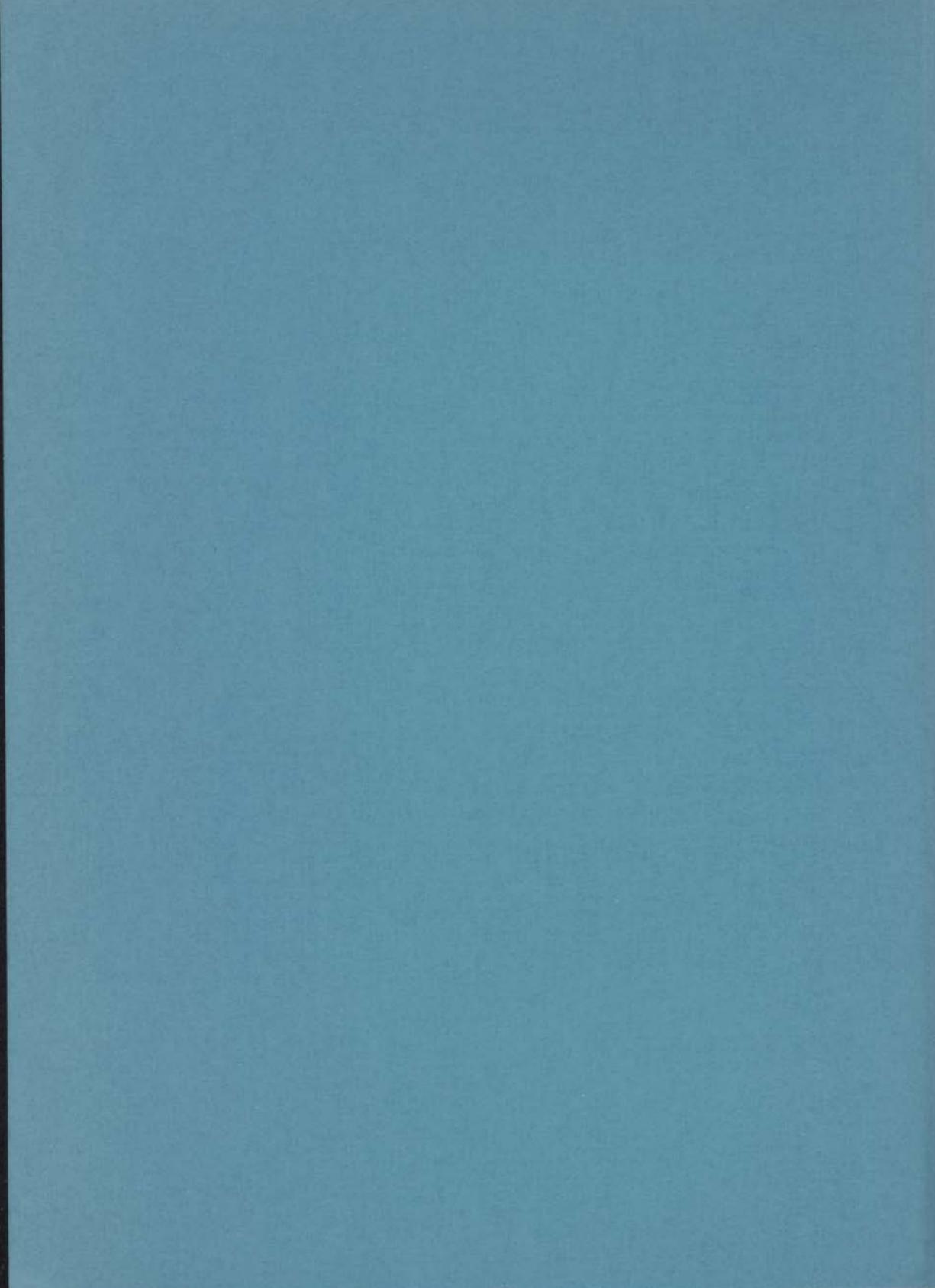


SOME ASPECTS OF THE INFLUENCE OF
A MAGNETIC FIELD ON TRANSPORT
PHENOMENA IN DILUTE GASES

25 JUN 1968

INSTITUUT-LORENTZ
voor theoretische natuurkunde
Nieuwsteeg 13-Leiden-Nederland

A. TIP



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TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN DE
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UNIVERSITEIT TE LEIDEN, OP GEZAG VAN DE RECTOR
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ADRIAAN TIP

GEBOREN TE ALKMAAR IN 1940

*Promotoren: Professor dr J.J.M. Beenakker
Professor dr P. Mazur*

STELLINGEN

6. Voor een beschrijving van het Zonlicht-Beeld effect...
 - 1. Voor een beschrijving van het Zonlicht-Beeld effect...
 - 2. Met behulp van een magnetisch veld is het mogelijk...
 - 3. Voor een beschrijving van het Zonlicht-Beeld effect...
 - 4. De door Muriel en Dresden aangegeven magnetisch-...
 - 5. Teneinde een magnetische afwijking te verkrijgen...
 - 6. Dit is van groot belang bij experimenten...
 - 7. Dit is van groot belang bij experimenten...
 - 8. Dit is van groot belang bij experimenten...
 - 9. Dit is van groot belang bij experimenten...
 - 10. Dit is van groot belang bij experimenten...

