2} \langle 2 \underline{e}^{(i)} \cdot \underline{e}^{(i+2)} \rangle + \dots \\ &= N \langle \underline{e}^{(1)^2} \rangle + (N-1) \langle 2 \underline{e}^{(1)} \cdot \underline{e}^{(2)} \rangle + (N-2) \langle 2 \underline{e}^{(1)} \cdot \underline{e}^{(3)} \rangle + \dots \end{aligned}$$

using the results of calculation after (1 - 45).

Hence for large N we have

$$D_s = \frac{1}{6} \frac{\overline{(\Delta x)^2}}{\Delta t} = \frac{\langle \underline{e}^{(1)^2} \rangle}{6 \langle \tau_{12} \rangle} \left\{ 1 + \frac{\langle 2 \underline{e}^{(1)} \cdot \underline{e}^{(2)} \rangle}{\langle \underline{e}^{(1)^2} \rangle} + \frac{\langle 2 \underline{e}^{(1)} \cdot \underline{e}^{(3)} \rangle}{\langle \underline{e}^{(1)^2} \rangle} + \dots \right\} \quad (1 - 51)$$

Equation (1 - 51) shows clearly that the various terms of the series merely take into account the effect of the persistence of motion on the rate of diffusion in a rigorous manner.

To see that the value of D_s is not appreciably changed by choosing different ranges of interaction for any general force law between molecules when the chosen range is not too short, we rewrite (1 - 51) in the form

$$D_s = \frac{1}{6} \frac{\langle \underline{e}^{(1)^2} \rangle^{\frac{1}{2}}}{\langle \tau_{12} \rangle} \left\{ \langle \underline{e}^{(1)^2} \rangle^{\frac{1}{2}} + \frac{\langle 2 \underline{e}^{(1)} \cdot \underline{e}^{(2)} \rangle}{\langle \underline{e}^{(1)^2} \rangle^{\frac{1}{2}}} + \frac{\langle 2 \underline{e}^{(1)} \cdot \underline{e}^{(3)} \rangle}{\langle \underline{e}^{(1)^2} \rangle^{\frac{1}{2}}} + \dots \right\} \quad (1 - 52)$$

Increasing the range of interaction will tend to reduce the length of free path and mean time of free flight but leave their ratio, the average speed almost unchanged. This is approximately the factor $\frac{\langle \underline{e}^{(1)^2} \rangle^{\frac{1}{2}}}{\langle \tau_{12} \rangle}$ in (1 - 52). As to the series inside the bracket in (1 - 52) its sum is almost constant for sufficient long range of interaction, though the rate of convergence /

convergence does depend on this choice of range of interaction. The exact nature of convergence can not be discussed until μ and α have been calculated for some particular force law, but qualitatively one can see that as we increase the range of interaction, the first term tends to decrease, but then a small angular deflection between successive flights becomes more probable, hence the second term increases, etc.. A convenient limit for the range of interaction can be set up as follows: it must be larger than 2 to 3 times the molecular diameter found for example from measurements of the second virial coefficient in gases and it must not extend up to a distance comparable with the average distance between the molecules corresponding to the density of the gas considered. Formula (1 - 47) is valid so long as those two limits do not come close to each other which is always so in gases. Choosing a high upper limit to the range of interaction will give very slightly more accurate results, but this is entirely offset by the slowness of convergence of the series.

I. - 4. Ordinary and thermal diffusion in gas mixtures.

It has been found possible in I. - 1 to express the mutual diffusion velocity in non-uniform fluids in terms of the first and second moments of certain transition probabilities. It has also been shown in I. - 2 that in non-uniform gases one can follow the future course of /

of a chosen molecule provided the velocity distribution of the medium is known. Our statistics of motion is seen to be based on the knowledge of the velocity distribution throughout the medium. The mutual diffusion velocity according to (1 - 25) with β' 's and α' 's calculated from P_N (1 - 41) should be, and as shown in Appendix II is indeed equal to that calculated directly from the local velocity distribution i.e.

$$\alpha'_1 - \alpha'_2 = \frac{1}{n_1} \int f'_1(\xi_1) \xi_1 d\xi_1 - \frac{1}{n_2} \int f'_2(\xi_2) \xi_2 d\xi_2 \quad (1 - 53)$$

where $f'_1(\xi_1)$ and $f'_2(\xi_2)$ are the deviations from the Maxwellian velocity distribution due to the presence of the gradients of densities, temperature, etc., of molecules of the first and second kind respectively.

Nevertheless the present calculation shows the intrinsically different natures of self-diffusion on the one hand and mutual diffusion on the other, the former is simply a kind of Brownian motion, while the latter is entirely caused by the non-uniformity of the physical parameters. Though in non-uniform gas mixtures, self-diffusion still goes on, it has no effect on the mutual diffusion velocity which can be pictured as set up by forces arising from the local gradients of density, temperature etc. In order to obtain an exact value of mutual diffusion velocity it is indispensable to find the local deviation from Maxwellian velocity distribution consistent with the local gradients of the physical parameters.

When /

When the β 's are neglected in (1 - 25), the remaining part is seen to correspond to the free path theory. Though the present theory which takes account of the persistence of successive flights rigorously is much more refined than the old free path theory, they are both based on the same approximate assumption that molecules which collide during each element of time have a distribution after collision of the Maxwellian type. Mutual diffusion though entirely different from self-diffusion in nature can be approximately expressed in terms of self-diffusion. Equation (1-25) becomes when the β 's are neglected

$$u_1' - u_2' = -\frac{1}{3} \left\{ \frac{\partial n_1}{\partial x} \frac{\partial}{\partial n_1} + \frac{\partial n_2}{\partial x} \frac{\partial}{\partial n_2} + \frac{\partial T}{\partial x} \frac{\partial}{\partial T} \right\} (\alpha_1 - \alpha_2) + \left\{ \frac{\alpha_1}{n_1} \frac{\partial n_1}{\partial x} - \frac{\alpha_2}{n_2} \frac{\partial n_2}{\partial x} \right\} \quad (1 - 54)$$

With the aid of this equation, both ordinary and thermal diffusion receive simple explanations. The α_1 and α_2 appearing in (1 - 54) measure the tendency to diffuse for the two kinds of molecules. Mutual diffusion can be seen from (1 - 54) to arise in two ways. First, the number of molecules diffusing in one direction is not equal to that in the opposite direction, and second, the tendency for diffusion varies in different ways with n_1, n_2 and T for the two kinds of molecules. Equations (1 - 29) (1 - 30) become, when the β 's are neglected

$$\left. \begin{aligned} D_0 &= \frac{n_1 n_2}{3n} \left(\frac{\partial}{\partial n_1} - \frac{\partial}{\partial n_2} \right) (\alpha_1 - \alpha_2) + \left(\frac{\alpha_1}{n_1} + \frac{\alpha_2}{n_2} \right) \\ D_T &= \frac{n_1 n_2}{3n^2} \left\{ 1 + n_1 \frac{\partial}{\partial n_1} + n_2 \frac{\partial}{\partial n_2} - T \frac{\partial}{\partial T} \right\} (\alpha_1 - \alpha_2) \end{aligned} \right\} \quad (1 - 55)$$

Thus D_0 consists of contributions of both of the two /

two types described above under constant temperature and pressure, while D_T arises only from the second type under constant pressure. It may be mentioned here that the old free path theory does not give rise to thermal diffusion because there only the first effect is taken into account, Meyer's diffusion coefficient corresponds to

$$D_0 = \frac{n_1 n_2}{3n} \left(\frac{\alpha_1}{n_1} + \frac{\alpha_2}{n_2} \right) \quad (1 - 56)$$

Fürth's explanation of thermal diffusion considering only single free path corresponds to the second equation in (1 - 55).

It should be mentioned that for gas mixtures in which one component is comparatively rare, equation (1 - 55) would give good results. This suggests that a corresponding approximate theory exists in the liquid region which can be obtained without any knowledge of the deviation from Maxwellian velocity distribution.

I. - 5. Approximate theory of diffusion in liquids.

The recent development of the liquid state based on the analogue between the liquid and solid state reveals that the heat motion of molecules in liquids at temperature not far from the crystallization point may be regarded as of a vibration-diffusion type with a much more pronounced diffusion component than in the case of solids. Each molecule after performing a more or less large number of oscillations about the same /

same equilibrium position jumps to a new equilibrium position at a distance δ of the same order of magnitude as the distance between the neighbouring molecules. The average time τ of staying in the same equilibrium position is usually large compared to the period of oscillation. The velocity of the molecule at the end of τ can hardly be correlated with that at the beginning of τ . We can therefore conveniently identify this mean life τ with the time interval Δt used in I. - 1.

Each elementary shift of the equilibrium position can be analyzed into two stages, first the evaporation of the atom from its initial equilibrium position to an intermediate one, connected with a certain increase of its potential (better free) energy w , and secondly the condensation from this position into a new equilibrium position where it is surrounded, at least partially, by new neighbours among which the resulting extra kinetic energy of the given molecule is distributed so that it can no longer get back into its original position. Working with this picture of heat motion, the problem of self-diffusion has been qualitatively solved as summarized in Frenkel's Kinetic Theory of Liquids. We shall quote the results and apply them to the case of mutual diffusion.

The mean life τ can be expressed as

$$\tau = \tau_0 e^{w/kT} \quad (1 - 57)$$

where /

where τ_0 being of the order of 10^{-13} sec., can be identified with the period of free oscillation. The coefficient of self-diffusion D_s is then

$$D_s = \frac{1}{6} \frac{\delta^2}{\tau} = \frac{1}{6} \frac{\delta^2}{\tau_0} e^{-\frac{w}{kT}} \quad (1 - 58)$$

The form of this equation has been verified. By considering the change of free energy in the formation of holes and interstitial atoms, it is shown that

$$w = w_0 + b v_0 \left(\frac{1}{\kappa} p - a T \right)$$

where w_0 is the activation energy, κ the bulk modulus, a the coefficient of thermal expansion, v_0 the average volume occupied by each molecule for $p=0$, b a constant. For small pressure p the term involving p can be neglected. Equation (1 - 58) then becomes

$$D_s = \frac{1}{6} \frac{\delta^2}{\tau_0} e^{\gamma} e^{-\frac{w_0}{kT}} \quad (1 - 59)$$

where $\gamma = \frac{v_0 a b}{\kappa}$

To apply the results of self-diffusion in liquids we have to consider self-diffusion in a liquid mixture. In dilute solution the activation energy $w_0^{(1)}$ of molecules of the solute is almost equal to that of molecules of the solvent as found experimentally. In a mixture where the number densities of the components are comparable, the activation energy of each component must be a function of n_1, n_2 and T . This function has not been determined elsewhere nor shall we take it up here. All that can be said is that from the data of self-diffusion in an equilibrium mixture, one can estimate /

estimate the Coefficient of mutual diffusion of the same mixture. In particular thermal diffusion in dilute solution can be roughly estimated as follows

$$\left. \begin{aligned} \alpha_1 &= \frac{1}{2} \frac{\delta_1^2}{\tau_1} = \frac{1}{2} \frac{\delta_1^2}{\tau_0} e^{\gamma_1} e^{-\bar{w}_{20}/kT} = A_1 e^{-\bar{w}_{20}/kT} \\ \alpha_2 &= \frac{1}{2} \frac{\delta_2^2}{\tau_2} = \frac{1}{2} \frac{\delta_2^2}{\tau_0} e^{\gamma_2} e^{-\bar{w}_{20}/kT} = A_2 e^{-\bar{w}_{20}/kT} \end{aligned} \right\} (1-60)$$

The meaning of the quantities appearing in this equation is the same as in (1-59) with suffixes 1 and 2 to denote quantities of the solute and solvent molecules respectively.

From (1-28) we have, neglecting the β 's

$$D_T = \frac{n_1 n_2}{3n^2} \left\{ \frac{T}{\Delta p} \frac{\partial P}{\partial T} (1 + \beta) - T \frac{\partial}{\partial T} \right\} (\alpha_1 - \alpha_2) \quad (1-61)$$

We shall take A_1 , A_2 and \bar{w}_{20} as almost independent of temperature as found experimentally and $\beta(\alpha_1 - \alpha_2) \pm \frac{2}{3}(\alpha_1 - \alpha_2)$ as $\frac{n_1}{n} \rightarrow 0$. Hence

$$D_T \pm \frac{n_1}{3n} \left\{ \frac{T}{\Delta p} \frac{\partial P}{\partial T} - \frac{\bar{w}_{20}}{kT} \right\} (A_1 - A_2) e^{-\bar{w}_{20}/kT} \quad (1-62)$$

D_T is seen to be proportional to the difference of self-diffusion coefficient of the solute and solvent. A better estimation of mutual diffusion in liquids could be obtained if more about the self-diffusion in equilibrium were known.

Part II. Kinetic Theory of Liquid Mixtures.

II - 1. Notation and definitions.

Consider an assembly of two different kinds of molecules of total number N occupying a total volume V . Let N_1, N_2 be the numbers of molecules of the first and second kind respectively and m_1, m_2 their molecular masses. Of these $N = N_1 + N_2$ molecules, one can choose any k_1 of the first kind and any k_2 of the second kind for special consideration.

Let the velocity and acceleration of a molecule of the first kind at the position $x_1^{(i)}$ be denoted by $\xi_1^{(i)}$ and $\eta_1^{(i)}$ respectively. To abbreviate, we shall use x_1, ξ_1 and η_1 to denote all the position velocity and acceleration vectors of the k_1 molecules and x_2, ξ_2 and η_2 those of the k_2 molecules. The volume elements $\prod_{i=1}^{k_1} \prod_{j=1}^{k_2} dx_1^{(i)} dx_2^{(j)}$ will be denoted by $d\alpha_{k_1 k_2}$ and $\prod_{i=1}^{k_1} \prod_{j=1}^{k_2} d\xi_1^{(i)} d\xi_2^{(j)}$ by $d\xi_{k_1 k_2}$.

Next a set of multiple distribution functions symmetrized with respect to molecules of the same kind will be defined. The distribution functions

$n_{k_1 k_2} = n_{k_1 k_2}(t, x_1, x_2)$ is defined such that $n_{k_1 k_2} d\alpha_{k_1 k_2}$ is the probability of finding the volume elements

$dx_1^{(1)} \dots dx_1^{(k_1)}$ occupied by any k_1 molecules of the first kind and the volume elements $dx_2^{(1)} \dots dx_2^{(k_2)}$ by any

k_2 molecules of the second kind simultaneously at time t . Similarly $f_{k_1 k_2} = f_{k_1 k_2}(t, x_1, x_2, \xi_1, \xi_2)$ is defined such that $f_{k_1 k_2} d\alpha_{k_1 k_2} d\xi_{k_1 k_2}$ is the probability of finding the /

the volume elements $x_i^{(i)}, dx_i^{(i)}$ ($i=1,2,\dots,l_1$) occupied by any molecules of the first kind with velocities in $\xi_i^{(i)}, d\xi_i^{(i)}$ ($i=1,2,\dots,h_1$), and $x_2^{(j)}, dx_2^{(j)}$ ($j=1,2,\dots,h_2$) occupied by any molecules of the second kind with velocities in $\xi_2^{(j)}, d\xi_2^{(j)}$ ($j=1,2,\dots,h_2$) simultaneously at time t . One can proceed to define acceleration distribution functions $g_{h_1,h_2} = g_{h_1,h_2}(t, x_1, x_2, \xi_1, \xi_2, \eta_1, \eta_2)$ and distribution functions of still higher order in a precisely similar way.

It follows from the above definitions that

$$\left. \begin{aligned} \int f_{h_1,h_2} d\xi_{h_1,h_2} &= n_{h_1,h_2} \\ \int g_{h_1,h_2} d\eta_{h_1,h_2} &= f_{h_1,h_2} \end{aligned} \right\} (2-1)$$

Since the quotient $\left(\frac{n_{h_1+1,h_2} d\xi_1^{(h_1+1)}}{n_{h_1,h_2}}\right)$ represents the probability of finding a molecule of the first kind at $x_1^{(h_1+1)}, dx_1^{(h_1+1)}$ knowing that dx_{h_1,h_2} is occupied by l_1 molecules of the first kind and l_2 of the second kind, one has

$$\int n_{h_1+1,h_2} d\xi_1^{(h_1+1)} = (N_1 - l_1) n_{h_1,h_2} \quad (2-2)$$

Similarly

$$\int f_{h_1+1,h_2} d\xi_1^{(h_1+1)} d\xi_1^{(h_1)} = (N_1 - l_1) f_{h_1,h_2} \quad (2-3)$$

By repeating the above process it can be shown that

$$\left. \begin{aligned} \int n_{h_1,h_2} d\xi_{h_1,h_2} &= \frac{N_1! N_2!}{(N_1 - h_1)! (N_2 - h_2)!} \\ \iint f_{h_1,h_2} d\xi_{h_1,h_2} d\xi_{h_1,h_2} &= \frac{N_1! N_2!}{(N_1 - h_1)! (N_2 - h_2)!} \end{aligned} \right\} (2-4)$$

When one of h_1, h_2 vanishes and the other equals to one, we shall use single index notation i.e. n_{10}, f_{10} will /

will be replaced by n_1, f_1 respectively. In accordance with the usual notation n_1, n_2 are the number densities and f_1, f_2 the velocity distribution functions of the two kinds of molecules normalized with respect to their number densities. The total number density n and the total mass density ρ are

$$n = n_1 + n_2 \quad \text{and} \quad \rho = \rho_1 + \rho_2 \quad (2-5)$$

where

$$\rho_1 = m_1 n_1, \quad \rho_2 = m_2 n_2.$$

II - 2. The equation of continuity and the equation of motion.

The probability that the volume element $x_1^{(i)} dx_1^{(i)}$ is occupied by any molecule of the first kind at time t is equal to the integrated sum over all velocities of the probability of the same molecule having velocity in $\xi_1^{(i)} d\xi_1^{(i)}$ and position in $(x_1^{(i)} - \xi_1^{(i)} \delta t), d(x_1^{(i)} - \xi_1^{(i)} \delta t)$ at time $(t - \delta t)$. The same consideration applies also to each of the others in the set h_1, h_2 . Thus we have

$$\int f_{h_1, h_2}(t - \delta t, x_1 - \xi_1 \delta t, x_2 - \xi_2 \delta t, \xi_1, \xi_2) d\xi_{h_1, h_2} = n_{h_1, h_2}(t, x_1, x_2).$$

Expanding in powers of δt and using (2-1) we

obtain

$$\int \left\{ \frac{\partial}{\partial t} f_{h_1, h_2} + \left(\sum_{i=1}^{h_1} \xi_1^{(i)} \frac{\partial}{\partial x_1^{(i)}} + \sum_{j=1}^{h_2} \xi_2^{(j)} \frac{\partial}{\partial x_2^{(j)}} \right) f_{h_1, h_2} \right\} d\xi_{h_1, h_2} = 0$$

or

$$\frac{\partial}{\partial t} n_{h_1, h_2} + \sum_{i=1}^{h_1} \frac{\partial}{\partial x_1^{(i)}} (n_{h_1, h_2} u_{h_1, h_2}^{(i)}) + \sum_{j=1}^{h_2} \frac{\partial}{\partial x_2^{(j)}} (n_{h_1, h_2} u_{h_1, h_2}^{(j)}) = 0 \quad (2-6)$$

where /

where

$$\left. \begin{aligned} \bar{u}_{h_1, h_2}^{(i)} &= \frac{1}{n_{h_1, h_2}} \int f_{h_1, h_2} \xi_1^{(i)} d\xi_{h_1, h_2} \\ \bar{u}_{h_1, h_2}^{(j)} &= \frac{1}{n_{h_1, h_2}} \int f_{h_1, h_2} \xi_2^{(j)} d\xi_{h_1, h_2} \end{aligned} \right\} (2-7)$$

$\bar{u}_{h_1, h_2}^{(i)}$ is the average velocity of a molecule of the first kind at $\underline{x}_1^{(i)}, d\underline{x}_1^{(i)}$ in the set h_1, h_2 whose positions are specified. By introducing the convective time derivative $\frac{d}{dt}$ defined by

$$\frac{d}{dt} = \frac{\partial}{\partial t} + \sum_{i=1}^{h_1} \bar{u}_{h_1, h_2}^{(i)} \cdot \frac{\partial}{\partial \underline{x}_1^{(i)}} + \sum_{j=1}^{h_2} \bar{u}_{h_1, h_2}^{(j)} \cdot \frac{\partial}{\partial \underline{x}_2^{(j)}} \quad (2-8)$$

equation (2-6) can be rewritten in the form

$$\frac{d}{dt} n_{h_1, h_2} + n_{h_1, h_2} \left(\sum_{i=1}^{h_1} \frac{\partial}{\partial \underline{x}_1^{(i)}} \cdot \bar{u}_{h_1, h_2}^{(i)} + \sum_{j=1}^{h_2} \frac{\partial}{\partial \underline{x}_2^{(j)}} \cdot \bar{u}_{h_1, h_2}^{(j)} \right) = 0 \quad (2-9)$$

In a similar way one can derive

$$\begin{aligned} \frac{\partial}{\partial t} f_{h_1, h_2} + \left(\sum_{i=1}^{h_1} \xi_1^{(i)} \cdot \frac{\partial}{\partial \underline{x}_1^{(i)}} + \sum_{j=1}^{h_2} \xi_2^{(j)} \cdot \frac{\partial}{\partial \underline{x}_2^{(j)}} \right) f_{h_1, h_2} \\ + \sum_{i=1}^{h_1} \frac{\partial}{\partial \underline{x}_1^{(i)}} \cdot (f_{h_1, h_2} \eta_{h_1, h_2}^{(i)}) + \sum_{j=1}^{h_2} \frac{\partial}{\partial \underline{x}_2^{(j)}} \cdot (f_{h_1, h_2} \eta_{h_1, h_2}^{(j)}) = 0 \end{aligned} \quad (2-10)$$

where

$$\eta_{h_1, h_2}^{(i)} = \frac{1}{f_{h_1, h_2}} \int g_{h_1, h_2} \eta_i^{(i)} d\eta_{h_1, h_2} \quad (2-11)$$

with a similar expression for $\eta_{h_1, h_2}^{(j)}$. In the following we shall reserve i, k for indicating quantities pertaining to the first kind of molecules and j, ℓ for the second kind of molecules.