S T E L L I N G E N

1. De door di Giacomo aangegeven voorwaarden waaronder de elektrische polarisatie in een verdund polair gas mag worden gelineariseerd in het drijvend tijdafhankelijk elektrisch veld zijn onvolledig.

A. Di Giacomo, *Il Nuovo Cimento* 34, 473 (1964).

2. Met behulp van een magnetisch veld is het mogelijk experimentele aanwijzingen te verkrijgen over het optreden van een "visceuze" terugstroom bij het thermomoleculair druk-effect.

3. Voor een beschrijving van het Senftleben-Beenakker effect verdient de parameter B/n , de verhouding van magnetische inductie en dichtheid, de voorkeur boven H/p , de verhouding van magnetische veldsterkte en druk.

4. De door Muriel en Dresden aangegeven master-vergelijking is in zijn algemeenheid onjuist.

A. Muriel en M. Dresden, *Physics Letters* 27A, 16 (1968).

R.M. Wilcox, *J.Math.Phys.* 8, 962 (1967).

5. Teneinde een gunstige signaal-ruisverhouding te verkrijgen bij vlucht- of verblijftijd-experimenten verdient het aanbeveling gebruik te maken van een (kruis)correlatiemethode. Dit is van groot belang bij experimenten, waarbij gebruik wordt gemaakt van door middel van kathodeverstuiving verkregen atomaire bundels.

6. Voor een theoretische verklaring van het optreden van twee maxima in de transversale transport-coëfficiënten van zuurstof in een magneetveld is het niet noodzakelijk het optreden van "spin-omklap"-botsingen te veronderstellen.

L.L. Gorelik, V.G. Nikolaev en V.V. Sinitsyn,
Zh.Eksperim. i Teor.Fiz. Pis'ma v Redaktsiyu
4, 456 (1966);

I.K. Kikoin, K.I. Balashov, S.D. Lasarev en R.E. Neushtadt, Physics Letters 24a, 165 (1967);

Yu. Kagan en L.A. Maksimov, Zh.Eksperim. i Teor.Fiz.
51, 1893 (1966) (Engelse vertaling: Soviet Physics
JETP 24, 1272 (1967)).

7. Naar aanleiding van de onlangs aangegeven regels betreffende het promoveren op publicaties dient het verbod van de Rijksuniversiteit te Leiden, een dankwoord te richten tot aan deze universiteit verbonden personen, herzien te worden.
Acta et Agenda, 5 december 1968.

8. De toename in de effectieve werking van ultra-centrifuges bij toenemende hoekfrequentie wordt bij hoge hoekfrequentie-gasdichtheidverhouding begrensd door het optreden van Corioliskrachten.

9. Voor de theoretische beschrijving van Debye-relaxatie in verdunde meer-atomige gassen kan met vrucht gebruik worden gemaakt van de door Waldmann en Snider opgestelde transportvergelijking.

L. Waldmann, Z.Naturforschg 12a, 660 (1957).

R.F. Snider, J.Chem.Phys. 32, 1051 (1960).

CHAPTER I

Chapter I. The first part of the book is devoted to a general introduction to the subject of the history of the United States. The author discusses the various factors that have influenced the development of the country, including geography, climate, and the actions of its people. He also touches upon the early colonial period and the struggle for independence.

The second part of the chapter deals with the political and social changes that have shaped the nation. The author examines the role of the government, the influence of the courts, and the impact of the various parties and movements that have emerged over time. He also discusses the role of the press and the public in the development of the country.

The third part of the chapter is devoted to a discussion of the economic and social conditions of the United States. The author examines the various industries and the role of the government in the economy. He also discusses the social conditions of the country, including the role of education and the impact of the various social movements that have emerged over time.

The fourth part of the chapter is devoted to a discussion of the foreign relations of the United States. The author examines the various treaties and agreements that have been entered into by the country and the role of the government in the conduct of foreign affairs. He also discusses the impact of the various international organizations and movements that have emerged over time.

The fifth part of the chapter is devoted to a discussion of the future of the United States. The author examines the various challenges that the country faces and the role of the government in addressing these challenges. He also discusses the role of the people in the development of the country and the impact of the various social and economic movements that have emerged over time.