$\eta_{h_1, h_2}^{(i)}$ is the average acceleration of a molecule of the first kind at $\underline{x}_1^{(i)}, d\underline{x}_1^{(i)}$ in the set h_1, h_2 whose positions and velocities are specified. This acceleration can also be given a simple explicit expression /

expression if we assume that the intermolecular forces are central and depend only on the distances between the mass centres of the molecules. Let $\phi_1^{(kl)} = \phi_1(|x_1^{(k)} - x_1^{(l)}|)$ be the mutual potential energy of two molecules of the first kind, $\phi_2^{(kl)} = \phi_2(|x_1^{(k)} - x_2^{(l)}|)$ that of two molecules of the second kind and $\psi^{(ij)} = \psi(|x_1^{(i)} - x_2^{(j)}|)$ that of two molecules of different kinds. We may also consider the whole assembly to be in an external force field conservative or otherwise and denote by $\underline{F}_1^{(i)} = \underline{F}_1^{(i)}(x_1^{(i)}, t)$ the force exerted on a molecule of the first kind at $x_1^{(i)}$ at time t . Let $\mathcal{W}^{(N)}$ be the total interval potential energy, then

$$\mathcal{W}^{(N)} = \Phi_1(N_1) + \Phi_2(N_2) + \Psi(N_1, N_2) \quad (2-12)$$

where

$$\begin{aligned} \Phi_1(N_1) &= \frac{1}{2} \sum_{i, l=1}^{N_1} \phi_1^{(il)} & \Phi_2(N_2) &= \frac{1}{2} \sum_{j, l=1}^{N_2} \phi_2^{(jl)} \\ \Psi(N_1, N_2) &= \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \psi^{(ij)} \end{aligned} \quad (2-13)$$

If we know the position of all the N molecules at t , then the acceleration of a given molecule of the first kind at $x_1^{(i)}$ is

$$\eta_1^{(i)} = -\frac{1}{m_1} \left(\frac{\partial \mathcal{W}^{(N)}}{\partial x_1^{(i)}} - \underline{F}_1^{(i)} \right) \quad (2-14)$$

If we know only the positions of the set h_1, h_2 at time t , the acceleration of a molecule of the first kind at $x_1^{(i)}$ belonging to the set h_1, h_2 consists of two parts; the first part is the sum of the intermolecular forces due to the rest of the set h_1, h_2 and the external force $\underline{F}_1^{(i)}$ and the second part is the average /

average force due to the set $(N_1 - h_1)$, $(N_2 - h_2)$ whose positions are unknown. Hence

$$\eta_{h_1 h_2}^{(i)} = -\frac{1}{m_1} \left\{ \frac{\partial W(h)}{\partial x_1^{(i)}} - F_1^{(i)} \right\} - \frac{1}{m_1} \left\{ \iint \frac{f_{h_1 h_2}}{f_{h_1 h_2}} \frac{\partial \phi_1^{(i, h_1+1)}}{\partial x_1^{(i)}} d\underline{x}_1^{(h_1+1)} d\underline{z}_1^{(h_1+1)} \right. \\ \left. + \iint \frac{f_{h_1 h_2+1}}{f_{h_1 h_2}} \frac{\partial \psi^{(i, h_2+1)}}{\partial x_1^{(i)}} d\underline{x}_2^{(h_2+1)} d\underline{z}_2^{(h_2+1)} \right\} \quad (2-15)$$

where

$$\begin{aligned} W(h) &= \Phi_1(h_1) + \Phi_2(h_2) + \Psi(h_1, h_2), \quad h = h_1 + h_2, \\ \Phi_1(h_1) &= \frac{1}{2} \sum_{i, k=1}^{h_1} \phi_1^{(i, k)}, \quad \Phi_2(h_2) = \frac{1}{2} \sum_{j, k=1}^{h_2} \phi_2^{(j, k)}, \\ \Psi(h_1, h_2) &= \sum_{i=1}^{h_1} \sum_{j=1}^{h_2} \psi^{(i, j)} \end{aligned} \quad (2-16)$$

The meaning of the integrals in the second bracket in (2-15) is clear, for instance, the integrand of the first integral means the probability that the molecule at $\underline{x}_1^{(i)}$ will suffer a force $-\frac{\partial \phi_1^{(i, h_1+1)}}{\partial x_1^{(i)}}$ due to a molecule at $\underline{x}_1^{(h_1+1)}$, $d\underline{x}_1^{(h_1+1)}$ with velocity in $\underline{z}_1^{(h_1+1)}$, $d\underline{z}_1^{(h_1+1)}$ knowing that the volume elements $d\underline{x}_{h_1 h_2}$ are occupied by a set h_1, h_2 with velocity in $d\underline{z}_{h_1 h_2}$. Similar expression for $\eta_{h_1 h_2}^{(i)}$ can be written down.

Substituting (2-15) in (2-10) we obtain the equation of motion

$$\left\{ \frac{\partial}{\partial t} + \sum_i \underline{z}_1^{(i)} \cdot \frac{\partial}{\partial \underline{x}_1^{(i)}} + \sum_j \underline{z}_2^{(j)} \cdot \frac{\partial}{\partial \underline{x}_2^{(j)}} \right\} f_{h_1 h_2} = \frac{1}{m_1} \sum_i \left(\frac{\partial W(h)}{\partial x_1^{(i)}} - F_1^{(i)} \right) \frac{\partial f_{h_1 h_2}}{\partial \underline{x}_1^{(i)}} + \frac{1}{m_2} \sum_j \left(\frac{\partial W(h)}{\partial x_2^{(j)}} - F_2^{(j)} \right) \frac{\partial f_{h_1 h_2}}{\partial \underline{x}_2^{(j)}} \\ + \iint \left(\frac{1}{m_1} \sum_i \frac{\partial \phi_1^{(i, h_1+1)}}{\partial x_1^{(i)}} \cdot \frac{\partial}{\partial \underline{z}_1^{(i)}} + \frac{1}{m_2} \sum_j \frac{\partial \psi^{(j, h_2+1)}}{\partial x_2^{(j)}} \cdot \frac{\partial}{\partial \underline{z}_2^{(j)}} \right) f_{h_1 h_2} d\underline{x}_1^{(h_1+1)} d\underline{z}_1^{(h_1+1)} \\ + \iint \left(\frac{1}{m_2} \sum_j \frac{\partial \phi_2^{(j, h_2+1)}}{\partial x_2^{(j)}} \cdot \frac{\partial}{\partial \underline{z}_2^{(j)}} + \frac{1}{m_1} \sum_i \frac{\partial \psi^{(i, h_1+1)}}{\partial x_1^{(i)}} \cdot \frac{\partial}{\partial \underline{z}_1^{(i)}} \right) f_{h_1 h_2} d\underline{x}_2^{(h_2+1)} d\underline{z}_2^{(h_2+1)}. \quad (2-17)$$

II - 3. The equations of conservation of momentum and energy.

Let $\varphi_i(t, \underline{x}_1^{(i)}, \underline{z}_1^{(i)}) = \varphi_i^{(i)}$ be any molecular property pertaining to a molecule of the first kind at $\underline{x}_1^{(i)}$ with velocity $\underline{z}_1^{(i)}$. $\varphi_i^{(i)}$ may be a scalar, a vector or a tensor. Multiplying (2-17) by $\varphi_i^{(i)} d\underline{x}_{h_1 h_2}$ and integrating over /

over all the velocities, we shall show that for $\varphi_1^{(i)} = 1$, $\left(\frac{\xi_1^{(i)}}{m_1}\right)$ and $\frac{1}{2} (\xi_1^{(i)})^2$ the equation of continuity, of conservation of momentum and energy will follow.

For $\varphi_1^{(i)} = 1$, we obtain exactly (2 - 6) after integration. For $\varphi_1^{(i)} = \xi_1^{(i)}$ we obtain

$$\frac{\partial}{\partial t} (n_{h_1 h_2} u_{h_1 h_2}^{(i)}) + \sum_{k=1}^{h_1} \frac{\partial}{\partial \xi_1^{(k)}} \left(f_{h_1 h_2} \xi_1^{(k)} \xi_1^{(i)} d\xi_{h_1 h_2} \right) + \sum_{\ell=1}^{h_2} \frac{\partial}{\partial \xi_2^{(\ell)}} \left(f_{h_1 h_2} \xi_2^{(\ell)} \xi_1^{(i)} d\xi_{h_1 h_2} \right) = n_{h_1 h_2} \gamma_{h_1 h_2}^{(i)} \quad (2 - 18)$$

where

$$\gamma_{h_1 h_2}^{(i)} = -\frac{1}{m_1} \left(\frac{\partial W(h)}{\partial \xi_1^{(i)}} - F_1^{(i)} \right) - \frac{1}{m_1} \left\{ \int \frac{n_{h_1 h_2} h_2}{n_{h_1 h_2}} \frac{\partial \phi^{(i, h_1+1)}}{\partial \xi_1^{(i)}} d\xi_{h_1 h_2}^{(h_1+1)} + \int \frac{n_{h_1 h_2} h_1}{n_{h_1 h_2}} \frac{\partial \psi^{(i, h_2+1)}}{\partial \xi_2^{(i)}} d\xi_{h_1 h_2}^{(h_2+1)} \right\} \quad (2 - 19)$$

The meaning of $\gamma_{h_1 h_2}^{(i)}$ is similar to $\eta_{h_1 h_2}^{(i)}$ except that in the case of $\gamma_{h_1 h_2}^{(i)}$ our information concerning the set h_1, h_2 is limited to a knowledge of their positions only. From (2 - 6) and (2 - 8) it follows that

$$\frac{\partial}{\partial t} (n_{h_1 h_2} u_{h_1 h_2}^{(i)}) = n_{h_1 h_2} \frac{d}{dt} u_{h_1 h_2}^{(i)} - \left\{ \sum_k \frac{\partial}{\partial \xi_1^{(k)}} (n_{h_1 h_2} u_{h_1 h_2}^{(k)} u_{h_1 h_2}^{(i)}) + \sum_{\ell} \frac{\partial}{\partial \xi_2^{(\ell)}} (n_{h_1 h_2} u_{h_1 h_2}^{(\ell)} u_{h_1 h_2}^{(i)}) \right\} \quad (2 - 20)$$

Comparing (2 - 19) with (2 - 20), we have

$$\frac{d}{dt} (m_1 u_{h_1 h_2}^{(i)}) + \frac{1}{n_{h_1 h_2}} \left(\sum_k \frac{\partial}{\partial \xi_1^{(k)}} K_{h_1 h_2}^{(ki)} + \sum_{\ell} \frac{\partial}{\partial \xi_2^{(\ell)}} K_{h_1 h_2}^{(\ell i)} \right) = m_1 \gamma_{h_1 h_2}^{(i)} \quad (2 - 21)$$

where

$$\left. \begin{aligned} K_{h_1 h_2}^{(ki)} &= m_1 \int f_{h_1 h_2} v_{h_1 h_2}^{(k)} v_{h_1 h_2}^{(i)} d\xi_{h_1 h_2}, & v_{h_1 h_2}^{(i)} &= \xi_1^{(i)} - u_{h_1 h_2}^{(i)}, \\ K_{h_1 h_2}^{(\ell i)} &= m_1 \int f_{h_1 h_2} v_{h_1 h_2}^{(\ell)} v_{h_1 h_2}^{(i)} d\xi_{h_1 h_2}, & v_{h_1 h_2}^{(\ell)} &= \xi_2^{(\ell)} - u_{h_1 h_2}^{(\ell)}. \end{aligned} \right\} \quad (2 - 22)$$

Similarly we obtain

$$\frac{d}{dt} (m_2 u_{h_1 h_2}^{(j)}) + \frac{1}{n_{h_1 h_2}} \left(\sum_k \frac{\partial}{\partial \xi_1^{(k)}} K_{h_1 h_2}^{(kj)} + \sum_{\ell} \frac{\partial}{\partial \xi_2^{(\ell)}} K_{h_1 h_2}^{(\ell j)} \right) = m_2 \gamma_{h_1 h_2}^{(j)} \quad (2 - 23)$$

where

$$\left. \begin{aligned} K_{h_1 h_2}^{(kj)} &= m_2 \int f_{h_1 h_2} v_{h_1 h_2}^{(k)} v_{h_1 h_2}^{(j)} d\xi_{h_1 h_2} \\ K_{h_1 h_2}^{(\ell j)} &= m_2 \int f_{h_1 h_2} v_{h_1 h_2}^{(\ell)} v_{h_1 h_2}^{(j)} d\xi_{h_1 h_2} \\ K_{h_1 h_2}^{(ki)} &\text{ etc. are the generalized kinetic pressure} \end{aligned} \right\} \quad (2 - 24)$$

tensors /

tensors for the sets of molecules h_1, h_2 etc.

Further if we define $\underline{P}_{h_1 h_2}^{(k_i)}$, $\underline{P}_{h_1 h_2}^{(e_i)}$ by the equations

$$\sum_k \left(\frac{\partial}{\partial x_1^{(k)}} \cdot \underline{P}_{h_1 h_2}^{(k_i)} \right) = n_{h_1 h_2} \left(\frac{\partial \Phi_1(h_1)}{\partial x_1^{(k)}} + \int \frac{n_{h_1 h_2}}{n_{h_1 h_2}} \frac{\partial \psi_1^{(h_1, h_2)}}{\partial x_1^{(k)}} dx_1^{(h_1, h_2)} \right),$$

$$\sum_k \left(\frac{\partial}{\partial x_2^{(k)}} \cdot \underline{P}_{h_1 h_2}^{(e_i)} \right) = n_{h_1 h_2} \left(\frac{\partial \Phi_2(h_2)}{\partial x_2^{(k)}} + \int \frac{n_{h_1 h_2}}{n_{h_1 h_2}} \frac{\partial \psi_2^{(h_1, h_2)}}{\partial x_2^{(k)}} dx_2^{(h_1, h_2)} \right),$$

with similar expressions defining $\underline{P}_{h_1 h_2}^{(k_j)}$, $\underline{P}_{h_1 h_2}^{(e_j)}$ equations

(2 - 21), (2 - 23) can be written in the form

$$\left. \begin{aligned} \frac{d}{dt} \left(m_1 \frac{u_{h_1 h_2}^{(i)}}{n_{h_1 h_2}} \right) + \frac{1}{n_{h_1 h_2}} \left\{ \sum_k \frac{\partial}{\partial x_1^{(k)}} \cdot \underline{P}_{h_1 h_2}^{(k_i)} + \sum_k \frac{\partial}{\partial x_2^{(k)}} \cdot \underline{P}_{h_1 h_2}^{(e_i)} \right\} &= F_1^{(i)} \\ \frac{d}{dt} \left(m_2 \frac{u_{h_1 h_2}^{(j)}}{n_{h_1 h_2}} \right) + \frac{1}{n_{h_1 h_2}} \left\{ \sum_k \frac{\partial}{\partial x_1^{(k)}} \cdot \underline{P}_{h_1 h_2}^{(k_j)} + \sum_k \frac{\partial}{\partial x_2^{(k)}} \cdot \underline{P}_{h_1 h_2}^{(e_j)} \right\} &= F_2^{(j)} \end{aligned} \right\} \quad (2 - 25)$$

where

$$\underline{P}_{h_1 h_2}^{(k_i)} = \underline{K}_{h_1 h_2}^{(k_i)} + \underline{L}_{h_1 h_2}^{(k_i)} \quad \text{etc.} \quad (2 - 26)$$

The total pressure tensors $\underline{P}_{h_1 h_2}^{(k_i)}$ etc. for the sets of molecules h_1, h_2 etc. are seen to consist of two parts, the kinetic part $\underline{K}_{h_1 h_2}^{(k_i)}$ etc. and the potential part $\underline{L}_{h_1 h_2}^{(k_i)}$ etc. arising from intermolecular forces.

For $\varphi_1^{(i)} = \frac{1}{2} (\xi_1^{(i)})^2$ we obtain

$$\begin{aligned} \frac{\partial}{\partial t} \left[\frac{1}{2} n_{h_1 h_2} (u_{h_1 h_2}^{(i)})^2 + \frac{3}{2} k n_{h_1 h_2} T_{h_1 h_2}^{(i)} \right] + \sum_{k=1}^{h_1} \left(\frac{\partial}{\partial x_1^{(k)}} \cdot f_{h_1 h_2} \xi_1^{(k)} \frac{1}{2} \xi_1^{(i)2} d\xi_{h_1 h_2}^{(k)} \right) \\ + \sum_{k=1}^{h_2} \left(\frac{\partial}{\partial x_2^{(k)}} \cdot f_{h_1 h_2} \xi_2^{(k)} \frac{1}{2} \xi_1^{(i)2} d\xi_{h_1 h_2}^{(k)} \right) = n_{h_1 h_2} u_{h_1 h_2}^{(i)} \cdot \underline{P}_{h_1 h_2}^{(i)} \\ - \frac{1}{n_1} \left\{ \int \frac{\partial \psi_1^{(h_1, h_2)}}{\partial x_1^{(i)}} \cdot (u_{h_1+1, h_2}^{(i)} - u_{h_1 h_2}^{(i)}) n_{h_1+1, h_2} dx_1^{(h_1, h_2)} + \int \frac{\partial \psi_2^{(h_1, h_2)}}{\partial x_2^{(i)}} \cdot (u_{h_1 h_2}^{(i)} - u_{h_1, h_2+1}^{(i)}) n_{h_1, h_2+1} dx_2^{(h_1, h_2)} \right\} \end{aligned} \quad (2 - 27)$$

where

$$\frac{3}{2} k n_{h_1 h_2} T_{h_1 h_2}^{(i)} = \int f_{h_1 h_2} \frac{1}{2} m_1 (x_{h_1 h_2}^{(i)})^2 d\xi_{h_1 h_2} \quad (2 - 28)$$

defines the generalized temperature of a molecule of the first kind at $x_1^{(i)}$ in the set h_1, h_2 . After some transformation equation (2 - 27) can be rewritten in the form

$$\begin{aligned} \frac{3}{2} k n_{h_1 h_2} \frac{d}{dt} T_{h_1 h_2}^{(i)} + \sum_k \left\{ \left(\underline{K}_{h_1 h_2}^{(k_i)} \cdot \frac{\partial}{\partial x_1^{(k)}} \right) \cdot u_{h_1 h_2}^{(i)} + \frac{\partial}{\partial x_1^{(k)}} n_{h_1 h_2}^{(k_i)} \right\} + \sum_k \left\{ \left(\underline{K}_{h_1 h_2}^{(e_i)} \cdot \frac{\partial}{\partial x_2^{(k)}} \right) \cdot u_{h_1 h_2}^{(i)} + \frac{\partial}{\partial x_2^{(k)}} n_{h_1 h_2}^{(e_i)} \right\} \\ = - \int n_{h_1+1, h_2} \frac{\partial \psi_1^{(h_1, h_2)}}{\partial x_1^{(i)}} \cdot (u_{h_1+1, h_2}^{(i)} - u_{h_1 h_2}^{(i)}) dx_1^{(h_1, h_2)} - \int n_{h_1, h_2+1} \frac{\partial \psi_2^{(h_1, h_2)}}{\partial x_2^{(i)}} \cdot (u_{h_1 h_2}^{(i)} - u_{h_1, h_2+1}^{(i)}) dx_2^{(h_1, h_2)}, \end{aligned} \quad (2 - 29)$$

where /

where

$$\left. \begin{aligned} \underline{m}_{h_1 h_2}^{(k)} &= m_1 \int f_{h_1 h_2} v_{h_1 h_2}^{(k)} \frac{1}{2} (v_{h_1 h_2}^{(k)})^2 d\xi_{h_1 h_2} \\ \underline{m}_{h_1 h_2}^{(e)} &= m_1 \int f_{h_1 h_2} v_{h_1 h_2}^{(e)} \frac{1}{2} (v_{h_1 h_2}^{(e)})^2 d\xi_{h_1 h_2} \end{aligned} \right\} (2-30)$$

The external force $\underline{F}_1^{(k)}$ which affects only the mass motion velocity and the internal forces due to the rest of the set h_1, h_2 do not enter into (2-29) as one would expect. By strict analogy with the gas theory we see that the vectors $\underline{m}_{h_1 h_2}^{(k)}$, $\underline{m}_{h_1 h_2}^{(e)}$ are the generalized kinetic thermal energy flux connected with a molecule of the first kind at $\underline{x}_1^{(k)}$, $d\xi_1^{(k)}$ in the set h_1, h_2 .