The author concludes the chapter by discussing the role of the United States in the world. He examines the various international organizations and movements that have emerged over time and the impact of the country's actions on the world. He also discusses the role of the United States in the development of the world and the impact of the various social and economic movements that have emerged over time.

CONTENTS

- Chapter I : General introduction.
- Chapter II : The influence of angular momentum anisotropy on the heat conductivity of dilute diatomic gases (Physica 37 (1967) 82-96).
- Chapter III : On the Senftleben-Beenakker effect in mixtures; 1. The magnetic field dependence of the shear viscosity tensor in mixtures of diamagnetic gases (Physica 37 (1967) 411-422).
- Chapter IV : Dispersion relations and sum rules for the transport coefficients of dilute ionized gases in a magnetic field (Physica, to be published).
- Chapter V : Magnetic dispersion relations in the Senftleben-Beenakker effect (Physica 40 (1968) 435-445).
- Samenvatting : (Summary in Dutch).

GENERAL INTRODUCTION

Many physical experiments consist of studying the variation of some physical phenomenon as a function of certain external parameters. Specializing to the field of transport phenomena in dilute gases one can mention the measurement of transport coefficients as a function of temperature. For noble gases this yields a quite precise knowledge of the parameters that enter into the expression for the intermolecular potential ¹⁾.

Ionized and polyatomic gases, however, offer additional possibilities, due to the circumstance that the motion of the individual particles can be influenced by means of external electric and magnetic fields. Charged particles feel Coulomb and Lorentz forces when placed in such fields. The electric field, if not too strong, acts as a driving force causing an electric current, the proportionality coefficient $\underline{\sigma}$ (the conductivity tensor) being independent of the electric field \underline{E} ²⁾. A magnetic field \underline{B} contributes to the driving force via $\underline{v}_0 \times \underline{B}$, \underline{v}_0 being the stream velocity of the gas, but it also influences the transport coefficients. Thus $\underline{\sigma} = \underline{\sigma}(\underline{B})$ is no longer an isotropic tensor. In a similar way the heat conductivity tensor $\underline{\lambda}$ and shear viscosity tensor $\underline{\eta}$ are affected ²⁾.

For neutral polyatomic molecules the situation is different. Homogeneous external fields no longer influence the translational motion of the molecules. However, if the molecules carry an electric or magnetic dipole moment they affect the time development of the internal state of the molecules due to the field contribution:

$$H^{(\text{field})} = - \underline{\mu}^{(e)} \cdot \underline{E} - \underline{\mu}^{(m)} \cdot \underline{B} \quad (1)$$

to the Hamiltonian. Here is $\underline{\mu}^{(e)}$ the electric and $\underline{\mu}^{(m)}$ the magnetic dipole moment.

A direct consequence of the presence of an external field is that a polarization or magnetization of the gas can take place. In time dependent external fields this leads to absorption phenomena which can be of both resonant and non-resonant nature.

An example of the first type is the collision broadening of spectral lines with the important special case of nuclear magnetic resonance in low density gases. Non-resonant absorption or Debye relaxation has also been observed in a number of gases. Recent reviews of both nuclear magnetic resonance and Debye relaxation in dilute polyatomic gases can be found in ref. 3.

In these cases the time dependent field acts as a driving force and is not contained in the parameters (relaxation times) that enter into expressions for the shape of the absorption curve as a function of frequency, provided the field is not too strong.

A static homogeneous external field can lead to effects of a quite different nature. It was observed by Senftleben in the 1930's⁴⁾ that the heat conductivity and viscosity of the paramagnetic gases O_2 and NO decrease slightly (0.5 - 1%) upon application of a magnetic field.

Denoting by ΔL the change in a transport coefficient L due to the field,

$$\Delta L(\underline{B}) = L(\underline{B}) - L(0) \quad (2)$$

one can state the following features, as they were found

experimentally by Senftleben:

- a) ΔL is even in B ;
- b) ΔL depends on the angle between B and transport direction;
- c) ΔL depends on $B = |B|$ via the parameter B/n , n being the gas density;
- d) For large B/n ΔL tends to a saturation value.

At this point it is of interest to note that a similar behaviour is found for the transport coefficients of ionized gases ²⁾. Indeed both phenomena are of a related nature and precisely these effects are the subject of the present investigation.

The field effect in an ionized gas is caused by the precession of the velocity vector around the field axis. This leads to a partial averaging of the anisotropy in velocity of the non-equilibrium distribution function. As the transport coefficients are connected to weighted averages of the distribution function, they are affected in turn. The effectiveness of the averaging process is determined by the number of precessions that are performed between two successive collisions. This number is given by the ratio ω_p / ω_c of precession frequency ω_p and collision frequency ω_c , which quantity is proportional to B/n .

An explanation of the Senftleben effect along these lines was given by Gorter ⁵⁾ in 1938. In a magnetic field the magnetic moment of a paramagnetic molecule precesses around the field axis. This magnetic moment is coupled to the rotational angular momentum, which is perpendicular to the plane in which the molecule rotates. Gorter now remarks that without a field the transport coefficient is proportional to the inverse of the collision cross-section, averaged

over all orientations (here all directions of the angular momentum vector) of the molecule. The situation alters if a magnetic field is applied, for now the precession causes a (partial) averaging over the orientations of the molecules about to collide. Thus in this case one first averages the cross-section over all orientations and the transport coefficient equals the inverse of this averaged quantity. It can easily be shown that the second averaging procedure yields a smaller transport coefficient than the first, thus explaining its decrease in a magnetic field. It is also clear that, as for the ionized gas, the averaging efficiency depends on the number of precessions between two successive collisions, thus explaining the B/n -law. Corter's ideas were worked out further by Zernike and van Lier⁶⁾, who obtained quantitative results for the B/n -dependence as well as the dependence on the angle between field and transport directions. However, the saturation values $(\Delta\lambda/\lambda)_{\text{sat}}$ and $(\Delta n/n)_{\text{sat}}$ were found to be equal, in contradiction with experiment⁴⁾.

Further theoretical progress had to wait until 1961 in which year a paper appeared by Kagan and Maksimov (KM 1)⁷⁾. These authors consider the case of gases consisting of linear paramagnetic molecules of which the paramagnetism is due to the spin magnetic moment only (this applies for oxygen). The gas is considered to be a mixture, each component corresponding to a different projection of the spin angular momentum \underline{S} on the total (spin + rotational) angular momentum \underline{J} . Starting from a Boltzmann equation for the one particle distribution function f , the Chapman-Enskog method is used to obtain an explicit formula for the

heat conductivity tensor $\underline{\lambda}(\underline{B})$. f is assumed to be a function of \underline{J} in addition to its dependence on time t , position \underline{x} and velocity \underline{v} . The precessional motion of \underline{J} around the field axis is taken care of by adding a corresponding flow term to the left hand side of the transport equation. For the orientation dependence of the collision cross-section a model similar to that used by Zernike and van Lier ⁶⁾ is introduced. It consists of approximating the (in general unknown) collision cross-section by a product of the corresponding cross-section for monatomic gases and a second factor which contains a term depending upon the angles between the rotational angular momenta and the relative velocity of the collision partners. It is further assumed that during collisions the angular momenta do not change in both magnitude and direction. The shape of the saturation curve (B/n -dependence) is in reasonable agreement with experiment, as is the case for the ratio $(\Delta\lambda)_{//} / (\Delta\lambda)_{\perp}$ at saturation. Here $//$ and \perp stand for \underline{B} parallel and perpendicular to the temperature gradient respectively.

It will be clear from Gorter's explanation of the Senftleben effect that any phenomenon which disturbs the internal state of the molecules between collisions may lead to a change in the transport coefficients of polyatomic gases. For the case of homogeneous magnetic and electric fields a coupling between magnetic or electric dipole moment and the other internal state variables such as the rotational angular momentum \underline{N} , is needed (\underline{N} is replaced by \underline{J} in the further discussion whenever it is the only angular momentum connected to the internal state of the molecule).

Moreover the molecules must be non-spherical. That is,

collision cross-sections (in quantum mechanical treatments; the transition operator) must depend on the internal states of the colliding molecules. In the absence of an external field this can give rise to an anisotropy in the dependence of f (in quantum treatments; the one particle density matrix) on \underline{N} . The action of the field leads to a change in the initial condition for each binary collision that takes place and as a consequence the velocity distribution and hence the transport coefficients are altered.

The first to realize that field effects are not restricted to paramagnetic gases, were Beenakker and coworkers who showed in 1962 that the viscosity of N_2 decreases upon application of a magnetic field ⁸⁾. Due to its rotation, nitrogen, as does every other polyatomic molecule, possesses a small magnetic moment coupled to the rotational angular momentum \underline{N} . As this magnetic moment is in the order of a nuclear magneton instead of a Bohr magneton, as is the case for oxygen, one needs a roughly a thousand times larger B/n -ratio to achieve the same averaging efficiency. One might raise the question if nuclear spins, which carry a magnetic moment of the same magnitude as that due to rotation, can play a role. This is usually not the case as the coupling between spin \underline{I} and rotational angular momentum \underline{N} is weak and the dependence of the interaction potential on I negligible. Thus at any appreciable field \underline{I} and \underline{N} precess independently around \underline{B} and one may neglect \underline{I} altogether in a description of the Senftleben-Beenakker effect.