An equation similar to (2-29) can be written for the rate of change of $T_{h_1 h_2}^{(e)}$, the generalized temperature of a molecule of the second kind at $\underline{x}_2^{(e)}$, $d\xi_2^{(e)}$ in the set h_1, h_2 . To find the corresponding equation for the internal potential energy we write $I_{h_1 h_2}^{(k)}$ for the internal potential energy of a molecule of the first kind at $\underline{x}_1^{(k)}$, $d\xi_1^{(k)}$ in the set h_1, h_2 .

$$\begin{aligned} I_{h_1 h_2}^{(k)} &= \frac{1}{2} \sum_{k=1}^{h_1} \phi_1^{(k)} + \frac{1}{2} \sum_{e=1}^{h_2} \psi^{(e)} \\ &+ \frac{1}{2} \int \frac{n_{h_1 h_2}}{n_{h_1 h_2}} \phi_1^{(k, h_1)} d\xi_1^{(k, h_1)} + \frac{1}{2} \int \frac{n_{h_1 h_2}}{n_{h_1 h_2}} \psi^{(e, h_2)} d\xi_2^{(e, h_2)}, \end{aligned} \quad (2-31)$$

where the factor $\frac{1}{2}$ signifies that the mutual potential energy is shared by each pair.

Using (2-6) and (2-8), we have

$$\begin{aligned} n_{h_1 h_2} \frac{d}{dt} I_{h_1 h_2}^{(k)} + \sum_k \frac{\partial}{\partial x_1^{(k)}} \cdot n_{h_1 h_2}^{(k)} + \sum_e \frac{\partial}{\partial x_2^{(e)}} \cdot n_{h_1 h_2}^{(e)} \\ = \int n_{h_1 h_2} \frac{\partial \phi_1^{(k, h_1)}}{\partial x_1^{(k)}} \cdot (u_{h_1 h_2}^{(k)} - u_{h_1 h_2}^{(e)}) d\xi_1^{(k, h_1)} + \int n_{h_1 h_2} \frac{\partial \psi^{(e, h_2)}}{\partial x_2^{(e)}} \cdot (u_{h_1 h_2}^{(k)} - u_{h_1 h_2}^{(e)}) d\xi_2^{(e, h_2)}, \end{aligned} \quad (2-32)$$

where /

where

$$\left. \begin{aligned} \sum_k \frac{\partial}{\partial x_1^{(k)}} n_{h_1 h_2}^{(k)} &= \frac{1}{2} n_{h_1 h_2} \sum_k (u_{h_1 h_2}^{(k)} - u_{h_1 h_2}^{(i)}) \cdot \frac{\partial \psi_1^{(i, k)}}{\partial x_1^{(i)}} \\ &+ \frac{1}{2} \int n_{h_1 h_2} (u_{h_1 h_2}^{(h_1+1, h_2)} + u_{h_1 h_2}^{(i)} - 2 u_{h_1 h_2}^{(i)}) \cdot \frac{\partial \psi_1^{(i, h_1+1)}}{\partial x_1^{(i)}} d x_1^{(h_1+1)} \\ &+ \frac{1}{2} \sum_k \frac{\partial}{\partial x_1^{(k)}} \left\{ \int n_{h_1 h_2} \psi_1^{(i, h_1+1)} (u_{h_1 h_2}^{(k)} - u_{h_1 h_2}^{(i)}) d x_1^{(h_1+1)} + \int n_{h_1 h_2+1} \psi_1^{(i, h_2)} (u_{h_1 h_2+1}^{(k)} - u_{h_1 h_2+1}^{(i)}) d x_2^{(h_2)} \right\} \end{aligned} \right\} (2-33)$$

$$\left. \begin{aligned} \sum_k \frac{\partial}{\partial x_2^{(k)}} n_{h_1 h_2}^{(k)} &= \frac{1}{2} n_{h_1 h_2} \sum_k (u_{h_1 h_2}^{(k)} - u_{h_1 h_2}^{(i)}) \cdot \frac{\partial \psi_2^{(i, k)}}{\partial x_2^{(i)}} \\ &+ \frac{1}{2} \int n_{h_1 h_2+1} (u_{h_1 h_2+1}^{(h_2+1)} + u_{h_1 h_2+1}^{(i)} - 2 u_{h_1 h_2+1}^{(i)}) \cdot \frac{\partial \psi_2^{(i, h_2+1)}}{\partial x_2^{(i)}} d x_2^{(h_2+1)} \\ &+ \frac{1}{2} \sum_k \frac{\partial}{\partial x_2^{(k)}} \left\{ \int n_{h_1 h_2} \psi_2^{(i, h_2+1)} (u_{h_1 h_2}^{(k)} - u_{h_1 h_2}^{(i)}) d x_2^{(h_2+1)} + \int n_{h_1 h_2+1} \psi_2^{(i, h_1)} (u_{h_1 h_2+1}^{(k)} - u_{h_1 h_2+1}^{(i)}) d x_1^{(h_1)} \right\} \end{aligned} \right\}$$

An equation similar to (2 - 32) can be written down for the rate of change of $I_{h_1 h_2}^{(i)}$ the internal potential energy of a molecule of the second kind at $x_2^{(i)}, d x_2^{(i)}$ in the set h_1, h_2 . On adding (2 - 29) and (2 - 32)

we obtain

$$\begin{aligned} n_{h_1 h_2} \frac{d}{dt} E_{h_1 h_2}^{(i)} + \sum_k \left\{ \left(\kappa_{h_1 h_2}^{(k)} \cdot \frac{\partial}{\partial x_1^{(k)}} \right) u_{h_1 h_2}^{(i)} + \frac{\partial}{\partial x_1^{(i)}} \cdot q_{h_1 h_2}^{(k)} \right\} \\ + \sum_k \left\{ \left(\kappa_{h_1 h_2}^{(k)} \cdot \frac{\partial}{\partial x_2^{(k)}} \right) u_{h_1 h_2}^{(i)} + \frac{\partial}{\partial x_2^{(i)}} \cdot q_{h_1 h_2}^{(k)} \right\} = 0 \end{aligned} \quad (2 - 34)$$

where

$$\left. \begin{aligned} E_{h_1 h_2}^{(i)} &= \frac{3}{2} k T_{h_1 h_2}^{(i)} + I_{h_1 h_2}^{(i)} \\ \underline{q}_{h_1 h_2}^{(k)} &= \underline{m}_{h_1 h_2}^{(k)} + \underline{n}_{h_1 h_2}^{(k)} \\ \underline{q}_{h_1 h_2}^{(i)} &= \underline{m}_{h_1 h_2}^{(i)} + \underline{n}_{h_1 h_2}^{(i)} \end{aligned} \right\} (2 - 35)$$

By analogy to the equations of ordinary hydrodynamics

we see $\underline{q}_{h_1 h_2}^{(k)}$ is the total energy flux connected with a molecule of the first kind at $x_1^{(i)}, d x_1^{(i)}$ in the set

h_1, h_2 , (and similarly for $\underline{q}_{h_1 h_2}^{(i)}$.) It consists of two parts, the kinetic part $\underline{m}_{h_1 h_2}^{(k)}$ and the potential part

$\underline{n}_{h_1 h_2}^{(k)}$. The total internal energy E also consists of two parts, the kinetic part $\frac{3}{2} k T_{h_1 h_2}^{(i)}$ and the potential part $I_{h_1 h_2}^{(i)}$. The terms $\sum_k \left(\kappa_{h_1 h_2}^{(k)} \cdot \frac{\partial}{\partial x_1^{(k)}} \right) u_{h_1 h_2}^{(i)}$ etc. in

(2 - 34) represent the dissipation of mechanical energy into heat due to internal friction.

II /

II - 4. The equilibrium solution.

In the equilibrium state $\frac{d}{dt} f_{h_1, h_2} = 0$ must hold, equation (2 - 17) becomes

$$\begin{aligned} & \left(\sum_i v_{h_1, h_2}^{(i)} \frac{\partial}{\partial x_1^{(i)}} + \sum_j v_{h_1, h_2}^{(j)} \frac{\partial}{\partial x_2^{(j)}} \right) f_{h_1, h_2} = \frac{1}{m_1} \left(\sum_i \frac{\partial W(h)}{\partial x_1^{(i)}} - F_1^{(i)} \right) \frac{\partial f_{h_1, h_2}}{\partial F_1^{(i)}} + \frac{1}{m_2} \left(\sum_j \frac{\partial W(h)}{\partial x_2^{(j)}} - F_2^{(j)} \right) \frac{\partial f_{h_1, h_2}}{\partial F_2^{(j)}} \\ & + \left\{ \left(\frac{1}{m_1} \sum_i \frac{\partial \psi^{(i, h+1)}}{\partial x_1^{(i)}} \frac{\partial}{\partial F_1^{(i)}} + \frac{1}{m_2} \sum_j \frac{\partial \psi^{(j, h+1)}}{\partial x_2^{(j)}} \frac{\partial}{\partial F_2^{(j)}} \right) f_{h_1, h_2} dZ_1^{(h+1)} dZ_2^{(h+1)} \right. \\ & \left. + \left\{ \left(\frac{1}{m_2} \sum_j \frac{\partial \psi^{(j, h+1)}}{\partial x_2^{(j)}} \frac{\partial}{\partial F_2^{(j)}} + \frac{1}{m_1} \sum_i \frac{\partial \psi^{(i, h+1)}}{\partial x_1^{(i)}} \frac{\partial}{\partial F_1^{(i)}} \right) f_{h_1, h_2} dZ_2^{(h+1)} dZ_1^{(h+1)} \right\} \right. \end{aligned} \quad (2 - 36)$$

From statistical mechanics it is known that the solution of the above equation must be of the form

$$f_{h_1, h_2} = n_{h_1, h_2} \left(\frac{m_1}{2\pi kT} \right)^{\frac{3}{2} h_1} \left(\frac{m_2}{2\pi kT} \right)^{\frac{3}{2} h_2} \exp - \left\{ \frac{m_1}{2kT} \sum_i (v_{h_1, h_2}^{(i)})^2 + \frac{m_2}{2kT} \sum_j (v_{h_1, h_2}^{(j)})^2 \right\} \quad (2 - 37)$$

where $T (= T_{h_1, h_2}^{(i)} = T_{h_1, h_2}^{(j)})$ is the equilibrium temperature of the assembly.

After substitution from (2 - 37) in (2 - 36) we obtain

$$\begin{aligned} & \sum_i \left\{ \frac{\partial n_{h_1, h_2}}{\partial x_1^{(i)}} + \frac{n_{h_1, h_2}}{kT} \left(\frac{\partial W(h)}{\partial x_1^{(i)}} - F_1^{(i)} \right) + \left[\frac{n_{h_1, h_2}}{kT} \frac{\partial \psi^{(i, h+1)}}{\partial x_1^{(i)}} dZ_1^{(h+1)} + \frac{n_{h_1, h_2+1}}{kT} \frac{\partial \psi^{(i, h+1)}}{\partial x_1^{(i)}} dZ_2^{(h+1)} \right] \right\} v_{h_1, h_2}^{(i)} \\ & + \sum_j \left\{ \frac{\partial n_{h_1, h_2}}{\partial x_2^{(j)}} + \frac{n_{h_1, h_2}}{kT} \left(\frac{\partial W(h)}{\partial x_2^{(j)}} - F_2^{(j)} \right) + \left[\frac{n_{h_1, h_2+1}}{kT} \frac{\partial \psi^{(j, h+1)}}{\partial x_2^{(j)}} dZ_2^{(h+1)} + \frac{n_{h_1, h_2}}{kT} \frac{\partial \psi^{(j, h+1)}}{\partial x_2^{(j)}} dZ_1^{(h+1)} \right] \right\} v_{h_1, h_2}^{(j)} = 0 \end{aligned}$$

Since n_{h_1, h_2} is independent of $v_{h_1, h_2}^{(i)}$ and $v_{h_1, h_2}^{(j)}$, the above equation can be separated. For $h_1 = N_1$, $h_2 = N_2$, we have

$$\left. \begin{aligned} \frac{\partial n_{N_1, N_2}}{\partial x_1^{(i)}} + \frac{n_{N_1, N_2}}{kT} \left(\frac{\partial W(N)}{\partial x_1^{(i)}} - F_1^{(i)} \right) &= 0 \quad (i = 1, 2, \dots, N_1) \\ \frac{\partial n_{N_1, N_2}}{\partial x_2^{(j)}} + \frac{n_{N_1, N_2}}{kT} \left(\frac{\partial W(N)}{\partial x_2^{(j)}} - F_2^{(j)} \right) &= 0 \quad (j = 1, 2, \dots, N_2) \end{aligned} \right\} \quad (2 - 38)$$

The integrability of the above equation requires

$F_1^{(i)}, F_2^{(j)}$ to be conservative.

Let /

Let

$$\left. \begin{aligned} F_1^{(i)} &= -\frac{\partial E(N)}{\partial x_1^{(i)}} \quad , \quad F_2^{(j)} = -\frac{\partial E(N)}{\partial x_2^{(j)}} \quad , \\ E(N) &= E_1(N_1) + E_2(N_2) \\ E_1(N_1) &= \sum_{i=1}^{N_1} E_1^{(i)}(x_1^{(i)}) \quad , \quad E_2(N_2) = \sum_{j=1}^{N_2} E_2^{(j)}(x_2^{(j)}) \end{aligned} \right\} \quad (2-39)$$

We can similarly define the total potential energy in the external force field for a set of molecules

$$h = h_1 + h_2 .$$

Integrating (2-38) we obtain

$$Q_0 n_{N_1, N_2} = \exp\left\{-\frac{1}{kT}(W(N) + E(N))\right\} \quad (2-40)$$

where

$$Q_0 = \frac{1}{N_1! N_2!} \int e^{-\frac{1}{kT}(W(N) + E(N))} dZ_{N_1, N_2} \quad (2-41)$$

By means of (2-2), equation (2-40) gives

$$\begin{aligned} Q_0 n_{N_1, N_2} &= \frac{1}{(N_1 - h_1)! (N_2 - h_2)!} \int e^{-\frac{1}{kT}(W(N) + E(N))} \frac{dZ_{N_1, N_2}}{dZ_{h_1, h_2}} \quad (2-42) \\ &= \frac{e^{-\frac{1}{kT}E(h)}}{(N_1 - h_1)! (N_2 - h_2)!} \int e^{-\frac{1}{kT}(W(N) + E(N-h))} \frac{dZ_{N_1, N_2}}{dZ_{h_1, h_2}} \end{aligned}$$

II - 5. Reduction of the molecular conservation equations to ordinary hydrodynamical equations.

In an assembly consisting of only one kind of molecules, the generalized definitions of kinetic pressure, temperature and thermal flux reduce for $\lambda = 1$ in each case to their respective ordinary definitions. This is not so in a mixture where the generalized definitions of the above quantities reduce for $h_1 = 1, h_2 = 0$ to quantities referring to the first kind of molecules only which can not be directly observed. What one directly /

directly observes in a mixture instead of the above mentioned quantities are the average properties contributed by a small group of molecules of various types in a small time interval. We can nevertheless find connections between these two sets of quantities so that either of them can be expressed in terms of the other.

There are two different average velocities in a mixture i.e. the directly observable mass velocity \underline{u} from which the peculiar velocities (or thermal velocities) and therefore the kinetic pressure, temperature and thermal flux in a mixture are defined, and the number velocity \underline{u}_n used in connection with the transport of molecular properties,

$$\underline{u} = \frac{\rho_1 \underline{u}_1 + \rho_2 \underline{u}_2}{\rho} \quad , \quad \underline{u}_n = \frac{n_1 \underline{u}_1 + n_2 \underline{u}_2}{n} \quad (2 - 43)$$

where

$$\underline{u}_1 = \int \frac{f_1}{n_1} \underline{\xi}_1 d\underline{\xi}_1 \quad , \quad \underline{u}_2 = \int \frac{f_2}{n_2} \underline{\xi}_2 d\underline{\xi}_2 \quad (2 - 44)$$

f_i, n_i and $\underline{\xi}_i$ stand for $f_{i0}(\underline{z}''', \underline{\xi}_i'', t)$, $n_{i0}(\underline{z}''', t)$ and $\underline{\xi}_{i0}''$ respectively.

Let \underline{k}, T and \underline{m} be the kinetic pressure, temperature and thermal flux in a mixture. These are defined as

$$\begin{aligned} \underline{k} &= m_1 \int f_1 v_1 v_1 d\underline{v}_1 + m_2 \int f_2 v_2 v_2 d\underline{v}_2 = \underline{k}_1 + \underline{k}_2 \quad , \\ \frac{3}{2} k T n &= \frac{m_1}{2} \int f_1 v_1^2 d\underline{v}_1 + \frac{m_2}{2} \int f_2 v_2^2 d\underline{v}_2 = \frac{3}{2} k (n_1 T_1 + n_2 T_2) \quad , \\ \underline{m} &= \frac{m_1}{2} \int f_1 v_1 v_1^2 d\underline{v}_1 + \frac{m_2}{2} \int f_2 v_2 v_2^2 d\underline{v}_2 = \underline{m}_1 + \underline{m}_2 \quad , \end{aligned} \quad (2 - 45)$$

where /

where

$$v_1 = \xi_1 - u, \quad v_2 = \xi_2 - u. \quad (2-46)$$

\underline{k}_1 and \underline{m}_1 are the partial kinetic pressure and the thermal flux of the molecules of the first kind, T_1 the partial temperature such that $\frac{1}{2}kT_1$ is the average heat energy for each degree of freedom of a molecule of the first kind. \underline{k}_2 , \underline{m}_2 and T_2 have similar meanings for the second type of molecules.

On the other hand we obtain from (2-22), (2-28) and (2-30) for $h_1=1, h_2=0$

$$\left. \begin{aligned} \underline{k}_{10} &= m_1 \int f_1 v_{10} v_{10} dv_{10}, \\ \frac{3}{2}kT_{10} &= \frac{m_1}{2} \int \frac{f_1}{m_1} v_{10}^2 dv_{10}, \\ \underline{m}_{10} &= \frac{m_1}{2} \int f_1 v_{10} v_{10}^2 dv_{10}, \end{aligned} \right\} (2-47)$$

with similar equations for $\underline{k}_{01}, T_{01}$ and \underline{m}_{01} .

From the definitions given above it can be shown that

$$\left. \begin{aligned} \underline{k} &= \underline{k}_1 + \underline{k}_2 = \underline{k}_{10} + \underline{k}_{01} + \rho_1 u_1' u_1' + \rho_2 u_2' u_2', \\ \frac{3}{2}nkT &= \frac{3}{2}k(n_1T_{10} + n_2T_{01}) + \frac{1}{2}\rho_1 (u_1')^2 + \frac{1}{2}\rho_2 (u_2')^2, \\ \underline{m} &= \underline{m}_1 + \underline{m}_2 = \underline{m}_{10} + \underline{m}_{01} + \underline{k}_{10} u_1' + \underline{k}_{01} u_2' + \frac{3}{2}kT(n_1 u_1' + n_2 u_2') \end{aligned} \right\} (2-48)$$

where

$$u_1' = u_1 - u, \quad u_2' = u_2 - u. \quad (2-49)$$

With these relations between $\underline{k}, T, \underline{m}$ and $\underline{k}_{10}, T_{10}, \underline{m}_{10}$ etc., it can be shown that the equation of continuity (2-6), the equation of conservation of momentum (2-25) and /

and of thermal energy (2 - 29) reduce for $h_1 = 1, h_2 = 0$ or $h_1 = 0, h_2 = 1$ to equations similar in form to the corresponding equations in a gas mixture. (c.f. Chapman & Cowling, Mathematical theory of non-uniform gases 1939). These are

$$\left. \begin{aligned} \frac{\partial}{\partial t} n_1 &= -\frac{\partial}{\partial x} \cdot (n_1 u_1) , \\ \frac{\partial}{\partial t} n &= -\frac{\partial}{\partial x} \cdot (n u) - \frac{\partial}{\partial x} \cdot (n_1 u_1' + n_2 u_2') , \\ \frac{\partial}{\partial t} u_1 &= -u_1 \frac{\partial}{\partial x} u_1 - \frac{1}{\rho} \frac{\partial}{\partial x} \cdot \underline{k}_{10} + \gamma_1 , \\ \frac{\partial}{\partial t} u &= -u \frac{\partial}{\partial x} u - \frac{1}{\rho} \frac{\partial}{\partial x} \cdot \underline{k} + \frac{1}{\rho} (\rho_1 \gamma_1 + \rho_2 \gamma_2) , \\ \frac{\partial}{\partial t} T &= -u \frac{\partial}{\partial x} T + \frac{T}{n} \frac{\partial}{\partial x} \cdot (n_1 u_1' + n_2 u_2') - \frac{2}{3kn} \left(\underline{k} : \frac{\partial}{\partial x} u + \frac{\partial}{\partial x} \cdot \underline{k} \right) \\ &\quad + \frac{2}{3kn} \left[(\rho_1 \gamma_1 \cdot u_1' + \rho_2 \gamma_2 \cdot u_2') - (\delta_1 + \delta_2) \right] . \end{aligned} \right\} (2 - 50)$$

where

$$\left. \begin{aligned} \rho_1 \gamma_1 &= n_1 E_1 - \left\{ \int \frac{\partial \phi}{\partial x_1''} n_{20} d x_1'' + \int \frac{\partial \psi}{\partial x_1''} n_{1T} d x_2'' \right\} = n_1 E_1 - \frac{\partial}{\partial x} \cdot \underline{L}_1 , \\ \delta_1 &= \left\{ \int n_{20} \frac{\partial \phi}{\partial x_1''} \cdot (u_{20}'' - u_1) d x_1'' + \int n_{1T} \frac{\partial \psi}{\partial x_1''} \cdot (u_{1T}'' - u_1) d x_2'' \right\} \end{aligned} \right\} (2 - 51)$$

n_{1T} stands for $n_{11}(x_1'', x_2'', t)$ and u_{1T}'', E_1 for $u_{11}''(x_1'', x_2'', t), E_1''$. If we interchange the two molecules concerned, we obtain n_{T1} and u_{T1}'' .