Following the historical development somewhat further the work of Gorelik and Sinitsyn must be mentioned next. In a paper published in 1964 these authors reported the

existence of a field effect on the heat conductivity of N_2 ⁹⁾. This was followed a year later by a second paper where results for H_2 and D_2 were given¹⁰⁾.

During the last four years progress has been rapid. Nowadays a large number of data on viscosity and heat conductivity exist for a number of gases (A review of both experiment and theory has been given recently by Beenakker¹¹⁾).

In 1965 Korving et al.¹²⁾ published results concerning the influence of a magnetic field on gases made up from spherical top molecules (CH_4 , CF_4), thus showing that field effects are not restricted to linear molecules. In the same year a paper by Senftleben¹³⁾ came out, where results were given about the influence of an electric field on the heat conductivity of gases consisting of polar symmetrical top molecules. In one case (CH_3CN) the field effect showed a positive sign. This was confirmed later by de Groot et al.¹⁴⁾, who also found a striking dependence of the effect on the dipole moment $\mu^{(e)}$, its sign being negative for small $\mu^{(e)}$ but becoming positive for large electric dipole moment.

An interesting behaviour is also shown by the hydrogen isotopic molecules H_2 , D_2 and HD in a magnetic field¹⁵⁾,¹⁶⁾. Not only is the field induced change in viscosity and heat conductivity of H_2 and D_2 much smaller than for other molecules, due to their nearly spherical shape, but also the viscosity change of the three hydrogen isotopes saturates at about ten times lower B/n -values than other diamagnetic gases (N_2 , CO). This turned out to be a very valuable piece of information in connection with the choice of trial

functions in series expansions of the molecular distribution function in theoretical considerations.

Another important development was the discovery of field effects, odd in the direction of \underline{B} (transverse effects) 17, 18, 19). In fact such phenomena were long known for electric conductivity (Hall-effect) and heat conductivity (Righi-Leduc-effect) in electrically conducting media. Also theoretical expressions already existed for transverse viscous flow in ionized gases ²⁾. In 1955, Hooyma, Mazur and de Groot ²⁰⁾ showed, in a phenomenological treatment, that in a magnetic field the viscosity tensor, relating the symmetric part of the stream velocity gradient tensor to the symmetric part of the pressure tensor, contains seven independent coefficients. Five of these, η_1 to η_5 , determine the shear viscosity tensor. η_1 , η_2 and η_3 are even, η_4 and η_5 odd in \underline{B} . The bulk viscosity coefficient η_v turns out to be even in \underline{B} . Moreover there exists a cross coefficient ζ , even in \underline{B} , which links shear and bulk viscosity. In the absence of a field η_4 , η_5 and ζ vanish. A similar classification can also be given for the heat conductivity tensor ²¹⁾. $\underline{\lambda}(\underline{B})$ is determined by three coefficients of which two are even and one is odd in \underline{B} . The latter determines the heat flow perpendicular to both \underline{B} and temperature gradient (transverse heat flow) whereas the two other coefficients are responsible for the heat flow in the plane of \underline{B} and temperature gradient (longitudinal heat flow). As far as gases with internal degrees of freedom are concerned, transverse effects were first described theoretically by Waldmann and Kupatt ²²⁾ in an investigation about the diffusion of spin $\frac{1}{2}$ particles in a magnetic field. Theoretical expressions for transverse Senftleben-Beenakker-effects in heat

conductivity and viscosity were obtained some years later, independently by Kagan and Maksimov²³⁾ and Knaap and Beenakker^{17, 24)}. It was shown that the transverse effect exhibits an absorptive behaviour (see figure 1), the maximum

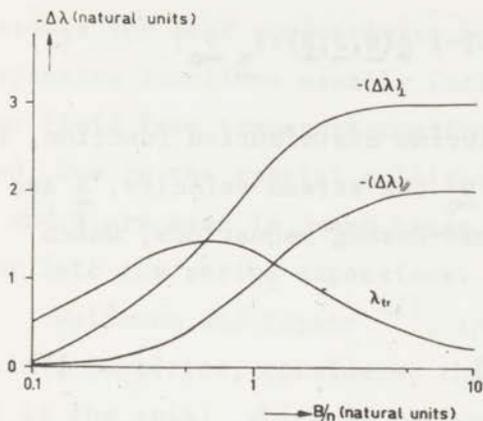


Figure 1.

The magnetic field dependence of the heat conductivity coefficients $(\Delta\lambda)_{\perp}$, $(\Delta\lambda)_{\parallel}$ and $(\Delta\lambda)_{tr} = \lambda_{tr}$ as given by equation (7) in the main text. B/n is given in units Θ and $\Delta\lambda$ in units C (natural units).

in its B/n -curve occurring at roughly the same B/n -value for which a point of inflection is found on the curves for the longitudinal effects. The sign of the transverse effect may be either positive or negative, depending on the sign of the Landé g -factor.