To compare the equations in (2 - 50) with the corresponding equations for gas mixtures, we notice that the part played by the divergence of the potential pressure corresponds the rate of change of momentum of a molecule in a gas mixture due to collision with other molecules. The condition that the total momentum of the molecules in a small volume element be unaltered by collisions among them - the consequence of binary encounter and the hypothesis of molecular chaos is no longer satisfied in the general case but the rate of change /

change of momentum is represented by the quantity

$$\left(\frac{\partial}{\partial x_1} \cdot \underline{L}_1 + \frac{\partial}{\partial x_2} \cdot \underline{L}_2 \right) \\ = \left\{ \int \frac{\partial \Phi}{\partial x_1} n_{20} dx_1^{(2)} + \int \frac{\partial \Psi}{\partial x_1} n_{11} dx_1^{(1)} \right\} + \left\{ \int \frac{\partial \Phi}{\partial x_2} n_{02} dx_2^{(2)} + \int \frac{\partial \Psi}{\partial x_2} n_{11} dx_2^{(1)} \right\}$$

which does not vanish owing to the interaction at a large number of molecules other than those at the point considered.

Similarly the part played by the potential transport of thermal energy corresponds to the rate of change of thermal energy of a given molecule due to collision with other molecules. The condition that the total energy of the molecules in a small volume element be unaltered by collisions among them - again a consequence of binary encounters and the hypothesis of molecular chaos is no longer satisfied in the general case, but the rate of change of energy is represented by the quantity

$$\left\{ u_1 \cdot \left(\frac{\partial}{\partial x_1} \cdot \underline{L}_1 \right) + u_2 \cdot \left(\frac{\partial}{\partial x_2} \cdot \underline{L}_2 \right) - (\sigma_1 + \sigma_2) \right\}$$

which does not vanish owing to the interaction of a large number of molecules other than those at the point considered.

II - 6. Method of Expansion.

The equation of motion (2 - 17) as it stands possesses solutions far too general for our purpose. The solution which we require is the so-called normal solution describable in terms of certain parameters which deviates but slightly from the Maxwellian distribution. We shall therefore divide f_{h_1, h_2} into parts /

parts

$$f_{h_1 h_2} = f_{h_1 h_2}^{\circ} + f_{h_1 h_2}' + f_{h_1 h_2}'' + \dots \quad (2 - 52)$$

such that $f_{h_1 h_2}^{\circ}$, the zeroth approximation to $f_{h_1 h_2}$, is that equilibrium solution for a homogeneous fluid with properly chosen constant parameters λ_0 which fits best the real $f_{h_1 h_2}$ in the region considered, $f_{h_1 h_2}'$ the difference of the first approximation to $f_{h_1 h_2}$ from $f_{h_1 h_2}^{\circ}$, is the correction for a non-uniform fluid with properly chosen constant gradients of the parameters $\frac{\partial \lambda_e}{\partial x}$ to fit the real $f_{h_1 h_2}$, etc.. A natural and convenient basis for choosing $\lambda_e, \frac{\partial \lambda_e}{\partial x}$ etc., is to identify them with the values at the centre of gravity of the set of molecules x_1, x_2 . Hence we postulate

$$f_{h_1 h_2} = F_{h_1 h_2} \left(x_1^{(i)}, x_2^{(j)}, \xi_1^{(i)}, \xi_2^{(j)}, \lambda_e, \frac{\partial \lambda_e}{\partial x}, \frac{\partial^2 \lambda_e}{\partial x \partial x}, \frac{\partial \lambda_e}{\partial x} \frac{\partial \lambda_e}{\partial x}, \dots \right) \quad (2 - 53)$$

where the capital F is used to denote the new functional dependence.

By separating quantities of different order in $F_{h_1 h_2}$, we have

$$f_{h_1 h_2} = F_{h_1 h_2} = F_{h_1 h_2}^{\circ} + F_{h_1 h_2}' + F_{h_1 h_2}'' + \dots \quad (2 - 52)a$$

where $F_{h_1 h_2}^{\circ}$ does not involve any gradient, $F_{h_1 h_2}'$ involves gradients to the first order and first degree, $F_{h_1 h_2}''$ involves gradients of the first order to the second degree or the second order to the first degree, etc..

As to the selection of parameters adequate for a complete /

complete specification of the macroscopic state of a liquid mixture, it can be said that since a drop of liquid mixture is but an ensemble of different kinds of molecules, besides their intrinsic properties such as the molecular masses (m_1, m_2) and the potential functions between pairs of molecules (ϕ, ψ), one can further specify the average numbers of molecules per unit volume of each kind (n_1, n_2) their average momentum (\underline{u}), average kinetic energy relative to their centre of mass (T) and the potential energy of each kind of molecules in the external force field (E_1, E_2). Hence λ_r in (2 - 52) represent the values of $n_1, n_2, \underline{u}, T, E_1$ and E_2 at the mass centre $\underline{x} = \frac{(\sum_i m_1 \underline{x}_1^{(i)} + \sum_j m_2 \underline{x}_2^{(j)})}{(h_1 m_1 + h_2 m_2)}$ of the set $\underline{r}_1, \underline{r}_2$.

The assumption that intermolecular forces are central and expressible as functions of the distance between the mass centres of the pair of molecules concerned suggests that $\underline{x}_1^{(i)}, \underline{x}_2^{(j)}$ appear in $F_{h_1 h_2}$ only in the combination $\underline{r}_1^{(ik)} = \underline{x}_1^{(k)} - \underline{x}_1^{(i)}, \underline{r}_2^{(jl)} = \underline{x}_2^{(l)} - \underline{x}_2^{(j)}$ and $\underline{s}^{(ij)} = \underline{x}_2^{(j)} - \underline{x}_1^{(i)} = -\underline{s}^{(ji)}$. Further $F_{h_1 h_2}$ must be symmetrical with respect to $\underline{r}_1^{(ik)}$ and to $\underline{r}_2^{(jl)}$, i.e. $F_{h_1 h_2}$ is unaltered by interchanging two molecules of the same kind. In consequence, we have

$$\begin{aligned} \sum_i \frac{\partial F_{h_1 h_2}}{\partial \underline{x}_1^{(i)}} + \sum_j \frac{\partial F_{h_1 h_2}}{\partial \underline{x}_2^{(j)}} &= \sum_i \left\{ \sum_k \frac{\partial F_{h_1 h_2}}{\partial \underline{r}_1^{(ki)}} + \sum_l \frac{\partial F_{h_1 h_2}}{\partial \underline{s}^{(li)}} \right\} + \sum_j \left\{ \sum_l \frac{\partial F_{h_1 h_2}}{\partial \underline{r}_2^{(lj)}} + \sum_k \frac{\partial F_{h_1 h_2}}{\partial \underline{s}^{(kj)}} \right\} \\ &= \sum_{ik} \frac{\partial F_{h_1 h_2}}{\partial \underline{r}_1^{(ki)}} + \sum_{jl} \frac{\partial F_{h_1 h_2}}{\partial \underline{r}_2^{(lj)}} + \sum_{ij} \left(\frac{\partial F_{h_1 h_2}}{\partial \underline{s}^{(ji)}} + \frac{\partial F_{h_1 h_2}}{\partial \underline{s}^{(ij)}} \right) = 0 \end{aligned} \quad (2 - 54)$$

The dependence of $F_{h_1 h_2}$ on \underline{x} and t is implicit in $\lambda_r, \frac{\partial \lambda_r}{\partial \underline{x}}$ etc.. /



etc. As λ_e involves \underline{u} , the dependence of $F_{h_1 h_2}$ on $\underline{x}_1^{(i)}$, $\underline{x}_2^{(j)}$ can be made in terms of $\underline{v}_1^{(i)} = \underline{x}_1^{(i)} - \underline{u}$ and $\underline{v}_2^{(j)} = \underline{x}_2^{(j)} - \underline{u}$. Equation (2 - 52) can therefore be written in the form

$$f_{h_1 h_2} = F_{h_1 h_2} \left(\underline{r}_1^{(i)}, \underline{r}_2^{(j)}, \underline{s}^{(ij)}, \underline{v}_1^{(i)}, \underline{v}_2^{(j)}, \lambda_e, \frac{\partial \lambda_e}{\partial \underline{x}}, \frac{\partial^2 \lambda_e}{\partial \underline{x} \partial \underline{x}}, \frac{\partial \lambda_e \partial \lambda_e}{\partial \underline{x} \partial \underline{x}}, \dots \right) \quad (2 - 53)a$$

The above consideration holds as well for all quantities derivable from $F_{h_1 h_2}$ such as $N_{h_1 h_2}$, $U_{h_1 h_2}^{(i)}$, $T_{h_1 h_2}^{(i)}$, $K_{h_1 h_2}^{(i)}$ etc. Let c denote any one of them, we have

$$\begin{aligned} c &= C \left(\underline{r}_1^{(i)}, \underline{r}_2^{(j)}, \underline{s}^{(ij)}, \underline{v}_1^{(i)}, \underline{v}_2^{(j)}, \lambda_e, \frac{\partial \lambda_e}{\partial \underline{x}}, \frac{\partial^2 \lambda_e}{\partial \underline{x} \partial \underline{x}}, \frac{\partial \lambda_e \partial \lambda_e}{\partial \underline{x} \partial \underline{x}}, \dots \right) \\ &= c^0 + c' + c'' + \dots \end{aligned} \quad (2 - 55)$$

where c^0 does not contain any space gradients $\frac{\partial \lambda_e}{\partial \underline{x}}$, c' contains $\frac{\partial \lambda_e}{\partial \underline{x}}$ to the first degree etc..

The space gradient $\frac{\partial c}{\partial \underline{x}} = \sum_e \frac{\partial \lambda_e}{\partial \underline{x}} \frac{\partial c}{\partial \lambda_e}$ and the time derivative $\frac{\partial c}{\partial t} = \sum_e \frac{\partial \lambda_e}{\partial t} \frac{\partial c}{\partial \lambda_e}$ can be expanded in a similar way.

$$\begin{aligned} \frac{\partial c}{\partial \underline{x}} &= \left(\sum_e \frac{\partial \lambda_e}{\partial \underline{x}} \frac{\partial c^0}{\partial \lambda_e} \right) + \left(\sum_e \frac{\partial \lambda_e}{\partial \underline{x}} \frac{\partial c'}{\partial \lambda_e} \right) + \dots \\ \frac{\partial c}{\partial t} &= \left(\sum_e \left(\frac{\partial \lambda_e}{\partial t} \right)^0 \frac{\partial c^0}{\partial \lambda_e} \right) + \sum_e \left\{ \left(\frac{\partial \lambda_e}{\partial t} \right)' \frac{\partial c^0}{\partial \lambda_e} + \left(\frac{\partial \lambda_e}{\partial t} \right)^0 \frac{\partial c'}{\partial t} \right\} + \dots \end{aligned}$$

where

$$\frac{\partial \lambda_e}{\partial t} = \left(\frac{\partial \lambda_e}{\partial t} \right)^0 + \left(\frac{\partial \lambda_e}{\partial t} \right)' + \dots$$

has to be calculated from (2 - 50) in the way shown in the next section.

c^0 , c' in (2 - 54) can be expressed in each case in terms of $f_{h_1 h_2}^0$, $f_{h_1 h_2}'$, ... namely:

namely :

$$n_{h_1 h_2}^0 = \int f_{h_1 h_2}^0 d\xi_{h_1 h_2}, \quad n_{h_1 h_2}' = \int f_{h_1 h_2}' d\xi_{h_1 h_2},$$

$$\underline{u}_{h_1 h_2}^{(j)0} = \int \frac{f_{h_1 h_2}^0}{n_{h_1 h_2}^0} \underline{u}_{h_1 h_2}^{(j)} d\xi_{h_1 h_2}, \quad \underline{u}_{h_1 h_2}^{(j)'} = \int \frac{f_{h_1 h_2}'}{n_{h_1 h_2}'} \underline{u}_{h_1 h_2}^{(j)0} d\xi_{h_1 h_2}$$

where $\underline{u}_{h_1 h_2}^{(j)0} = \underline{u}_{h_1 h_2}^{(j)} - \underline{u}_{h_1 h_2}^{(j)0}$,

$$\underline{u}_{h_1 h_2}^{(j)'} = - \underline{u}_{h_1 h_2}^{(j)0} \quad \left. \begin{array}{l} \\ \\ \\ \\ \\ \\ \\ \\ \\ \end{array} \right\} (2-56)$$

$$T_{h_1 h_2}^{(j)0} = \frac{2m_1}{3k} \int \frac{f_{h_1 h_2}^0}{n_{h_1 h_2}^0} \frac{1}{2} (\underline{u}_{h_1 h_2}^{(j)0})^2 d\xi_{h_1 h_2},$$

$$T_{h_1 h_2}^{(j)'} = \frac{2m_1}{3k} \int \frac{f_{h_1 h_2}'}{n_{h_1 h_2}'} \left\{ \frac{1}{2} (\underline{u}_{h_1 h_2}^{(j)0})^2 - \frac{3k}{2m_1} T_{h_1 h_2}^{(j)0} \right\} d\xi_{h_1 h_2},$$

$$\underline{K}_{h_1 h_2}^{(k)0} = m_1 \int f_{h_1 h_2}^0 \underline{u}_{h_1 h_2}^{(k)0} \underline{u}_{h_1 h_2}^{(j)0} d\xi_{h_1 h_2},$$

$$\underline{K}_{h_1 h_2}^{(k)'} = m_1 \int f_{h_1 h_2}' \underline{u}_{h_1 h_2}^{(k)0} \underline{u}_{h_1 h_2}^{(j)0} d\xi_{h_1 h_2},$$

$$\underline{m}_{h_1 h_2}^{(k)0} = m_1 \int f_{h_1 h_2}^0 \underline{u}_{h_1 h_2}^{(k)0} \frac{1}{2} (\underline{u}_{h_1 h_2}^{(j)0})^2 d\xi_{h_1 h_2},$$

$$\underline{m}_{h_1 h_2}^{(k)'} = m_1 \int f_{h_1 h_2}' \left\{ \underline{u}_{h_1 h_2}^{(k)0} \left(\frac{1}{2} (\underline{u}_{h_1 h_2}^{(j)0})^2 - \frac{3k}{2m_1} T_{h_1 h_2}^{(j)0} \right) - \frac{\underline{u}_{h_1 h_2}^{(k)0} \underline{K}_{h_1 h_2}^{(k)0}}{n_{h_1 h_2}^0 m_1} \right\} d\xi_{h_1 h_2}$$

with corresponding formulae for $\underline{u}_{h_1 h_2}^{(j)}$, $T_{h_1 h_2}^{(j)}$ etc.

As C depends on λ_e at the mass centre \underline{x} of the set of molecules h_1, h_2 whenever C is integrated over the coordinates of one or more of the molecules in the set h_1, h_2 , it should be expanded inside the integral with respect to the new mass centre of the reduced set of molecules, for example

$$\int \frac{\partial \phi_1^{(j, h_1 h_2)}}{\partial \underline{x}^{(j)}} n_{h_1 h_2} d\underline{x}_1^{(h_1 h_2)} \quad (2-57)$$

$$= \int \frac{\partial \phi_1^{(j, h_1 h_2)}}{\partial \underline{x}^{(j)}} \left\{ [N_{h_1 h_2}] + d_1 \sum \frac{\partial \lambda_e}{\partial \underline{x}} \frac{\partial}{\partial \lambda_e} [N_{h_1 h_2}] + \dots \right\} d\underline{x}_1^{(h_1 h_2)}$$

where

$$d_1 = \frac{m_1}{M+m_1} (\underline{x}_1^{(h_1 h_2)} - \underline{x}), \quad M = h_1 m_1 + h_2 m_2, \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} (2-58)$$

$$\underline{x} = \left(\sum_i m_i \underline{x}_i^{(i)} + \sum_j m_j \underline{x}_j^{(j)} \right) / M$$

square brackets [] are used to show that quantities inside /

inside it depend on λ_e at the new mass centre after integration.

II - 7. Expansion of the equation of motion - zeroth approximation.

If we expand each term in the equation of motion (2 - 17) according to the rules outlined in the last section, we obtain a set of equations of motion for

$$F_{h_1, h_2}^0, F_{h_1, h_2}^1 \quad \text{etc.}$$

We observe first that all time derivatives vanish to the zeroth order i.e. they involve no term not containing $\frac{\partial \lambda_e}{\partial x}$. The zeroth order terms in

(2 - 17) are

$$\begin{aligned} \left(\sum_i \frac{\partial \psi_i^{(h_1)}}{\partial x_i^{(h_1)}} + \sum_j \frac{\partial \psi_j^{(h_2)}}{\partial x_j^{(h_2)}} \right) F_{h_1, h_2}^0 &= \frac{1}{m_1} \sum_i \frac{\partial W^{(h_1)}}{\partial x_i^{(h_1)}} \cdot \frac{\partial F_{h_1, h_2}^0}{\partial x_i^{(h_1)}} + \frac{1}{m_2} \sum_j \frac{\partial W^{(h_2)}}{\partial x_j^{(h_2)}} \cdot \frac{\partial F_{h_1, h_2}^0}{\partial x_j^{(h_2)}} \\ &+ \frac{1}{m_1} \sum_i \left(\frac{\partial \psi_i^{(h_1, h_2)}}{\partial x_i^{(h_1)}} \cdot \frac{\partial}{\partial x_i^{(h_1)}} [F_{h_1, h_2}^0] d_{x_2}^{(h_1)} d_{x_1}^{(h_2)} \right) + \frac{1}{m_2} \sum_j \left(\frac{\partial \psi_j^{(h_1, h_2)}}{\partial x_j^{(h_2)}} \cdot \frac{\partial}{\partial x_j^{(h_2)}} [F_{h_1, h_2}^0] d_{x_2}^{(h_2)} d_{x_1}^{(h_1)} \right) \quad (2 - 59) \\ &+ \frac{1}{m_1} \sum_i \left(\frac{\partial \psi_i^{(h_1, h_2)}}{\partial x_i^{(h_1)}} \cdot \frac{\partial}{\partial x_i^{(h_1)}} [F_{h_1, h_2}^0] d_{x_2}^{(h_1)} d_{x_1}^{(h_2)} \right) + \frac{1}{m_2} \sum_j \left(\frac{\partial \psi_j^{(h_1, h_2)}}{\partial x_j^{(h_2)}} \cdot \frac{\partial}{\partial x_j^{(h_2)}} [F_{h_1, h_2}^0] d_{x_2}^{(h_2)} d_{x_1}^{(h_1)} \right) \end{aligned}$$

where the L.H.S. of the above equation reduces to

$$\left(\sum_i \frac{\partial \psi_i^{(h_1)}}{\partial x_i^{(h_1)}} + \sum_j \frac{\partial \psi_j^{(h_2)}}{\partial x_j^{(h_2)}} \right) F_{h_1, h_2}^0 \quad \text{by virtue of (2 - 54). Equation}$$

(2 - 57) is then formally the same as equation (2 - 36)

except for the term involving the external force.

Our solution F_{h_1, h_2}^0 therefore corresponds to the homogeneous equilibrium state in the absence of any external force field. Equilibrium under an external force field acting with equal intensity on the two kinds of molecules is the result of two opposing dynamic effects: the drift caused by the external force field is balanced by the diffusion velocity due to the non-homogeneity of composition and density gradients. /

gradients. The true equilibrium solution $F_{h_1 h_2}^{\circ}$ is

$$F_{h_1 h_2}^{\circ} = N_{h_1 h_2}^{\circ} \left(\frac{m_1}{2\pi kT} \right)^{\frac{3}{2} h_1} \left(\frac{m_2}{2\pi kT} \right)^{\frac{3}{2} h_2} \exp - \left\{ \frac{m_1}{2kT} \sum_i (v_i^{(j)})^2 + \frac{m_2}{2kT} \sum_j (v_j^{(i)})^2 \right\} \quad (2-60)$$

Substituting equation (2-60) in (2-59), we obtain after separating as shown in II-4, the typical equation

$$- \frac{KT}{N_{h_1 h_2}^{\circ}} \frac{\partial N_{h_1 h_2}^{\circ}}{\partial x_i^{(j)}} + \frac{\partial w(h)}{\partial x_i^{(j)}} + \int \frac{\partial \phi^{(i, h_1+1)}}{\partial x_i^{(j)}} \frac{[N_{h_1 h_2}^{\circ}]}{N_{h_1 h_2}^{\circ}} dx_1^{(h_1+1)} + \int \frac{\partial \psi^{(i, h_2+1)}}{\partial x_i^{(j)}} \frac{[N_{h_1 h_2}^{\circ}]}{N_{h_1 h_2}^{\circ}} dx_2^{(h_2+1)} = 0 \quad (2-61)$$

(2-42) shows that $N_{h_1 h_2}^{\circ}$ must be equal to

$$N_{h_1 h_2}^{\circ} = \frac{1}{Q_0 (N_1 - h_1)! (N_2 - h_2)!} \iint e^{-\frac{w(N)}{kT}} dx_1^{(h_1)} \dots dx_1^{(N)} dx_2^{(h_2)} \dots dx_2^{(N_2)} \quad (2-62)$$

$N_{h_1 h_2}^{\circ}$ can only depend on $n_1^{(i)}, n_2^{(j)}, T, n_1$ and n_2 but not on u , as a constant motion of the whole assembly can obviously have no effect on $N_{h_1 h_2}^{\circ}$.

By means of (2-56), we obtain

$$\left. \begin{aligned} \underline{u}_{h_1 h_2}^{(i)} &= \underline{u} = \underline{u}_{h_1 h_2}^{(j)}, \quad \underline{v}_{h_1 h_2}^{(i)} = \underline{v}_1^{(j)}, \quad \underline{v}_{h_1 h_2}^{(j)} = \underline{v}_2^{(i)}, \\ T_{h_1 h_2}^{(i)} &= T = T_{h_1 h_2}^{(j)}, \quad \underline{k}_{h_1 h_2}^{(i)} = N_{h_1 h_2}^{\circ} kT \delta_{ik} \underline{1}, \\ \underline{k}_{h_1 h_2}^{(j)} &= N_{h_1 h_2}^{\circ} kT \delta_{ej} \underline{1}, \quad \underline{m}_{h_1 h_2}^{(i)} = 0 = \underline{m}_{h_1 h_2}^{(j)} \end{aligned} \right\} \quad (2-63)$$

In particular for $h_1=1, h_2=0$ or $h_1=0, h_2=1$ we have

$$\left. \begin{aligned} n_1^{\circ} &= n_1, \quad n_2^{\circ} = n_2, \quad \underline{u}_1^{\circ} = \underline{u} = \underline{u}_2^{\circ} \\ T_1^{\circ} &= T = T_2^{\circ}, \quad \underline{k}_1^{\circ} = n_1 kT \underline{1}, \quad \underline{k}_2^{\circ} = n_2 kT \underline{1}, \quad \underline{m}_1^{\circ} = \underline{m}_2^{\circ} = 0 \end{aligned} \right\} \quad (2-64)$$

The time derivative $\left(\frac{\partial \lambda e}{\partial t} \right)'$ of the first order may now be calculated.

$$\begin{aligned} \left(\frac{\partial n_1}{\partial t} \right)' &= -\frac{\partial}{\partial x} \cdot (n_1 u), \quad \left(\frac{\partial n_2}{\partial t} \right)' = -\frac{\partial}{\partial x} \cdot (n_2 u), \\ \left(\frac{\partial u}{\partial t} \right)' &= -u \frac{\partial u}{\partial x} - \frac{1}{\rho} \frac{\partial \kappa^{\circ}}{\partial x} + \frac{1}{\rho} (\rho_1 \gamma_1' + \rho_2 \gamma_2') = -u \frac{\partial u}{\partial x} - \frac{1}{\rho} \frac{\partial \rho^{\circ}}{\partial x} + \frac{1}{\rho} \rho^{\circ} \underline{1}, \\ \left(\frac{\partial T}{\partial t} \right)' &= -u \frac{\partial T}{\partial x} - \frac{2}{3k} \left(\underline{k}^{\circ} : \frac{\partial u}{\partial x} + \underline{d} + \underline{d} \right) = -u \frac{\partial T}{\partial x} - \frac{2}{3} T (1-\sigma) \frac{\partial u}{\partial x}, \end{aligned} \quad (2-65)$$

where /

where

$$\begin{aligned}
 \underline{\underline{L}}^0 &= \underline{\underline{L}}_1^0 + \underline{\underline{L}}_2^0 = nkT \underline{\underline{1}} , \\
 p_1 r_1' &= n_1 \underline{\underline{F}}_1 - \left\{ \frac{\partial}{\partial \underline{\underline{x}}_1} \cdot \underline{\underline{L}}_1^0 + \int [N_{1T}'] \frac{\partial \psi}{\partial \underline{\underline{x}}_1^{(1)}} d\underline{\underline{x}}_2^{(1)} \right\} , \\
 \underline{\underline{L}}_1^0 &= \frac{1}{2} \int r_1 \frac{\partial \phi_1}{\partial \underline{\underline{x}}_1^{(1)}} [N_{20}^0] d\underline{\underline{x}}_1^{(1)} + \frac{m_2}{m_1 + m_2} \int \underline{\underline{L}}_1 \frac{\partial \psi}{\partial \underline{\underline{x}}_1^{(1)}} [N_{1T}] d\underline{\underline{x}}_2^{(1)} \\
 \underline{\underline{r}}_1 &= \underline{\underline{x}}_1^{(1)} - \underline{\underline{x}}_1^{(2)} , \quad \underline{\underline{r}}_2 = \underline{\underline{x}}_2^{(1)} - \underline{\underline{x}}_1^{(1)} , \\
 p_1 r_1' + p_2 r_2' &= \underline{\underline{F}} - \frac{\partial}{\partial \underline{\underline{x}}} \cdot \underline{\underline{L}}^0 , \\
 \underline{\underline{F}} &= n_1 \underline{\underline{F}}_1 + n_2 \underline{\underline{F}}_2 , \quad \underline{\underline{L}}^0 = \underline{\underline{L}}_1^0 + \underline{\underline{L}}_2^0 , \\
 \underline{\underline{P}}^0 &= \underline{\underline{K}}^0 + \underline{\underline{L}}^0 , \\
 \delta_1' + \delta_2' &= -\sigma nkT \frac{\partial}{\partial \underline{\underline{x}}} \cdot \underline{\underline{u}} , \\
 \sigma &= \frac{(n_1 \frac{\partial}{\partial n_1} + n_2 \frac{\partial}{\partial n_2} + \frac{2}{3} T \frac{\partial}{\partial T} - 1) I}{(nkT + \frac{2}{3} T \frac{\partial}{\partial T} I)} \\
 I &= \frac{1}{2} \left\{ n_1 \left(\int \frac{[N_{20}^0]}{n_1} \phi_1 d\underline{\underline{x}}_1^{(1)} + \int \frac{[N_{1T}']}{n_1} \psi d\underline{\underline{x}}_2^{(1)} \right) + n_2 \left(\int \frac{[N_{02}^0]}{n_2} \phi_2 d\underline{\underline{x}}_2^{(1)} + \int \frac{[N_{1T}']}{n_2} \psi d\underline{\underline{x}}_1^{(1)} \right) \right\}
 \end{aligned} \tag{2-66}$$

The last three equations in (2-66) will be proved presently. It has to be pointed out that $\underline{\underline{L}}_1^0$ is not the whole of the partial potential pressure to the zeroth order but only part of it, the divergence of the rest which is chiefly responsible for neutral diffusion in non-uniform fluids is $\int [N_{1T}'] \frac{\partial \psi}{\partial \underline{\underline{x}}_1^{(1)}} d\underline{\underline{x}}_2^{(1)}$. This does not vanish because N_{1T}' is not symmetric with respect to the two different molecules concerned. The sum $(N_{1T}' + N_{2T}')$ is symmetric with respect to the two different molecules concerned, hence $\int (N_{1T}' + N_{2T}') \frac{\partial \psi}{\partial \underline{\underline{x}}_1} d\underline{\underline{x}}_1 = 0$ and $\underline{\underline{L}}^0$ does not contain terms of this type.

With the aid of (2-66), we can investigate $\left(\frac{\partial}{\partial t} n_{h_1 h_2}\right)^0$ $\left(\frac{\partial}{\partial t} u_{h_1 h_2}\right)^0$ and $\left(\frac{\partial}{\partial t} T_{h_1 h_2}\right)^0$ to the zeroth order by expanding (2-6), (2-23) and (2-29). They are all found to vanish. The expansion of $\left(\frac{\partial}{\partial t} \psi_{h_1 h_2}\right)^0$ leads to equation (2-61). The expansion of $\left(\frac{\partial}{\partial t} \psi_{h_1 h_2}\right)'$ may be used /

used to obtain the last three expressions in (2 - 66)

thus

$$\begin{aligned} \left(\frac{\partial}{\partial T} n_{h_1 h_2}\right) &= \left(\frac{\partial n_1}{\partial T}\right)' \frac{\partial N_{h_1 h_2}^0}{\partial n_1} + \left(\frac{\partial n_2}{\partial T}\right)' \frac{\partial N_{h_1 h_2}^0}{\partial n_2} + \left(\frac{\partial T}{\partial T}\right)' \frac{\partial N_{h_1 h_2}^0}{\partial T} \\ &= -\frac{\partial}{\partial x} \cdot (h_1 u) \frac{\partial N_{h_1 h_2}^0}{\partial n_1} - \frac{\partial}{\partial x} \cdot (h_2 u) \frac{\partial N_{h_1 h_2}^0}{\partial n_2} \\ &\quad + \left\{ u \frac{\partial}{\partial x} T - \frac{2}{3kn} (nkT \frac{\partial}{\partial x} u + \delta_1' + \delta_2') \right\} \frac{\partial N_{h_1 h_2}^0}{\partial T}, \\ &\left\{ \sum_i \frac{\partial}{\partial x_i^{(i)}} (n_{h_1 h_2} u_{h_1 h_2}^{(i)}) + \sum_j \frac{\partial}{\partial x_j^{(j)}} (n_{h_1 h_2} u_{h_1 h_2}^{(j)}) \right\}' = N_{h_1 h_2}^0 \frac{\partial}{\partial x} \cdot u \\ &\quad + \sum_i \frac{\partial}{\partial x_i^{(i)}} (N_{h_1 h_2}^0 u_{h_1 h_2}^{(i)})' + \sum_j \frac{\partial}{\partial x_j^{(j)}} (N_{h_1 h_2}^0 u_{h_1 h_2}^{(j)})' \\ &\quad + u \cdot \left(\frac{\partial n_1}{\partial x} \frac{\partial}{\partial n_1} + \frac{\partial n_2}{\partial x} \frac{\partial}{\partial n_2} + \frac{\partial T}{\partial x} \frac{\partial}{\partial T} \right) N_{h_1 h_2}^0 \end{aligned}$$

Combining the above two expressions, we find

$$\begin{aligned} \left\{ 1 - (n_1 \frac{\partial}{\partial n_1} + n_2 \frac{\partial}{\partial n_2} + \frac{2}{3} T \frac{\partial}{\partial T}) \right\} N_{h_1 h_2}^0 \frac{\partial}{\partial x} \cdot u - \frac{2}{3kn} (\delta_1' + \delta_2') \frac{\partial N_{h_1 h_2}^0}{\partial T} \\ + \sum_i \frac{\partial}{\partial x_i^{(i)}} (N_{h_1 h_2}^0 u_{h_1 h_2}^{(i)})' + \sum_j \frac{\partial}{\partial x_j^{(j)}} (N_{h_1 h_2}^0 u_{h_1 h_2}^{(j)})' = 0 \end{aligned} \quad (2 - 67)$$

For $h_1 = 2, h_2 = 0$ the above equation becomes

$$\frac{\partial}{\partial x_1} \cdot \left\{ N_{20}^0 (u_{20}^{(2)'} - u_{20}^{(1)'}) \right\} = \Gamma N_{20}^0 \frac{\partial}{\partial x} \cdot u - \frac{2}{3kn} (\delta_1' + \delta_2') \frac{\partial N_{20}^0}{\partial T} \quad (2 - 68)$$

where

$$\Gamma = \left(n_1 \frac{\partial}{\partial n_1} + n_2 \frac{\partial}{\partial n_2} + \frac{2}{3} T \frac{\partial}{\partial T} - 1 \right). \quad (2 - 69)$$

Multiplying (2 - 68) by $\frac{1}{2} \phi_1$ and integrating over $d r_1$ we obtain

$$\begin{aligned} \frac{1}{2} \int \phi_1 \frac{\partial}{\partial x_1} \cdot [N_{20}^0 (u_{20}^{(2)'} - u_{20}^{(1)'})] d r_1 &= -\frac{1}{2} \int \frac{\partial \phi_1}{\partial x_1} \cdot [N_{20}^0 (u_{20}^{(2)'} - u_{20}^{(1)'})] d r_1 \\ &= -\int \frac{\partial \phi_1}{\partial x_1^{(1)}} \cdot [(u_{20}^{(1)} - u) N_{20}^0] d x_1^{(1)} = \Gamma I_1^{(1)} \frac{\partial}{\partial x} \cdot u - \frac{2}{3kn} (\delta_1' + \delta_2') \frac{\partial}{\partial T} I_1^{(1)} \end{aligned} \quad (2 - 70)$$

where

$$I_1^{(1)} = \frac{1}{2} \int [N_{20}^0] \phi_1 d x_1^{(1)}$$

Similarly it can be shown that

$$\begin{aligned} -\int \frac{\partial \phi_2}{\partial x_2^{(2)}} \cdot [(u_{02}^{(2)} - u) N_{02}^0] d x_2^{(2)} &= \Gamma I_2^{(2)} \frac{\partial}{\partial x} \cdot u + \frac{2}{3kn} (\delta_1' + \delta_2') \frac{\partial}{\partial T} I_2^{(2)} \\ -\int \frac{\partial \phi_1}{\partial x_1^{(1)}} \cdot [(u_{11}^{(1)} - u) N_{11}^0] d x_1^{(1)} &= \Gamma I_1^{(1)} \frac{\partial}{\partial x} \cdot u + \frac{2}{3kn} (\delta_1' + \delta_2') \frac{\partial}{\partial T} I_1^{(1)} \\ -\int \frac{\partial \phi_2}{\partial x_2^{(2)}} \cdot [(u_{11}^{(2)} - u) N_{11}^0] d x_2^{(2)} &= \Gamma I_2^{(2)} \frac{\partial}{\partial x} \cdot u + \frac{2}{3kn} (\delta_1' + \delta_2') \frac{\partial}{\partial T} I_2^{(2)} \end{aligned} \quad (2 - 70)a$$

where /

where

$$I_1^{(2)} = \frac{1}{2} \int [N_{1T}^0] \psi dx_2'' , \quad I_2^{(2)} = \frac{1}{2} \int [N_{2T}^0] \psi dx_1'' , \quad I_3^{(2)} = \int [N_{22}^0] \psi_2 dx_2''$$

$$\frac{u_{T1}^{(2)}}{n_{T1}} = \iint f_{T1} \xi_2'' d\xi_2'' d\xi_1''$$

Adding (2 - 70) and (2 - 70)a together, we obtain

$$-(\delta_1' + \delta_2') = \Gamma I \frac{\partial u}{\partial x} + \frac{2}{3kn} (\delta_1' + \delta_2') \frac{\partial}{\partial T} I$$

Hence

$$(\delta_1' + \delta_2') = -\sigma n k T \frac{\partial u}{\partial x} ,$$

where

$$\sigma = \frac{\Gamma I}{(n k T + \frac{1}{3} T \frac{\partial}{\partial T} I)} , \quad I = (I_1^{(2)} + I_2^{(2)}) + (I_3^{(2)} + I_1^{(2)})$$

The last three relations in (2 - 66) are thus proved.

II - 8. Expansion of the equation of motion - first approximation.

The first order terms of the expansion of (2 - 17)

are

$$\begin{aligned} \left(\frac{\partial f_{nh_1}}{\partial t} \right)' &= \left(\frac{\partial n_1}{\partial t} \right)' \frac{\partial F_{nh_1}^0}{\partial n_1} + \left(\frac{\partial n_2}{\partial t} \right)' \frac{\partial F_{nh_1}^0}{\partial n_2} + \left(\frac{\partial T}{\partial t} \right)' \frac{\partial F_{nh_1}^0}{\partial T} + \left(\frac{\partial u}{\partial t} \right)' \frac{\partial F_{nh_1}^0}{\partial u} \\ &= \left(\frac{\partial}{\partial x} \cdot (n_1 u) \frac{\partial N_{nh_1}^0}{\partial n_1} + \frac{\partial}{\partial x} \cdot (n_2 u) \frac{\partial N_{nh_1}^0}{\partial n_2} \right) \frac{F_{nh_1}^0}{N_{nh_1}^0} + \left(-u \frac{\partial u}{\partial x} - \frac{1}{\rho} \frac{\partial P}{\partial x} + \frac{E}{\rho} \right) \cdot \frac{\mathcal{G}}{kT} \frac{F_{nh_1}^0}{N_{nh_1}^0} \\ &\quad + \left(-u \frac{\partial T}{\partial x} - \frac{2}{3} (1-\sigma) T \frac{\partial u}{\partial x} \right) \left(\frac{T}{N_{nh_1}^0} \frac{\partial N_{nh_1}^0}{\partial T} + \frac{E}{kT} - \frac{3}{2} h \right) \frac{F_{nh_1}^0}{T} \end{aligned}$$

where

$$\mathcal{G} = \sum_i m_i v_i^{(i)} + \sum_j m_j v_j^{(j)} , \quad E = \frac{1}{2} \left(\sum_i m_i (v_i^{(i)})^2 + \sum_j m_j (v_j^{(j)})^2 \right) ,$$

$$M = \epsilon_1 m_1 + \epsilon_2 m_2 ,$$

$$\begin{aligned} \left\{ \left(\sum_i \xi_i^{(i)} \frac{\partial}{\partial x_i^{(i)}} + \sum_j \xi_j^{(j)} \frac{\partial}{\partial x_j^{(j)}} \right) F_{nh_1}^0 \right\}' &= \left(u + \frac{\mathcal{G}}{M} \right) \cdot \left\{ \left(\frac{\partial n_1}{\partial x} \frac{\partial N_{nh_1}^0}{\partial n_1} + \frac{\partial n_2}{\partial x} \frac{\partial N_{nh_1}^0}{\partial n_2} \right) \frac{F_{nh_1}^0}{N_{nh_1}^0} \right. \\ &\quad \left. + \frac{\partial}{\partial x} \cdot u \cdot \frac{\mathcal{G}}{kT} \frac{F_{nh_1}^0}{N_{nh_1}^0} + \frac{\partial T}{\partial x} \left(\frac{T}{N_{nh_1}^0} \frac{\partial N_{nh_1}^0}{\partial T} + \frac{E}{kT} - \frac{3}{2} h \right) \frac{F_{nh_1}^0}{T} \right\} + \sum_i (u + v_i^{(i)}) \frac{\partial F_{nh_1}^0}{\partial x_i^{(i)}} + \sum_j (u + v_j^{(j)}) \frac{\partial F_{nh_1}^0}{\partial x_j^{(j)}} \end{aligned}$$

The right hand side of (2 - 17) contributes

$$\begin{aligned} &\frac{1}{m_1} \sum_i \frac{\partial \omega(h)}{\partial x_i^{(i)}} \frac{\partial F_{nh_1}^0}{\partial \xi_i^{(i)}} + \frac{1}{m_2} \sum_j \frac{\partial \omega(h)}{\partial x_j^{(j)}} \frac{\partial F_{nh_1}^0}{\partial \xi_j^{(j)}} + \left(\sum_i \xi_i^{(i)} v_i^{(i)} + \sum_j \xi_j^{(j)} v_j^{(j)} \right) \frac{F_{nh_1}^0}{kT} \\ &\quad + \iint \left(\frac{1}{m_1} \sum_i \frac{\partial f_{nh_1}^{(i, h+1)}}{\partial x_i^{(i)}} \frac{\partial}{\partial \xi_i^{(i)}} + \frac{1}{m_2} \sum_j \frac{\partial f_{nh_1}^{(j, h+1)}}{\partial x_j^{(j)}} \frac{\partial}{\partial \xi_j^{(j)}} \right) \left[F_{nh_1, h_2}^0 + d_1 \sum_i \frac{\partial \lambda_i}{\partial x} \frac{\partial}{\partial \lambda_i} F_{nh_1, h_2}^0 \right] dx_1^{(h+1)} dx_2^{(h+1)} \\ &\quad + \iint \left(\frac{1}{m_2} \sum_j \frac{\partial f_{nh_1}^{(j, h+1)}}{\partial x_j^{(j)}} \frac{\partial}{\partial \xi_j^{(j)}} + \frac{1}{m_1} \sum_i \frac{\partial f_{nh_1}^{(i, h+1)}}{\partial x_i^{(i)}} \frac{\partial}{\partial \xi_i^{(i)}} \right) \left[F_{nh_1, h_2}^0 + d_2 \sum_j \frac{\partial \lambda_j}{\partial x} \frac{\partial}{\partial \lambda_j} F_{nh_1, h_2}^0 \right] dx_2^{(h+1)} dx_1^{(h+1)} , \end{aligned}$$

where /

where

$$d_1 = \frac{m_1}{M+m_1} (x_1^{(h_1+1)} - x), \quad d_2 = \frac{m_2}{M+m_2} (x_2^{(h_2+1)} - x).$$

Combining the above results and rearranging terms, we obtain for the first order equation of motion of the set h_1, h_2 .