Next some attention will be paid to theoretical developments. On these the paper by Kagan and Maksimov⁷⁾ has had a profound influence. In this paper, and also in a second one by Kagan and Afanas'ev²⁵⁾, it was stressed that the molecular distribution function not only depends on the velocity but also on the angular momentum of the rotating molecules. Thus in series expansions both variables should be present. A convenient way to take both into account is an expansion into products of irreducible tensors constructed from the reduced peculiar velocity \underline{W} and the angular momentum \underline{J} respectively. (Sometimes \underline{J} is replaced by the reduced quantity $\underline{M} = (2 I kT)^{-\frac{1}{2}} \underline{J}$, I being the moment of

inertia of a linear molecule.)

According to the Chapman-Enskog approach the molecular distribution function is (to first order in the macroscopic gradients) given by

$$f = f^{(0)} \cdot \{ 1 - \underline{A}(\underline{W}, \underline{J}, \underline{B}) \cdot \partial_{\underline{x}} \ln T - 2 \underline{B}(\underline{W}, \underline{J}, \underline{B}) : \partial_{\underline{x}} \underline{v}_0 \} \quad (3)$$

Here $f^{(0)}$ is the local equilibrium distribution function, T the absolute temperature and \underline{v}_0 the stream velocity. \underline{A} and \underline{B} obey the appropriate "Chapman-Enskog"-equations, which can be written formally as

$$\underline{\Psi} = (J^{(0)} + J^{(1)}) \underline{\Phi} = J \underline{\Phi} \quad (4)$$

where $\underline{\Psi}$ is a given function of \underline{W}^2 , \underline{J}^2 and \underline{W} , $J^{(0)}$ is the linearized collision operator, $J^{(1)}$ a streaming operator connected to angular momentum flow (precession of \underline{J} around \underline{B}) and $\underline{\Phi}$ stands for \underline{A} and \underline{B} respectively. The expansion for $\underline{\Phi}$ now reads

$$\underline{\Phi}(\underline{W}, \underline{J}, \underline{B}) = \sum_{p,q} \underline{A}^{(p,q)}(\underline{W}^2, \underline{J}^2, \underline{B}) \Theta^{(p+q)}[\underline{W}]^{(p)}[\underline{J}]^{(q)} \quad (5)$$

where the symbol $[]^{(p)}$ indicates the p^{th} rank irreducible tensor (in Cartesian representation) constructed from the vector within the brackets.

After further expansion into suitable polynomials in \underline{W}^2 and \underline{J}^2 (5) is introduced into (4). Multiplication of left and right hand side of (4) with $f^{(0)}$ and each of the expansion functions and integration leads to an infinite set of equations for the expansion coefficients, which are now tensors depending on \underline{B} . Truncation of the series expansion leads to a finite set of equations from which the re-

maintaining expansion coefficients can be determined. As the transport coefficients are given by integrals of $f^{(0)} \cdot \underline{\psi} \cdot \underline{\phi}$ over \underline{W} and \underline{J} , they are finally obtained in terms of these coefficients. Kagan and Maksimov ⁷⁾ thus obtained acceptable results for heat conductivity by adding $\underline{W}[\underline{J}]^{(2)}$ to the expansion functions usually included in similar calculations for field free transport coefficients and which all have $q=0$. Due to the special collision model used by these authors \underline{A} and \underline{B} are even in \underline{J} and hence no functions with odd q enter into the series expansions.

Waldmann and Kupatt ²²⁾, in their note on diffusion of spin $\frac{1}{2}$ particles, considered the expansion function $\underline{W} \underline{S}$ (\underline{S} is the spin), which is the only possible function with $q \neq 0$ as no higher spin tensors can occur for spin $\frac{1}{2}$. Here a positive field effect was found. This is due to the general rule, connected with the time reversal invariance properties of $J^{(0)}$, that inclusion of functions even in \underline{J} in the expansions for \underline{A} and \underline{B} gives rise to an increase of the field free transport coefficients, whereas functions odd in \underline{J} lead to a decrease. As the effect of the field is a partial destruction of the contribution of the functions $[\underline{W}]^{(p)} [\underline{J}]^{(q)}$ with $q \neq 0$ it follows that inclusion of functions with even q leads to a decrease of the longitudinal coefficients whereas functions with odd q give an increase. For a further discussion of these matters, see ref. 26.

Early in 1966 an unpublished report by the author appeared ²⁷⁾ in which some general aspects of transport phenomena of mixtures of diatomic gases in a magnetic field were discussed. Using the space reflection and time reversal invariance properties of the binary collision dynamics (no

model assumptions for the collision operator were made) the results for the viscosity tensor given by Hooyman, Mazur and de Groot ²⁰⁾ are reproduced for this special case. Also an Onsager relation is established, connecting thermal diffusion and diffusion thermo coefficients in a magnetic field. In addition it is shown that for diatomic molecules no cross effects between viscous flow and heat flow can occur in a magnetic field and it is stated that such effects can be expected only for optically active molecules. (In the presence of electric fields the situation is different. Here cross effects may occur but transverse effects are restricted to optical isomers.)