$$\begin{aligned} F_{h_1 h_2}^0 \subseteq \left\{ \frac{1}{M N_{h_1 h_2}^0} \left(\frac{\partial n_1}{\partial x} \frac{\partial}{\partial n_1} + \frac{\partial n_2}{\partial x} \frac{\partial}{\partial n_2} \right) N_{h_1 h_2}^0 - \frac{1}{\rho} \frac{\partial n}{\partial x} - \frac{1}{\rho k T} \left(\frac{\partial n_1}{\partial x} \frac{\partial}{\partial n_1} + \frac{\partial n_2}{\partial x} \frac{\partial}{\partial n_2} \right) L^0 \right\} \\ - F_{h_1 h_2}^0 \left\{ \frac{1}{N_{h_1 h_2}^0} \left(n_1 \frac{\partial}{\partial n_1} + n_2 \frac{\partial}{\partial n_2} \right) N_{h_1 h_2}^0 + \frac{2}{3} (1-\sigma) \left(\frac{T}{N_{h_1 h_2}^0} \frac{\partial N_{h_1 h_2}^0}{\partial T} + \frac{E}{k T} - \frac{3}{2} h \right) - \frac{1}{3} \frac{G^2}{M k T} \right\} \frac{\partial}{\partial x} u \\ + \frac{F_{h_1 h_2}^0}{M k T} \left\{ \frac{\partial}{\partial x} u + \frac{F_{h_1 h_2}^0}{T} \left[\frac{T}{N_{h_1 h_2}^0} \frac{\partial N_{h_1 h_2}^0}{\partial T} + \frac{E}{k T} - \frac{3}{2} h - \frac{M n}{\rho} - \frac{M}{\rho k} \frac{\partial L^0}{\partial T} \right] \frac{\partial}{\partial T} \right\} \frac{\partial}{\partial x} u \quad (2-71) \\ + \frac{F_{h_1 h_2}^0}{k T} \left\{ \frac{E \cdot G}{\rho} + \frac{G_1 \cdot F_1}{m_1} + \frac{G_2 \cdot F_2}{m_2} \right\} + \sum_i v_i^{(j)} \frac{\partial F_{h_1 h_2}^0}{\partial x_i^{(j)}} + \sum_j v_2^{(j)} \frac{\partial F_{h_1 h_2}^0}{\partial x_2^{(j)}} = \left(\frac{1}{m_1} \sum_i \frac{\partial \psi^{(h_1+1)}_i}{\partial x_i^{(j)}} \frac{\partial}{\partial x_i^{(j)}} + \frac{1}{m_2} \sum_j \frac{\partial \psi^{(h_2+1)}_j}{\partial x_2^{(j)}} \frac{\partial}{\partial x_2^{(j)}} \right) F_{h_1 h_2}^0 \\ + \left\{ \left(\frac{1}{m_1} \sum_i \frac{\partial \psi^{(h_1+1)}_i}{\partial x_i^{(j)}} \frac{\partial}{\partial x_i^{(j)}} + \frac{1}{m_2} \sum_j \frac{\partial \psi^{(h_2+1)}_j}{\partial x_2^{(j)}} \frac{\partial}{\partial x_2^{(j)}} \right) \left[F'_{h_1 h_2} + d_1 \sum_e \frac{\partial \lambda_e}{\partial x} \frac{\partial}{\partial \lambda_e} F_{h_1 h_2}^0 \right] d x_1^{(h_1+1)} d x_1^{(h_1+1)} \right. \\ \left. + \left\{ \left(\frac{1}{m_1} \sum_i \frac{\partial \psi^{(h_1+1)}_i}{\partial x_i^{(j)}} \frac{\partial}{\partial x_i^{(j)}} + \frac{1}{m_2} \sum_j \frac{\partial \psi^{(h_2+1)}_j}{\partial x_2^{(j)}} \frac{\partial}{\partial x_2^{(j)}} \right) \left[F'_{h_1 h_2} + d_2 \sum_e \frac{\partial \lambda_e}{\partial x} \frac{\partial}{\partial \lambda_e} F_{h_1 h_2}^0 \right] d x_2^{(h_2+1)} d x_2^{(h_2+1)} \right\} \right. \end{aligned}$$

where

$$G_1 = \sum_i m_1 v_i^{(j)}, \quad G_2 = \sum_j m_2 v_2^{(j)}.$$

For $h_1=1, h_2=0$ equation (2-71) becomes

$$\begin{aligned} f_1^0 \left\{ \frac{1}{\rho} \frac{\partial n_1}{\partial x} - \frac{1}{\rho} \frac{\partial n}{\partial x} - \frac{1}{\rho k T} \left(\frac{\partial n_1}{\partial x} \frac{\partial}{\partial n_1} + \frac{\partial n_2}{\partial x} \frac{\partial}{\partial n_2} \right) L^0 \right\} \cdot m_1 v_1 + f_1^0 \frac{m_1}{k T} v_1 = \frac{\partial}{\partial x} u \\ + f_1^0 \left\{ \sigma \left(\frac{m_1 v_1^2}{3 k T} - 1 \right) \frac{\partial}{\partial x} u + \frac{f_1^0}{T} \left[\frac{m_1 v_1^2}{2 k T} - \frac{5}{2} + \frac{\rho - n m_1}{\rho} - \frac{m_1}{\rho k} \frac{\partial L^0}{\partial T} \right] \frac{\partial T}{\partial x} v_1 + \frac{f_1^0}{k T} \left(\frac{m_1 E}{\rho} - F_2 \right) \cdot v_1 \right. \\ = \frac{1}{m_1} \left\{ \frac{\partial \psi}{\partial x_1^{(1)}} \frac{\partial}{\partial x_1^{(1)}} \left[F'_{20} + \frac{r_1}{2} \sum_e \frac{\partial \lambda_e}{\partial x} \frac{\partial}{\partial \lambda_e} F_{20}^0 \right] d x_1^{(1)} d x_1^{(1)} \right. \\ \left. + \frac{1}{m_2} \left\{ \frac{\partial \psi}{\partial x_2^{(1)}} \frac{\partial}{\partial x_2^{(1)}} \left[F'_{1T} + \frac{5}{2} \sum_e \frac{\partial \lambda_e}{\partial x} \frac{\partial}{\partial \lambda_e} F_{1T}^0 \right] d x_2^{(1)} d x_2^{(1)} \right\} \right. \quad (2-72) \end{aligned}$$

The R.H.S. after substituting the known solutions

F_{20}^0, F_{1T}^0 and performing integration becomes

$$\begin{aligned} - \frac{1}{m_1} \left\{ \frac{\partial \psi}{\partial x_1^{(1)}} \frac{\partial}{\partial x_1^{(1)}} \left[F'_{20} \right] d x_1^{(1)} d x_1^{(1)} - \frac{1}{m_2} \left\{ \frac{\partial \psi}{\partial x_2^{(1)}} \frac{\partial}{\partial x_2^{(1)}} \left[F'_{1T} \right] d x_2^{(1)} d x_2^{(1)} \right. \right. \\ - f_1^0 \frac{v_1}{n_1 k T} \left(\frac{5}{2} \sum_e \frac{\partial \lambda_e}{\partial x} \frac{\partial L_1^0}{\partial \lambda_e} \right) - \frac{f_1^0}{T} \frac{L_1^0}{n_1 k T} \left(\frac{m_1 v_1^2}{2 k T} - \frac{5}{2} \right) \frac{\partial T}{\partial x} v_1 \\ - f_1^0 \frac{L_1^0}{n_1 k T} \left(\frac{m_1}{k T} \right) v_1 v_1 = \frac{\partial}{\partial x} u - f_1^0 \frac{L_1^0}{n_1 k T} \left(\frac{m_1 v_1^2}{3 k T} - 1 \right) \frac{\partial}{\partial x} u. \quad (2-73) \end{aligned}$$

Combining (2-72) with (2-73), we have

$$\begin{aligned} \frac{f_1^0}{m_1} \frac{\rho_1 \rho_2}{\rho} \left\{ \frac{1}{\rho} + \frac{1}{k T} \left(\frac{1}{\rho_1} \frac{\partial L_1^0}{\partial n_1} - \frac{1}{\rho_2} \frac{\partial L_2^0}{\partial n_2} \right) \right\} v_1 \frac{\partial n_1}{\partial x} - \left\{ \frac{d_1^2}{k T} + \frac{1}{k T} \left(\frac{1}{\rho_1} \frac{\partial L_1^0}{\partial n_1} - \frac{1}{\rho_2} \frac{\partial L_2^0}{\partial n_2} \right) \right\} v_1 \frac{\partial n_2}{\partial x} \\ + f_1^0 \frac{m_1}{k T} \left(1 + \frac{L_1^0}{n_1 k T} \right) v_1 v_1 = \frac{\partial}{\partial x} u + f_1^0 \left(\sigma + \frac{L_1^0}{n_1 k T} \right) \left(\frac{m_1 v_1^2}{3 k T} - 1 \right) \frac{\partial}{\partial x} u + \frac{f_1^0 \rho_1 \rho_2}{m_1 \rho k T} a \cdot v_1 \quad (2-74) \\ + \frac{f_1^0}{T} \left\{ \left(1 + \frac{L_1^0}{n_1 k T} \right) \left(\frac{m_1 v_1^2}{2 k T} - \frac{5}{2} \right) + \frac{1}{m_1} \left[\frac{n_1 m_2}{\rho} (m_2 - m_1) + \frac{\rho_1 \rho_2}{\rho} \left(\frac{1}{\rho_1} \frac{\partial L_1^0}{\partial T} - \frac{1}{\rho_2} \frac{\partial L_2^0}{\partial T} \right) \right] \right\} v_1 \frac{\partial T}{\partial x} \\ = - \frac{1}{m_1} \left\{ \left\{ \frac{\partial \psi}{\partial x_1^{(1)}} \frac{\partial}{\partial x_1^{(1)}} \left[F'_{20} \right] d x_1^{(1)} d x_1^{(1)} + \left\{ \frac{\partial \psi}{\partial x_2^{(1)}} \frac{\partial}{\partial x_2^{(1)}} \left[F'_{1T} \right] d x_2^{(1)} d x_2^{(1)} \right\} \right. \right. \end{aligned}$$

where

where

$$\underline{a} = \frac{F_2}{m_2} - \frac{F_1}{m_1}$$

is the difference of acceleration of the two kinds of molecules in the external field.

A similar equation can by symmetry be written down for f_2° , $f_{2'}^{\circ}$ and $f_{1'}^{\circ}$. Equation (2 - 74) is an exact analogue of the corresponding equations in gas theory. (c.f. Chapman and Cowling, The Mathematical Theory of non-uniform gases, 1939). Though equation (2 - 74) is successful in expressing the rate of change of f_1° in terms of $f_{2'}^{\circ}$ and $f_{1'}^{\circ}$ corresponding to the collision integral in the gas theory, yet in contrast to the latter where the statistical effect of the predominant mechanism of interaction (binary encounter) has actually been taken into account, it has only formal value as it stands. However there are two possible ways of solving the problem: the first is to proceed to equations containing more than two molecules in the set h_1, h_2 and use approximations similar to Kirkwood's for n_{30} , thus closed equations are obtained. The complications there involved in a mixture are likely to be considerable. The second and much more practical approach to the problem consists in transforming the R.H.S. of (2 - 74) to the form of the Maxwell and Boltzmann's Collision integral and using the resultant force due to molecules surrounding the incoming molecule as well as the scatterer molecule in calculating the trajectory of the incoming molecule. For instance when both the incoming and scatter molecule are of the first /

first kind the resultant force is (c.f. (2 - 61)

$$\frac{kT}{n_{20}} \frac{\partial n_{20}}{\partial x_1^{(1)}} = - \frac{\partial \phi_1}{\partial x_1^{(1)}} - \int \frac{n_{30}}{n_{20}} \frac{\partial \phi_1}{\partial x_1^{(1)}} dx_1^{(2)} - \int \frac{n_{2T}}{n_{20}} \frac{\partial \psi}{\partial x_1^{(1)}} dx_2^{(1)} = - \frac{\partial \phi_1^*}{\partial x_1^{(1)}}$$

where ϕ_1^* is the apparent potential. The trajectory thus calculated would represent the average behaviour of a molecule in the vicinity of a given molecule though in each individual case the path might be very different. In a liquid, the assumption of binary molecular encounter never holds, but by using the apparent potentials ϕ_1^* etc., we can take account of the influence of the surrounding molecules upon the velocity distribution of a molecule at a given position one at a time. The apparent potential ϕ_1^* has been worked out for a liquid at particular temperatures consisting only of one kind of molecules in equilibrium by E.A. Rodriguez and A.G. Melchian in the same department. The approximation made in the above procedure is the neglect of the dependence of the apparent potentials on the velocities of the two molecules concerned. Detailed calculation and the complete elucidation of this aspect of the situation remains to be a subject of further research.

II - 9. General expressions for the coefficient of ordinary and thermal diffusion and of viscosity and thermal conduction in liquid mixtures.

The quantities required for calculating the coefficient /

efficient of ordinary and thermal diffusion are F_1' and F_2' those for calculating the coefficient of viscosity are $F_1', F_2', N_{20}', N_{1T}'$ etc, and for the coefficient of thermal conduction $F_1', F_2', N_{20}', N_{1T}', \dots, N_{20}' U_{20}''', N_{20}' (U_{20}'' + U_{20}'''), \dots$ etc. From quite general considerations the form of the above quantities can be determined.

First consider F_1' and F_2' : they are linear in $\frac{\partial \lambda_e}{\partial x}$ and satisfy the conditions

$$\left. \begin{aligned} n_1' &= \int F_1' dv_1 = 0, & n_2' &= \int F_2' dv_2 = 0 \\ p_1 u_1' + p_2 u_2' &= m_1 \int F_1' v_1 dv_1 + m_2 \int F_2' v_2 dv_2 = 0 \\ n_1 T_1' + n_2 T_2' &= \frac{2m_1}{3k} \int F_1' \left(\frac{1}{2} v_1^2 - \frac{3k}{2m_1} T \right) dv_1 + \frac{2m_2}{3k} \int F_2' \left(\frac{1}{2} v_2^2 - \frac{3k}{2m_2} T \right) dv_2 \\ &= \frac{1}{3k} \left\{ m_1 \int F_1' v_1^2 dv_1 + m_2 \int F_2' v_2^2 dv_2 \right\} = 0 \end{aligned} \right\} (2-75)$$

which says that any further correction to the velocity distributions F_1^0 and F_2^0 shall not alter the values of the local parameters λ_e (For the present purpose, the presence of an external force field will not be considered.) v_1 and v_2 are used for v_1'' and v_2'' respectively for simplicity.

Hence F_1' and F_2' are of the form

$$\left. \begin{aligned} F_1' &= \varphi_1^{(1)} v_1 \frac{\partial m}{\partial x} + \varphi_1^{(2)} v_1 \frac{\partial m}{\partial x} + \varphi_1^{(3)} v_1 \frac{\partial T}{\partial x} + \varphi_1^{(4)} v_1 v_1 = \frac{\partial}{\partial x} \psi_1 \\ F_2' &= \varphi_2^{(1)} v_2 \frac{\partial m}{\partial x} + \varphi_2^{(2)} v_2 \frac{\partial m}{\partial x} + \varphi_2^{(3)} v_2 \frac{\partial T}{\partial x} + \varphi_2^{(4)} v_2 v_2 = \frac{\partial}{\partial x} \psi_2 \end{aligned} \right\} (2-76)$$

where

$$m_1 \int \varphi_1^{(i)} v_1^2 dv_1 + m_2 \int \varphi_2^{(i)} v_2^2 dv_2 = 0, \quad (i=1, 2, 3). \quad (2-77)$$

Next /

Next consider N_{20}' : it is linear in $\frac{\partial \lambda_e}{\partial x}$, even in r_1 ($= x_1^{(2)} - x_1^{(1)}$) and satisfies $\int N_{20}' d r_1 = 0$ hence it must be of the form

$$N_{20}' = \nu_{20}^{(4)} \frac{r_1 r_2}{r_1^2} = \frac{\partial \mu}{\partial x} \quad (2-78)$$

where $\nu_{20}^{(4)}$ is a function of r_1 and λ_e .

Similarly, we have for N_{02}'

$$N_{02}' = \nu_{02}^{(4)} \frac{r_1 r_2}{r_2^2} = \frac{\partial \mu}{\partial x} \quad (2-79)$$

N_{1T}' and N_{T1}' are however not so simple since neither of them is even in the relative position vector or symmetrical with respect to the two molecules concerned; but the sum ($N_{1T}' + N_{T1}'$) is an even function of s_1 ($= x_2^{(1)} - x_1^{(1)}$) and the difference ($N_{1T}' - N_{T1}'$) an odd function of s_1 . Hence

$$N_{1T}' + N_{T1}' = 2 \nu_{11}^{(4)} s_1 s_2 = \frac{\partial \mu}{\partial x}$$

$$N_{1T}' - N_{T1}' = 2 \nu_{11}^{(1)} s_1 \frac{\partial n_1}{\partial x} + 2 \nu_{11}^{(2)} s_1 \frac{\partial n_2}{\partial x} + 2 \nu_{11}^{(3)} s_1 \frac{\partial T}{\partial x}$$

It follows from the above equations that

$$\left. \begin{aligned} N_{1T}' &= \nu_{11}^{(1)} s_1 \frac{\partial n_1}{\partial x} + \nu_{11}^{(2)} s_1 \frac{\partial n_2}{\partial x} + \nu_{11}^{(3)} s_1 \frac{\partial T}{\partial x} + \nu_{11}^{(4)} s_1 s_2 = \frac{\partial \mu}{\partial x} \\ N_{T1}' &= \nu_{11}^{(1)} s_2 \frac{\partial n_1}{\partial x} + \nu_{11}^{(2)} s_2 \frac{\partial n_2}{\partial x} + \nu_{11}^{(3)} s_2 \frac{\partial T}{\partial x} + \nu_{11}^{(4)} s_2 s_1 = \frac{\partial \mu}{\partial x} \end{aligned} \right\} (2-80)$$

where $s_2 = -s_1$.

To find an expression for $N_{20} U_{20}^{(1) \prime}$ we notice that $N_{20}^0 (U_{20}^{(1) \prime} + U_{20}^{(2) \prime})$ is even in r_1 , and $N_{20}^0 (U_{20}^{(1) \prime} - U_{20}^{(2) \prime})$ is odd in r_1 , hence

$$\left. \begin{aligned} N_{20}^0 (U_{20}^{(1) \prime} + U_{20}^{(2) \prime}) &= 2 \left(\nu_{20}^{(1)} \frac{r_1 r_2}{r_1^2} + \nu_{20}^{(2)} \frac{r_1 r_2}{r_2^2} \right) \frac{\partial n_1}{\partial x} \\ &\quad + 2 \left(\nu_{20}^{(3)} \frac{r_1 r_2}{r_1^2} + \nu_{20}^{(4)} \frac{r_1 r_2}{r_2^2} \right) \frac{\partial n_2}{\partial x} + 2 \left(\nu_{20}^{(5)} \frac{r_1 r_2}{r_1^2} + \nu_{20}^{(6)} \frac{r_1 r_2}{r_2^2} \right) \frac{\partial T}{\partial x} \\ N_{20}^0 (U_{20}^{(1) \prime} - U_{20}^{(2) \prime}) &= 2 \nu_{20}^{(1)} \frac{\partial \mu}{\partial x} r_1 + 2 \nu_{20}^{(2)} r_1 \frac{r_1 r_2}{r_1^2} = \frac{\partial \mu}{\partial x} \\ &\quad + 2 \nu_{20}^{(3)} r_1^2 \frac{\partial \mu}{\partial x} r_1 \end{aligned} \right\} (2-81)$$

It /

It follows therefore

$$\begin{aligned}
 N_{20}^0 \underline{U}_{20}^{(i)'} &= (\omega_{20}^{(i)} r_1^0 + \omega_{20}^{(i)'} r_1^2 \perp) \cdot \frac{\partial n_1}{\partial x} + (\omega_{20}^{(i)} r_1^0 + \omega_{20}^{(i)'} r_1^2 \perp) \cdot \frac{\partial n_2}{\partial x} \\
 &+ (\omega_{20}^{(i)} r_1^0 + \omega_{20}^{(i)'} r_1^2 \perp) \cdot \frac{\partial I}{\partial x} \\
 &- \left(\omega_{20}^{(i)} \frac{\partial}{\partial x} \cdot r_1 + \omega_{20}^{(i)'} r_1 \cdot \frac{\partial}{\partial x} + \omega_{20}^{(i)'} r_1^2 \frac{\partial}{\partial x} \cdot r_1 \right)
 \end{aligned} \quad (2-82)$$

Similarly one can write down the expressions for

$N_{02}^0 (\underline{U}_{02}^{(i)'} + \underline{U}_{02}^{(i)'})$ and $N_{02}^0 \underline{U}_{02}^{(i)'}$. To find an expression for $N_{1T}^0 \underline{U}_{1T}^{(i)'}$, we notice that $(N_{1T}^0 \underline{U}_{1T}^{(i)'} + N_{T1}^0 \underline{U}_{T1}^{(i)'})$ is even in \underline{s}_1 , and $(N_{1T}^0 \underline{U}_{1T}^{(i)'} - N_{T1}^0 \underline{U}_{T1}^{(i)'})$ odd in \underline{s}_1 , therefore we have

$$\begin{aligned}
 N_{1T}^0 \underline{U}_{1T}^{(i)'} &= (\omega_1^{(i)} \underline{s}_1 \underline{s}_1 + \omega_1^{(i)'} s_1^2 \perp) \cdot \frac{\partial n_1}{\partial x} + (\omega_1^{(i)} \underline{s}_1 \underline{s}_1 + \omega_1^{(i)'} s_1^2 \perp) \cdot \frac{\partial n_2}{\partial x} \\
 &+ (\omega_1^{(i)} \underline{s}_1 \underline{s}_1 + \omega_1^{(i)'} s_1^2 \perp) \cdot \frac{\partial I}{\partial x} + \omega_1^{(i)} \frac{\partial}{\partial x} \cdot \underline{s}_1 \\
 &+ \omega_1^{(i)'} \underline{s}_1 \underline{s}_1 \cdot \frac{\partial}{\partial x} \cdot \underline{s}_1 + \omega_1^{(i)'} s_1^2 \frac{\partial}{\partial x} \cdot \underline{s}_1 \\
 N_{T1}^0 \underline{U}_{T1}^{(i)'} &= (\omega_1^{(i)} \underline{s}_2 \underline{s}_2 + \omega_1^{(i)'} s_2^2 \perp) \cdot \frac{\partial n_1}{\partial x} + (\omega_1^{(i)} \underline{s}_2 \underline{s}_2 + \omega_1^{(i)'} s_2^2 \perp) \cdot \frac{\partial n_2}{\partial x} \\
 &+ (\omega_1^{(i)} \underline{s}_2 \underline{s}_2 + \omega_1^{(i)'} s_2^2 \perp) \cdot \frac{\partial I}{\partial x} + \omega_1^{(i)} \frac{\partial}{\partial x} \cdot \underline{s}_2 \\
 &+ \omega_1^{(i)'} \underline{s}_2 \underline{s}_2 \cdot \frac{\partial}{\partial x} \cdot \underline{s}_2 + \omega_1^{(i)'} s_2^2 \frac{\partial}{\partial x} \cdot \underline{s}_2
 \end{aligned} \quad (2-83)$$

By similar reasoning we can obtain

$$\begin{aligned}
 N_{T1}^0 \underline{U}_{T1}^{(i)'} &= (\omega_2^{(i)} \underline{s}_2 \underline{s}_2 + \omega_2^{(i)'} s_2^2 \perp) \cdot \frac{\partial n_1}{\partial x} + (\omega_2^{(i)} \underline{s}_2 \underline{s}_2 + \omega_2^{(i)'} s_2^2 \perp) \cdot \frac{\partial n_2}{\partial x} \\
 &+ (\omega_2^{(i)} \underline{s}_2 \underline{s}_2 + \omega_2^{(i)'} s_2^2 \perp) \cdot \frac{\partial I}{\partial x} + \omega_2^{(i)} \frac{\partial}{\partial x} \cdot \underline{s}_2 \\
 &+ \omega_2^{(i)'} \underline{s}_2 \underline{s}_2 \cdot \frac{\partial}{\partial x} \cdot \underline{s}_2 + \omega_2^{(i)'} s_2^2 \frac{\partial}{\partial x} \cdot \underline{s}_2
 \end{aligned} \quad (2-84)$$

and $N_{1T}^0 \underline{U}_{1T}^{(i)'}$ is obtainable from $N_{T1}^0 \underline{U}_{T1}^{(i)'}$ by changing \underline{s}_2 to \underline{s}_1 . Further the condition $\underline{u}' = 0$ requires that

$$\begin{aligned}
 \frac{m_1}{n_1} \int N_{20}^0 \underline{U}_{20}^{(i)'} d\underline{r}_1 + \frac{m_2}{n_2} \int N_{02}^0 \underline{U}_{02}^{(i)'} d\underline{r}_2 &= 0 \\
 \rho_1 \int N_{1T}^0 \underline{U}_{1T}^{(i)'} d\underline{s}_1 + \rho_2 \int N_{T1}^0 \underline{U}_{T1}^{(i)'} d\underline{s}_2 &= 0
 \end{aligned}$$

Hence

$$\begin{aligned}
 \frac{m_1}{n_1} \int \omega_{20}^{(i)'} r_1^2 d\underline{r}_1 + \frac{m_2}{n_2} \int \omega_{02}^{(i)'} r_2^2 d\underline{r}_2 &= 0 \quad (i=1,2,3) \\
 \rho_1 \int \omega_1^{(i)'} s_1^2 d\underline{s}_1 + \rho_2 \int \omega_2^{(i)'} s_2^2 d\underline{s}_2 &= 0 \quad (i=1,2,3)
 \end{aligned} \quad (2-85)$$

Concerning /

Concerning $\underline{u}_{02}^{(2)'}$, $\underline{u}_{r1}^{(2)'}$ etc., we adopt the convention that for $h_1=2, h_2=0$ or $h_1=0, h_2=2$ the subscript at the top right signifies the first or second molecule in the set, and for $h_1=1, h_2=1$ it specifies the type of the molecule concerned.