Also in 1966 McCourt ²⁸⁾, in a thesis, presented explicit formulae for the longitudinal part of the heat conductivity tensor of diamagnetic diatomic gases. Contrary to the work done so far (with the exception of ref. 22) the internal degrees of freedom are treated quantum mechanically, the underlying transport equation being the Waldmann-Snider-equation ²⁹⁾. Here no special collision model is employed and the choice of expansion functions corresponds with that of KM 1. Thus angular momentum anisotropy is introduced via $\underline{W}[\underline{J}]^{(2)}$, where now \underline{J} is a quantum mechanical operator.

It should be stressed that for diamagnetic diatomic gases quantum mechanical and classical treatments lead to comparable results. Only the collision integrals entering into the final formulae are defined in a different way. Quantum mechanical treatments are preferable in those cases where typical quantum effects play a role; hydrogen at low temperatures and paramagnetic molecules.

At the end of 1966 a second paper by Kagan and Maksi-

23) appeared. Instead of an expansion of \underline{A} and \underline{B} this work made an expansion of $J^{-1} = (J^{(0)} + J^{(1)})^{-1}$. For this purpose the collision operator (no model assumptions are made) is divided into two parts, $J^{(e)}$ and $J^{(p)}$, the first connected with elastic collisions and the second containing all polyatomic features. The eigenfunctions of the first part are approximated by products of Maxwellian eigenfunctions and suitable angular momentum dependent functions. The latter now contain irreducible tensors in spherical representation. This has the advantage of diagonalizing $J^{(1)}$. The expansion of J^{-1} is based upon the assumption

$$J^{(p)} \ll J^{(e)} \quad (6)$$

Unfortunately this assumption is incorrect. Sound absorption and Debye relaxation in polyatomic gases are both determined by relaxation times connected to diagonal matrix elements of $J^{(p)}$ and it follows from experiment that for many polyatomic gases these diagonal matrix elements can be as large as the diagonal matrix elements of $J^{(e)}$ (which determine λ and η for noble gases). Especially the results obtained by Kagan and Maksimov for the bulk viscosity in a magnetic field are unacceptable. This is due to the circumstance that bulk viscosity in dilute gases is of a truly polyatomic nature. It is, however, easy to modify the splitting of $J^{(0)}$ in such a way that the difficulties mentioned above can be overcome. This is discussed in chapter 5 of this thesis, where the improved perturbation expansion of J^{-1} is used to good advantage in an investigation concerning the analytic continuation in the complex B/n plane of the theoretical expressions for λ and η .

Kagan and Maksimov did obtain expressions for transverse effects. The results for viscosity are in agreement with ref. 20; seven independent viscosity coefficients are found of which two are odd in B.

In the beginning of 1967 a paper by Knaap and Beenakker²⁴⁾ appeared in which the magnetic field influence on the heat conductivity and viscosity of gases consisting of linear molecules was treated on the basis of the collision model, introduced by Kagan and Maksimov in their earlier paper⁷⁾. Both para- and diamagnetic gases were considered. (The original treatment by Kagan and Maksimov was for paramagnetic gases only. No experimental results for other gases were available at that date.) Due to some approximations in the treatment of the spin-rotation coupling Kagan and Maksimov did not find a transverse effect for paramagnetic gases. This was improved upon by Knaap and Beenakker, who showed that in oxygen transverse effects may exist, in agreement with experiment¹⁷⁾. Their expression for the transverse viscosity coefficient η_5 was already published a year earlier, together with the experimental results¹⁷⁾.

The expression for the field dependence of the heat conductivity of diamagnetic diatomic gases, as obtained by various authors^{24, 28, 30)}, reads:

$$\Delta \underline{\lambda}(\underline{B}) = - C \left\{ \left[\frac{\theta^2}{1+\theta^2} + 2 \frac{(2\theta)^2}{1+(2\theta)^2} \right] \underline{U} + \left[\frac{\theta^2}{1+\theta^2} - 2 \frac{(2\theta)^2}{1+(2\theta)^2} \right] \underline{b} \cdot \underline{b} - \left[\frac{\theta}{1+\theta^2} + 2 \frac{2\theta}{1+(2\theta)^2} \right] \underline{\varepsilon} \cdot \underline{b} \right\} \quad (7)$$