With these general expressions in hand, it is easy to find the coefficients of all transport processes in terms of them. Consider diffusion first: the mutual diffusion velocity is

$$\underline{u}'_1 - \underline{u}'_2 = \int \frac{F_1'}{n_1} v_1 dV_1 - \int \frac{F_2'}{n_2} v_2 dV_2 \quad (2-86)$$

As the coefficients of diffusion are measured under constant pressure, it is convenient first to transform the gradients $\frac{\partial n_1}{\partial x}$, $\frac{\partial n_2}{\partial x}$ and $\frac{\partial T}{\partial x}$ appearing in the formal expressions for F_1' and F_2' to $\frac{\partial c_1}{\partial x}$, $\frac{\partial p}{\partial x}$ and $\frac{\partial T}{\partial x}$ according to (1-22) with \underline{p} given by \underline{p}^0 in (2-66).

Thus

$$F_1' = \Omega_1^{(1)} v_1 \frac{\partial c_1}{\partial x} + \Omega_1^{(2)} v_1 \frac{\partial p}{\partial x} + \Omega_1^{(3)} v_1 \frac{\partial T}{\partial x} + \varphi_1^{(1)} v_1 = \frac{\partial \underline{u}}{\partial x} \quad (2-87)$$

where

$$\left. \begin{aligned} \Omega_1^{(1)} &= \frac{n_2}{\Delta p^0} \left(\varphi_1^{(1)} \frac{\partial p^0}{\partial n_2} - \varphi_1^{(2)} \frac{\partial p^0}{\partial n_1} \right) \\ \Omega_1^{(2)} &= \frac{1}{\Delta p^0} \left(\varphi_1^{(1)} n_1 + \varphi_1^{(2)} n_2 \right) \\ \Omega_1^{(3)} &= \varphi_1^{(3)} - \frac{\partial p^0}{\partial T} \frac{(n_1 \varphi_1^{(1)} + n_2 \varphi_1^{(2)})}{\Delta p^0} \\ \Delta &= n_1 \frac{\partial}{\partial n_1} + n_2 \frac{\partial}{\partial n_2} \\ p^0 &= nkT + \frac{1}{6} \left\{ \int N_{20}^0 \phi_1^{(1)}(n) n d\underline{r}_1 + \int N_{02}^0 \phi_2^{(2)}(n) n d\underline{r}_2 + 2 \int N_{1r}^0 \psi(r) S d\underline{s} \right\} \end{aligned} \right\} (2-88)$$

Similar transformation can be applied to F_2' . (2-86)

becomes then

$$\underline{u}'_1 - \underline{u}'_2 = \frac{1}{3} \left\{ \int \Omega_1^{(1)} \frac{v_1^2}{n_1} dV_1 + \int \Omega_2^{(1)} \frac{v_2^2}{n_2} dV_2 \right\} \frac{\partial c_1}{\partial x} + \frac{1}{3} \left\{ \int \Omega_1^{(2)} \frac{v_1^2}{n_1} dV_1 - \int \Omega_2^{(2)} \frac{v_2^2}{n_2} dV_2 \right\} \frac{\partial p}{\partial x} + \frac{1}{3} \left\{ \int \Omega_1^{(3)} \frac{v_1^2}{n_1} dV_1 + \int \Omega_2^{(3)} \frac{v_2^2}{n_2} dV_2 \right\} \frac{\partial T}{\partial x} \quad (2-89)$$

Under /

Under constant pressure, the term involving $\frac{\partial p}{\partial x}$ in (2 - 89) can be dropped. Upon comparing (2 - 89) with (1 - 26), we find

$$D_0 = -\frac{m_1 n_1}{3n^2} \left\{ \int \Omega_1^{(1)} \frac{v_1^2}{n_1} dv_1 + \int \Omega_2^{(1)} \frac{v_2^2}{n_2} dv_2 \right\} \quad (2 - 90)$$

$$D_T = -\frac{m_1 n_1 T}{3n^2} \left\{ \int \Omega_1^{(3)} \frac{v_1^2}{n_1} dv_1 - \int \Omega_2^{(3)} \frac{v_2^2}{n_2} dv_2 \right\}$$

Next consider viscosity: the pressure tensor in the presence of linear gradient $\frac{\partial \lambda_c}{\partial x}$ is $\underline{p} = \underline{p}^0 + \underline{p}'$ where \underline{p}^0 is given in (2 - 66) and

$$\begin{aligned} \underline{p}' &= \underline{k}' + \underline{l}', \\ \underline{k}' &= m_1 \int F_1' v_1 v_1 dv_1 + m_2 \int F_2' v_2 v_2 dv_2 \\ &= \frac{2}{15} \left\{ m_1 \int \varphi_1^{(4)} v_1^4 dv_1 + m_2 \int \varphi_2^{(4)} v_2^4 dv_2 \right\} \frac{\partial \lambda_c}{\partial x}, \\ \underline{l}' &= -\frac{1}{2} \int r_1 \frac{\partial \phi_1}{\partial r_1} N_{20}' dr_1 - \frac{m_2}{m_1 + m_2} \int s_1 \frac{\partial \psi}{\partial s_1} N_{1r}' ds_1 \\ &= -\frac{1}{2} \int r_2 \frac{\partial \phi_2}{\partial r_2} N_{02}' dr_2 - \frac{m_1}{m_1 + m_2} \int s_2 \frac{\partial \psi}{\partial s_2} N_{r1}' ds_2 \\ &= -\frac{1}{15} \left\{ \int v_{20}^{(4)} \phi_1(r_1) r_1^3 dr_1 + \int v_{02}^{(4)} \phi_2(r_2) r_2^3 dr_2 + 2 \int v_{11}^{(4)} \psi(s_1) s_1^3 ds_1 \right\} \end{aligned} \quad (2 - 91)$$

Now the viscosity coefficient μ is defined by the equation

$$\underline{p}' = -2\mu \frac{\partial \lambda_c}{\partial x} \quad (2 - 92)$$

Hence

$$\begin{aligned} \mu &= \mu_p + \mu_k \\ \mu_p &= \frac{1}{30} \left\{ \int v_{20}^{(4)} \phi_1(r_1) r_1^3 dr_1 + \int v_{02}^{(4)} \phi_2(r_2) r_2^3 dr_2 + 2 \int v_{11}^{(4)} \psi(s_1) s_1^3 ds_1 \right\} \\ \mu_k &= \frac{1}{15} \left\{ m_1 \int \varphi_1^{(4)} v_1^4 dv_1 + m_2 \int \varphi_2^{(4)} v_2^4 dv_2 \right\} \end{aligned} \quad (2 - 93)$$

where the first part is the potential viscosity and the second part is the kinetic viscosity, the former plays a predominant role in liquid mixtures.

To calculate the coefficient of thermal conductivity it is necessary to obtain first the energy flux vector

$$\underline{q}' \quad \text{From (2 - 35), (2 - 48), (2 - 56)}$$

$$\underline{q}' = \underline{m}' + \underline{n}' \quad (2-94)$$

$$\begin{aligned} \underline{m}' &= \underline{m}'_{10} + \underline{m}'_{01} + \frac{5}{2} kT (n_1 \underline{u}'_1 + n_2 \underline{u}'_2) \\ &= m_1 \left\{ F_1' \underline{v}_1 \left(v_1^2 - \frac{5}{2} \frac{kT}{m_1} \right) d\underline{v}_1 + m_2 \left\{ F_2' \underline{v}_2 \left(v_2^2 - \frac{5}{2} \frac{kT}{m_2} \right) d\underline{v}_2 \right. \right. \\ &\quad \left. \left. + \frac{5}{2} kT (n_1 \underline{u}'_1 + n_2 \underline{u}'_2) \right\} \right. \\ &= \left\{ \frac{m_1}{3} \int \Omega_1^{(1)} v_1^2 \left(v_1^2 - \frac{5}{2} \frac{kT}{m_1} \right) d\underline{v}_1 + \frac{m_2}{3} \int \Omega_2^{(1)} v_2^2 \left(v_2^2 - \frac{5}{2} \frac{kT}{m_2} \right) d\underline{v}_2 \right\} \frac{\partial c_1}{\partial x} \\ &\quad + \left\{ \frac{m_1}{3} \int \Omega_1^{(3)} v_1^2 \left(v_1^2 - \frac{5}{2} \frac{kT}{m_1} \right) d\underline{v}_1 + \frac{m_2}{3} \int \Omega_2^{(3)} v_2^2 \left(v_2^2 - \frac{5}{2} \frac{kT}{m_2} \right) d\underline{v}_2 \right\} \frac{\partial T}{\partial x} \\ &\quad + \frac{5}{2} kT (n_1 \underline{u}'_1 + n_2 \underline{u}'_2) \end{aligned} \quad (2-95)$$

It has been shown (c.f. Chapman and Cowling's book) that when diffusion is proceeding there is a kinetic heat flow resulting from the flux of $(n_1 \underline{u}'_1 + n_2 \underline{u}'_2)$ molecules per unit time relative to the mass velocity \underline{u} : each molecule carries on the average a quantity $\frac{5}{2} kT$ of heat energy. The thermal conductivity actually measured is under the conditions of constant pressure and steady composition consistent with the uniform temperature gradient i.e. $\frac{\partial p}{\partial x} = 0$, $\underline{u}'_1 = \underline{u}'_2 = 0$.

Thus we can eliminate $\frac{\partial c_1}{\partial x}$ in (2-95) by the equation.

$$\begin{aligned} \underline{u}'_1 - \underline{u}'_2 = 0 &= \frac{1}{3} \left\{ \left(\int \Omega_1^{(1)} \frac{v_1^2}{n_1} d\underline{v}_1 + \int \Omega_2^{(1)} \frac{v_2^2}{n_2} d\underline{v}_2 \right) \frac{\partial c_1}{\partial x} \right. \\ &\quad \left. + \left(\int \Omega_1^{(3)} \frac{v_1^2}{n_1} d\underline{v}_1 + \int \Omega_2^{(3)} \frac{v_2^2}{n_2} d\underline{v}_2 \right) \frac{\partial T}{\partial x} \right\} \end{aligned} \quad (2-96)$$

Hence equation (2-95) becomes

$$\begin{aligned} \underline{m}' &= \left\{ \frac{m_1}{3} \int \Omega_1^{(3)} v_1^2 \left(v_1^2 - \frac{5}{2} \frac{kT}{m_1} \right) d\underline{v}_1 + \frac{m_2}{3} \int \Omega_2^{(3)} v_2^2 \left(v_2^2 - \frac{5}{2} \frac{kT}{m_2} \right) d\underline{v}_2 \right. \\ &\quad \left. + \frac{\left(\int \Omega_1^{(3)} \frac{v_1^2}{n_1} d\underline{v}_1 - \int \Omega_2^{(3)} \frac{v_2^2}{n_2} d\underline{v}_2 \right)}{\left(\int \Omega_1^{(1)} \frac{v_1^2}{n_1} d\underline{v}_1 + \int \Omega_2^{(1)} \frac{v_2^2}{n_2} d\underline{v}_2 \right)} \left(\frac{m_1}{3} \int \Omega_1^{(1)} v_1^2 \left(v_1^2 - \frac{5}{2} \frac{kT}{m_1} \right) d\underline{v}_1 + \frac{m_2}{3} \int \Omega_2^{(1)} v_2^2 \left(v_2^2 - \frac{5}{2} \frac{kT}{m_2} \right) d\underline{v}_2 \right) \right\} \frac{\partial T}{\partial x} \end{aligned}$$

Now the coefficient of kinetic thermal conductivity λ_k is defined by the equation

$$\underline{m}' = -\lambda_k \frac{\partial T}{\partial x}, \quad (2-97)$$

where /

where

$$\lambda_k = - \left\{ \begin{aligned} & \left(\frac{m_1}{3} \int \Omega_1^{(1)} v_1^2 \left(v_1^2 - \frac{kT}{2m_1} \right) dv_1 + \frac{m_2}{3} \int \Omega_2^{(2)} v_2^2 \left(v_2^2 - \frac{kT}{2m_2} \right) dv_2 \right) \\ & - \epsilon \left(\frac{m_1}{3} \int \Omega_1^{(1)} v_1^2 \left(v_1^2 - \frac{kT}{2m_1} \right) dv_1 + \frac{m_2}{3} \int \Omega_2^{(2)} v_2^2 \left(v_2^2 - \frac{kT}{2m_2} \right) dv_2 \right) \end{aligned} \right\} \quad (2-98)$$

$$\epsilon = \left(\int \Omega_1^{(1)} \frac{v_1^2}{n_1} dv_1 - \int \Omega_2^{(2)} \frac{v_2^2}{n_2} dv_2 \right) / \left(\int \Omega_1^{(1)} \frac{v_1^2}{n_1} dv_1 + \int \Omega_2^{(2)} \frac{v_2^2}{n_2} dv_2 \right)$$

In calculating the potential part of the energy flux vector \underline{n}' , we impose at the beginning the conditions $\frac{\partial p}{\partial x} = 0$, $u_i' = u_i'' = 0$. From (2-33) we have

$$\begin{aligned} \frac{\partial}{\partial x} \cdot \underline{n}' = & \frac{1}{2} \left\{ \frac{\partial}{\partial x_1} \left[\int N_{20} u_{20}^{(1)} \phi_1 d\underline{x}_1^{(2)} + \int N_{1T} u_{1T}^{(1)} d\underline{x}_2^{(1)} \right] + \frac{\partial}{\partial x_2} \left[\int N_{02} u_{02}^{(2)} \phi_2 d\underline{x}_2^{(2)} + \int N_{T1} u_{T1}^{(2)} d\underline{x}_1^{(1)} \right] \right\} \\ & - \frac{1}{2} \frac{\partial}{\partial x} \left\{ \int \frac{1}{2} r_1 \frac{\partial \phi_1}{\partial r_1} N_{20} (u_{20}^{(1)} + u_{20}^{(2)}) d\underline{r}_1 + \int \frac{1}{2} r_2 \frac{\partial \phi_2}{\partial r_2} N_{02} (u_{02}^{(1)} + u_{02}^{(2)}) d\underline{r}_2 \right. \\ & \left. + \int \frac{1}{2} s_1 \frac{\partial \psi}{\partial s_1} N_{1T} (u_{1T}^{(1)} + u_{1T}^{(2)}) d\underline{s}_1 + \int \frac{1}{2} s_2 \frac{\partial \psi}{\partial s_2} N_{T1} (u_{T1}^{(1)} + u_{T1}^{(2)}) d\underline{s}_2 \right\} \end{aligned}$$

with terms involving u_i' and u_i'' neglected. Using (2-81) to (2-84) we obtain

$$\underline{n}' = -\theta_1 \frac{\partial n_1}{\partial x} - \theta_2 \frac{\partial n_2}{\partial x} - \theta_3 \frac{\partial T}{\partial x} \quad (2-99)$$

where

$$\begin{aligned} \theta_1 = & \frac{1}{2} \left\{ \left[\frac{1}{15} v_{20}^{(1)} \phi_1' r_1 + v_{20}^{(2)} \left(\frac{1}{3} \phi_1' r_1 - \phi_1 \right) \right] r_1^2 d\underline{r}_1 + \left[\frac{1}{15} v_{02}^{(2)} \phi_2' r_2 + v_{02}^{(1)} \left(\frac{1}{3} \phi_2' r_2 - \phi_2 \right) \right] r_2^2 d\underline{r}_2 \right\} \\ & + \frac{1}{2} \left\{ \left[\frac{1}{15} (\omega_1^{(1)} + \omega_2^{(1)}) \psi' s_1 + (\omega_1^{(2)} + \omega_2^{(2)}) \left(\frac{1}{3} \psi' s_1 - \psi \right) \right] s_1^2 d\underline{s}_1 \right. \end{aligned} \quad (2-100)$$

θ_2 and θ_3 can be obtained from θ_1 through replacing

$v_{20}^{(1)}, \omega_1^{(1)}, \omega_2^{(1)}, \dots$ by $v_{20}^{(2)}, \omega_1^{(2)}, \omega_2^{(2)}, \dots$ and $v_{20}^{(2)}, \omega_1^{(2)}, \omega_2^{(2)}, \dots$

respectively.

Applying transformation (1-22) to (2-99) and dropping terms involving $\frac{\partial p}{\partial x}$, we obtain

$$\underline{n}' = -(\mathbb{H})_1 \frac{\partial c_1}{\partial x} - (\mathbb{H})_3 \frac{\partial T}{\partial x},$$

where

$$(\mathbb{H})_1 = \frac{n^2}{\partial p^0} (\theta_1 \frac{\partial p^0}{\partial n_2} - \theta_2 \frac{\partial p^0}{\partial n_1}),$$

$$(\mathbb{H})_3 = \theta_3 - \frac{\partial p^0}{\partial T} \frac{(n_1 \theta_1 + n_2 \theta_2)}{\partial p^0}$$

Using /

Using the relation (2 - 96), we have

$$\zeta' = - \left\{ \Theta_3 - \epsilon \Theta_1 \right\} \frac{\partial T}{\partial x} \quad (2 - 101)$$

Since the coefficient of potential thermal conductivity λ_p is defined by the equation

$$\zeta' = - \lambda_p \frac{\partial T}{\partial x}, \quad (2 - 102)$$

hence

$$\lambda_p = \Theta_3 - \epsilon \Theta_1, \quad (2 - 103)$$

The coefficient of thermal conductivity λ is equal to the sum of λ_p and λ_k as given by (2 - 103) and (2 - 98).

As mentioned in the beginning of I - 1, the transport of molecular properties are made up of two parts, i.e., the potential and the kinetic part. It has been shown in the present section that both μ and λ can be resolved into two parts. In the case of diffusion,

\mathcal{D}_0 and \mathcal{D}_T consist only the kinetic part. The problem is completely solved once F_1' and F_2' are known. The practical method of solution as discussed in the last section makes possible a rigorous solution to the problem of diffusion in liquids.

I wish to express my thanks to Prof. M. Born who has suggested this problem to me, for his constant interest and encouragement and also to Dr. H.S. Green for many helpful suggestions and discussions.

Appendix I. Calculation of μ and χ for special models.

Consider a binary mixture, the velocities of the colliding molecules of the first and second kind before collision are denoted by v_1^u and v_2^u respectively, those after collision by $v_1^{u'}$, $v_2^{u'}$ respectively. As the collision frequency μ and the deflection probability χ are independent of the frame of reference chosen, we shall assume a frame of reference moving with the local mass motion velocity u . Since molecules of one kind may collide either with a molecule of the same kind or one of the other kind we shall find that both μ and χ consist of two parts (1 - 48), (1 - 49) i.e.

$$\mu_{(1)} = \mu_{11} + \mu_{12}$$

$$\chi_{(12)} = \chi_{11(12)} + \chi_{12(12)}$$

It is obviously sufficient to calculate μ_{12} and $\chi_{12(12)}$. Further each of them can be expanded

$$\mu_{12} = \mu_{12}^0 + \mu_{12}' + \dots$$

$$\chi_{12(12)} = \chi_{12(12)}^0 + \chi_{12(12)}' + \dots$$

where the first term represents the contribution from f_2^0 and the second term from f_2' pertaining to the second kind of molecule in the medium. As μ_{12}' , $\chi_{12(12)}'$ are not required in the present paper, only μ_{12}^0 $\chi_{12(12)}^0$ will be calculated in the following.

I. 1. Rigid sphere model.

The collision frequency of rigid spherical molecules calculated on the assumption of binary encounter and molecular chaos is given in most text books on the kinetic /

kinetic theory of gases. (c.f. Chapman and Cowling 1939). The result is

$$\chi_{12}^0(1) = \left(\frac{2\pi kT}{m_2}\right)^{\frac{1}{2}} \sigma_{12}^2 n_2 E(y_2) \quad (1)$$

where

$$\left. \begin{aligned} \sigma_{12} &= \frac{1}{2}(\sigma_1 + \sigma_2) \\ y_2 &= \sqrt{\frac{m_2}{2kT}} v_1'' \\ E(y_2) &= \left\{ e^{-y_2^2} + \left(2y_2 + \frac{1}{y_2}\right) \int_0^{y_2} e^{-x^2} dx \right\} \end{aligned} \right\} \quad (2)$$

σ_1 and σ_2 being the molecular diameters of the two kinds of molecules and m_1, m_2 the molecular masses.

To calculate χ we proceed at first in a similar manner as in the calculation of μ i.e. counting the probability of the occurrence of a specific type of collision but then integrating over all possible types of collision for which the chosen molecule is deflected into a specific velocity range $v_1^{(1)}, v_1^{(2)}$ after collision. Thus one obtains

$$\chi_{12}^0(12) dt dv_1^{(1)} = \iint_R f_2^0(v_2'') g dt b db d\epsilon dv_2^{(1)} \quad (3)$$

where $f_2^0(v_2'')$ is the Maxwellian velocity distribution of the second type of molecule normalized to its number density. $g = (v_2'' - v_1'')$ is the velocity of a molecule in the medium relative to the chosen molecule.

$b db d\epsilon$ is an elementary cross-section or "target area" in polar coordinates on a plane passing through the chosen molecule and perpendicular to g , b being the radius and ϵ the polar angle. The integration is to be carried out over a region R defined by

$$R: v_1^{(1)} \leq v_1''(v_1'', v_2'', b) \leq v_1^{(2)} + dv_1^{(1)}$$

For /

For binary encounter we have in general

$$v_1^{(2)} = v_1^{(1)} + \left(\frac{2m_2}{m_1 + m_2} \right) (v_2^{(1)} - v_1^{(1)}) \cdot \underline{k} \quad \underline{k}$$

or

$$\underline{p} = \frac{2m_2}{m_0} \underline{g} \cdot \underline{k} \quad \underline{k} \quad (4)$$

where $\underline{p} = v_1^{(2)} - v_1^{(1)}$ is the velocity of the chosen molecule after collision relative to its velocity before collision, $m_0 = m_1 + m_2$, $\underline{k} = \underline{p}/p$ is the unit vector in the direction of \underline{p} .

For rigid spheres, we have in particular

$$b = r_{12} \sin \psi$$

$$\begin{aligned} g b db d\epsilon &= \underline{g} \cdot \underline{k} r_{12}^2 \sin \psi d\psi d\epsilon \\ &= \underline{g} \cdot \underline{k} r_{12}^2 d\Omega_k \end{aligned}$$

where $d\Omega_k = \sin \psi d\psi d\epsilon$ is an elementary solid angle in the direction of \underline{k} (see Fig. 1)

Equation (1 - 3) becomes then

$$\chi_{12}^{(12)} d v_1^{(2)} = \int_{\mathcal{R}} f_2^0 (\underline{g} + v_1^{(1)}) r_{12}^2 \underline{g} \cdot \underline{k} d\Omega_k d\underline{g}$$

where the relative velocity \underline{g} has

replaced $v_2^{(1)}$ as integration variable. If \underline{k} is taken as the new x-axis the region can be described by two conditions. Firstly, \underline{p} must be inside $d\Omega_k$ and secondly, $\underline{g} \cdot \underline{k} = g_1$ must lie within the limits

$$\frac{m_0}{2m_2} p \leq g_1 \leq \frac{m_0}{2m_2} (p + dp)$$

Hence

$$\chi_{12}^{(12)} d v_1^{(2)} = d\Omega_k r_{12}^2 \int_{\frac{m_0}{2m_2} p}^{\frac{m_0}{2m_2} (p+dp)} g_1 dg_1 \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} f_2^0 (\underline{g} + v_1^{(1)}) dg_2 dg_3$$

where g_2, g_3 are the two components of \underline{g} in the plane /

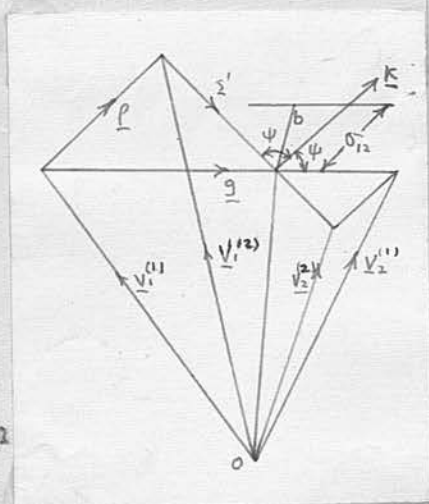


Fig. 1.

plane perpendicular to \underline{k} .

After performing integration over g_2, g_3 we obtain

$$\chi_{12}^0(12) d\underline{v}_1^{(2)} = d\underline{v}_1^{(2)} n_2 \sigma_{12}^2 \left(\frac{m_2}{2\pi kT}\right)^{\frac{1}{2}} \left(\frac{m_0}{2m_2}\right)^2 \frac{\exp\left\{-\frac{m_2}{2kT} \left[\frac{v_1^{(2)} - v_1^{(1)}}{2m_2} + v_1^{(1)} \cdot \underline{k} \right]^2\right\}}{|v_1^{(2)} - v_1^{(1)}|} \quad (5)$$

It may be verified that

$$\int \chi_{12}^0(12) d\underline{v}_1^{(2)} = \mu_{12}^0(1), \quad \int f_1^0(1) \chi_{12}^0(12) d\underline{v}_1^{(2)} = f_1^0(1) \mu_{12}^0(1)$$

as one would expect.

I. 2. General force law.

It has been mentioned in I - 2 that for the general force law the classical cross section diverges and the collision frequency μ also diverges due to the weak interaction of the distant molecules. Fortunately we do not need to consider such weak interaction: a proper distance r_0 can always be chosen as the limit of the range of interaction. Variation of r_0 will only result in the redistribution of the contribution from the successive terms in our final formula for the coefficient of self-diffusion (1 - 47).

Let $\phi(r)$ be the potential energy between two molecules expressed as a function of the distance between their centres of gravity.

We can take $\phi(r) = 0$ for $r > r_0$. The expression for $\mu_{12}^0(1)$ takes the same form as (1 - 1) with r_{12} replaced by r_0 . It is the function χ which takes the actual force law inside the distance r_0 into account. We shall indicate here how $\chi_{12}(12)$ for the general force law can be calculated. As before we have

$$\chi_{12}^0(12) d\underline{v}_1^{(2)} = \int_R f_2^0(\underline{v}_2^{(1)}) g b db d\underline{v}_2^{(1)}$$

$$\text{The } \int_R: \quad \underline{p} \leq \frac{2m_2}{m} \underline{g} \cdot \underline{k} \leq \underline{p} + d\underline{p}$$

The differential equation of the orbit of relative motion in polar coordinates is

$$\frac{d\theta}{dr} = \frac{b}{r^2} \left[1 - \frac{2\phi(r)}{Mg^2} - \frac{b^2}{r^2} \right]^{-\frac{1}{2}}$$

$$= \frac{b}{r} \left[\left(1 - \frac{2\phi(r)}{Mg^2} \right) r^2 - b^2 \right]^{-\frac{1}{2}}$$

where

$$M = \frac{m_1 m_2}{m_1 + m_2} \quad \text{is the reduced mass}$$

θ is the polar angle, and r the radius vector as shown in Fig. 2.

$$\text{At } \underline{R}, \psi, \text{ we have } \frac{\partial R}{\partial \theta} = 0$$

Hence

$$\frac{2\phi(r)}{Mg^2} = 1 - \frac{b^2}{R^2} \quad (6)$$

from which $R = R(b, g)$ can be found.

$$\text{At } r_0, \theta_0 \text{ we have } \theta_0 = \sin^{-1} \left(\frac{b}{r_0} \right)$$

Hence

$$\int_{\theta_0}^{\psi} d\theta = \int_R^{r_0} \frac{b}{r} \left[\left(1 - \frac{2\phi(r)}{Mg^2} \right) r^2 - b^2 \right]^{-\frac{1}{2}} dr$$

$$\psi = \theta_0 + \int_{R(b, g)}^{r_0} \frac{b}{r} \left[\left(1 - \frac{2\phi(r)}{Mg^2} \right) r^2 - b^2 \right]^{-\frac{1}{2}} dr = \psi(b, g) \quad (7)$$

from which $b = b(g, \psi)$ can be found.

$$\chi_{12}^0(u_2) dV_1^{(2)} = \int_R f_2(r_2) g \frac{b(g, \psi)}{\sin \psi} \left| \frac{\partial b}{\partial \psi} \right| \sin \psi d\psi dt dg$$

$$= \rho^2 d\Omega_K \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int \frac{m_0}{2m_2} \rho f_2(g + V_1^{(1)}) \frac{g}{\rho^2} \frac{b(g, \psi)}{\sin \psi} \left| \frac{\partial b}{\partial \psi} \right| dg_1 dg_2 dg_3 \quad (8)$$

where ψ inside the integral is expressed by $\psi = \cos^{-1} \frac{g_1}{g}$.

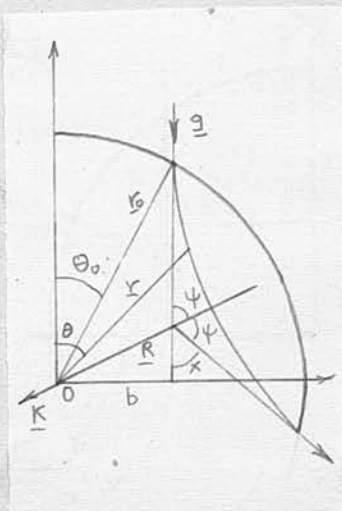


Fig. 2.

Appendix 2. Calculation of α_1, β_1' for non-uniform gas mixtures.

The assumption that the physical parameters λ_e vary only smoothly will be made in the calculation. One can always express λ_e in the vicinity of a given point x by means of Taylor's expansion. For the present purpose we shall neglect the presence of velocity gradient and assume a constant mass motion velocity in the region in which $\psi(x, t)$ is appreciable. The velocity distribution functions of the two kinds of molecules at x, t normalized to their local number densities $n_1(x, t), n_2(x, t)$ are denoted by $f_1(\xi_1, x, t)$ and $f_2(\xi_2, x, t)$. The following abbreviations will be used hereafter.

$$\left. \begin{aligned} f_1(z)_3 &= f_1(\xi_1^{(1)}, \xi_1^{(2)}, t_3), \quad \mu_1(z)_3 = \mu(\xi_1^{(1)}, \xi_1^{(2)}, t_3), \quad n_1(z^{(1)}, t) = n_1(z), \\ \chi_1(z)_4 &= \chi(\xi_1^{(1)}, \xi_1^{(2)}, x^4, t_4), \quad D_2^{(1)} = \xi_2^{(1)} \cdot \frac{\partial}{\partial x^{(1)}} + \frac{\partial}{\partial t_1}, \\ \frac{\partial}{\partial x^{(1)}} &= \sum_e \frac{\partial \lambda_e}{\partial x^{(1)}} \frac{\partial}{\partial \lambda_e}, \quad \frac{\partial}{\partial t} = \sum_e \frac{\partial \lambda_e}{\partial t} \frac{\partial}{\partial \lambda_e} \end{aligned} \right\} (9)$$

Further if we take the pressure to be constant during diffusion and suppose that no external force field is present, we find

$$\left(\frac{\partial}{\partial x^{(1)}} + \frac{\partial}{\partial t_1} \right) \lambda_e = 0 \quad \text{or} \quad D_2^{(1)} = v_2^{(1)} \cdot \frac{\partial}{\partial x^{(1)}} \quad (10)$$

where $\lambda_e = \mu_1, n_2, T, \dots$, $v_2^{(1)} = \xi_2^{(1)} - u$ is the peculiar velocity of molecules of the second kind on its i th flight relative to the local mass motion velocity u .

Both μ and χ at any later stage of the motion of the molecule can be expressed in terms of their values at /

at the starting point i.e.

$$\begin{aligned}
 \mu_i(t_j) &= \mu_i(t_0) + \sum_{\ell=1}^{j-1} \left(\sum_{\alpha=1}^{\ell} \tau_{\ell, \ell+\alpha} \frac{\partial}{\partial x_i^{(\alpha)}} + \tau_{\ell, \ell+1} \frac{\partial}{\partial t} \right) \mu_i(t_{\ell-1}) + \dots \\
 &= \mu_i(t_0) + \sum_{\ell=1}^{j-1} \tau_{\ell, \ell+1} D_i^{(\ell)} \mu_i(t_0) + \dots \\
 \chi_i(t_j, t_{j+1}) &= \chi_i(t_0, t_1) + \sum_{\ell=1}^{j-1} \left(\sum_{\alpha=1}^{\ell} \tau_{\ell, \ell+\alpha} \frac{\partial}{\partial x_i^{(\alpha)}} + \tau_{\ell, \ell+1} \frac{\partial}{\partial t} \right) \chi_i(t_0, t_{\ell-1}) + \dots \\
 &= \chi_i(t_0, t_1) + \sum_{\ell=1}^{j-1} \left(\tau_{\ell, \ell+1} D_i^{(\ell)} \chi_i(t_0, t_1) \right) + \dots
 \end{aligned} \tag{11}$$

By means of (2 - 3), $P_N(i, 2 \dots N)$ in (1 - 42) can be expressed in terms of the values of quantities at the starting point x'' , t_1 , neglecting gradients of the second and higher order. The mean time of flight, mean displacement and mean square displacement relative to a frame moving with \underline{v} can be found by simple calculations. The mean time of flight is found to depend on the direction of the velocity in this flight, but as the difference can at most be linear in the gradients, it will not affect our final result for α_i, β_i' which is obtained by using the average time of flight for all directions in each flight. Although such average times of individual flights are different, the difference can again be ignored for the same reason.

$$\langle \tau_{i, i+1} \rangle = \frac{1}{\mu_{0i}} + O\left(\frac{\partial \chi_0}{\partial x}\right) \tag{12}$$

where

$$\begin{aligned}
 \overline{\mu_{0i}} &= \frac{1}{\mu_i} \int f_i(v_i) \mu_i^0(v_i) dv_i'' \\
 \Delta t &= \left\langle \sum_{i=1}^N \tau_{i, i+1} \right\rangle = \frac{N}{\mu_{0i}}
 \end{aligned} \tag{13}$$

The successive mean displacements relative to the mean mass motion velocity \underline{v} are

$$\left\langle \frac{\underline{r}}{v} \right\rangle = \left\langle v_i'' \tau_2 \right\rangle = \frac{\iint P_i(v_i) \tau_{i2} v_i'' dv_i'' d\tau_{i2}}{\iint P_i(v_i) dv_i'' d\tau_{i2}} \tag{14}$$

where /

where

$$\begin{aligned}
 R(t) &= (\mu_1(t) + D_1^{(1)}) f_1^{(1)} \left\{ e^{-\int_0^t (\mu_1^{(1)} + \tau_2 D_1^{(1)}) dt} (\mu_1^{(1)} + \tau_2 D_1^{(1)}) \right. \\
 &= (\mu_1^{(1)})^2 \left(f_1^{(1)} + f_1^{\prime(1)} \right) \left(1 + \frac{D_1^{(1)} f_1^{(1)}}{\mu_1^{(1)} f_1^{(1)}} \right) e^{-\mu_1^{(1)} t} \left(1 - \frac{1}{2} \tau_2^2 D_1^{(1)2} \mu_1^{(1)} \right) \left(1 + \frac{\tau_2 D_1^{(1)} \mu_1^{(1)}}{\mu_1^{(1)}} \right) \quad (15) \\
 &= f_1^{(1)} (\mu_1^{(1)})^2 e^{-\mu_1^{(1)} t} \left\{ 1 + \frac{D_1^{(1)} f_1^{(1)}}{\mu_1^{(1)} f_1^{(1)}} - \frac{\tau_2^2}{2} D_1^{(1)2} \mu_1^{(1)} + \frac{\tau_2 D_1^{(1)} \mu_1^{(1)}}{\mu_1^{(1)}} + \frac{f_1^{\prime(1)}}{f_1^{(1)}} \right\}
 \end{aligned}$$

neglecting terms involving the second or higher powers of $\frac{\partial \lambda_e}{\partial z}$.

Using (2 - 7), equation (2 - 6) becomes

$$\langle \xi_1 \rangle = \frac{1}{n_1 \mu_1^{(1)}} \left\{ \int f_1^{\prime(1)} v_1^{(1)} dv_1^{(1)} + \int D_1^{(1)} \left(\frac{f_1^{(1)}}{\mu_1^{(1)}} \right) v_1^{(1)} dv_1^{(1)} \right\}$$

Similarly one can calculate $\langle \xi_2 \rangle \dots$

$$\begin{aligned}
 \langle \xi_2 \rangle &= \frac{1}{n_1 \mu_1^{(1)}} \left\{ \int f_1^{(1)} v_1^{(1)} dv_1^{(1)} + \int D_1^{(1)} \left(\frac{f_1^{(1)}}{\mu_1^{(1)}} \right) v_1^{(1)} dv_1^{(1)} \right. \\
 &\quad \left. + \int \left(D_1^{(1)} \left(\frac{f_1^{(1)}}{\mu_1^{(1)}} \right) \frac{\chi_1^{(1,2)}}{\mu_1^{(1)} \mu_1^{(2)}} \right) v_1^{(1)} dv_1^{(1)} dv_1^{(2)} \right\} \\
 &\dots
 \end{aligned}$$

Hence

$$\overline{(\Delta z)} = \sum_{i=1}^N \langle \xi_i \rangle \quad (16)$$

$$= \frac{1}{n_1 \mu_1^{(1)}} \left\{ N \int f_1^{\prime(1)} v_1^{(1)} dv_1^{(1)} + N \int D_1^{(1)} \left(\frac{f_1^{(1)}}{\mu_1^{(1)}} \right) v_1^{(1)} dv_1^{(1)} + (N-1) \int \left(D_1^{(1)} \left(\frac{f_1^{(1)}}{\mu_1^{(1)}} \right) \frac{\chi_1^{(1,2)}}{\mu_1^{(1)} \mu_1^{(2)}} \right) v_1^{(1)} dv_1^{(1)} dv_1^{(2)} \right\}$$

The mean square displacement when quantities

involving the gradients are neglected is found to be

the same as in the equilibrium state. We have

therefore

$$\overline{(\Delta z)^2} = \frac{2}{n_1 \mu_1^{(1)}} \left\{ N \int f_1^{(1)} \frac{v_1^{(1)2}}{\mu_1^{(1)}} dv_1^{(1)} + (N-1) \int \int f_1^{(1)} \frac{\chi_1^{(1,2)}}{\mu_1^{(1)} \mu_1^{(2)}} v_1^{(1)} v_1^{(2)} dv_1^{(1)} dv_1^{(2)} + \dots \right\} \quad (17)$$

The required expressions for α_1 and β_1' follow

from (2 - 5), (2 - 8) and (2 - 9) for large N

$$\alpha_1 = \int \frac{f_1^{(1)} (v_1^{(1)})^2}{n_1 \mu_1^{(1)}} dv_1^{(1)} + \iint \frac{f_1^{(1)} \chi_1^{(1,2)}}{n_1 \mu_1^{(1)} \mu_1^{(2)}} v_1^{(1)} v_1^{(2)} dv_1^{(1)} dv_1^{(2)} + \dots \quad (18)$$

$$\beta_1' = \frac{1}{n_1} \left\{ \int f_1^{(1)} v_1^{(1)} dv_1^{(1)} + \int D_1^{(1)} \left(\frac{f_1^{(1)}}{\mu_1^{(1)}} \right) v_1^{(1)} dv_1^{(1)} + \iint \left(D_1^{(1)} \left(\frac{f_1^{(1)}}{\mu_1^{(1)}} \right) \frac{\chi_1^{(1,2)}}{\mu_1^{(1)} \mu_1^{(2)}} \right) v_1^{(1)} dv_1^{(1)} dv_1^{(2)} + \dots \right\}$$

By using (2 - 2) β_1' can be reduced to the form

$$\beta_1' = \frac{1}{n_1} \int f_1^{(1)} v_1^{(1)} dv_1^{(1)} + \frac{1}{3 n_1} \frac{\partial}{\partial z} (n_1 \alpha_1) = v_1 + \frac{1}{3 n_1} \frac{\partial}{\partial z} (n_1 \alpha_1) \quad (19)$$

Substituting (19) in (1 - 16) we obtain an identity.

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