Here is U the second rank unit tensor, ε the third rank Levi-

Civita pseudo tensor and \underline{b} a unit vector along \underline{B} . C is a positive constant, determined from matrix elements of $J^{(0)}$. The dependence on the absolute value of \underline{B} , or precession frequency ω_p enters via θ , which can be written as

$$\theta = \omega_p \cdot \tau \quad (8)$$

where the "relaxation time" τ is inversely proportional to the diagonal matrix element of $J^{(0)}$ with respect to $\underline{W}[\underline{J}]^{(2)}$. From (7) it follows that in saturation ($\theta \rightarrow \infty$):

$$\frac{(\Delta\lambda)_{\parallel}}{(\Delta\lambda)_{\perp \text{sat}}} = \frac{2}{3} \quad (9)$$

A characteristic feature of (7) is the occurrence of single and double frequencies θ and 2θ . It was first thought²⁴⁾ that this was related to the special collision model employed. In model independent calculations^{28, 30)}, however, the same θ -dependence is found and thus there must be a more general reason behind this. From the expressions given by Kagan and Maksimov in their second paper²³⁾ one gets the impression that in general an expansion function $[\underline{W}]^{(p)}$ $[\underline{J}]^{(q)}$ leads to a range of frequencies $\theta, 2\theta \dots, q\theta$. A similar result is found for ionized gases, where only tensors $[\underline{W}]^{(p)}$ occur. For heat conductivity $p=1$ and only a single frequency is present, whereas for viscosity $p=2$ and single and double frequency are found²⁾.

As it is difficult to compare Kagan and Maksimov's method²³⁾ with the usual expansion method of \underline{A} and \underline{B} the author reconsidered the derivation of (7)³¹⁾. In earlier work^{24, 28, 30)} some approximations were made which are now avoided. It turns out, somewhat surprisingly, that in

the improved treatment the $\theta - 2\theta$ property is lost completely and (7) is replaced by a more complicated expression. Also (9) no longer holds. This work is presented in chapter 2. Here it is pointed out under which conditions (7) can be obtained. In fact its validity is related to a weak coupling between the directions of \underline{W} and \underline{J} via $J^{(0)}$. For rough spherical molecules this coupling is rather strong and significant deviations from (7) are found³²⁾. For a further discussion see also ref. 26.

In chapter 2 also a brief discussion is given of the various collision integrals (matrix elements of $J^{(0)}$) that determine C and τ . An attempt is made to derive the values of some of these from the experimental data.

For viscosity the quantity $\underline{\psi}$ at the left in (4) is proportional to the second rank irreducible tensor $[\underline{W}]^{(2)}$. Thus $\underline{\phi}$ is also second rank irreducible. Also, due to the space reflection invariance properties of J , $\underline{\phi}$ must be even in \underline{W} . In treatments not dealing with field effects $\underline{\phi}$ is usually approximated by $[\underline{W}]^{(2)}$. In order to obtain any field effect at all some \underline{J} dependent functions must be added. The simplest of these are $[\underline{J}]^{(2)}$, $[\underline{W}]^{(2)} \underline{J}$ and $[\underline{W}]^{(2)} [\underline{J}]^{(2)}$. $[\underline{W}]^{(2)} \underline{J}$ being odd in \underline{J} leads to a positive contribution to the field effect on the longitudinal coefficients.

As the experimentally observed field effect is negative, theoretical attention has been centered upon $[\underline{J}]^{(2)}$ and $[\underline{W}]^{(2)} [\underline{J}]^{(2)}$, Knaap and Beenakker²⁴⁾ have considered $[\underline{W}]^{(2)} [\underline{J}]^{(2)}$. As they used the elastic Kagan-Maksimov collision model, they were not able to treat $[\underline{J}]^{(2)}$, since matrix elements of $J^{(0)}$ containing this function vanish. This is different for $[\underline{W}]^{(2)} [\underline{J}]^{(2)}$ as \underline{W} changes during

collision. As in the case of heat conductivity the final results again exhibit the $\theta - 2\theta$ property, although the relaxation time $\tau = \theta/\omega_p$ is now different. Still it is of the same order of magnitude and hence one is not able to explain the early saturation found for the hydrogen isotopic molecules. It was already suggested in the paper containing the experimental results for the latter (see also ref. 33) that θ should contain a relaxation time corresponding to inelastic collisions (in particular; \underline{J} reorienting). As these are less frequent for hydrogen than for other molecules this would explain the experimental results. For this reason $[\underline{J}]^{(2)}$ is of importance as this quantity changes during inelastic collisions but not during elastic ones. The diagonal matrix element of $J^{(0)}$ with respect to $[\underline{J}]^{(2)}$ then gives the required (inelastic) relaxation time τ . Expressions for $\underline{\eta}$ based on this function were obtained independently by H.F.P. Knaap and the author in the later half of 1966.

Knaap and coworkers³⁴⁾ compared τ with data drawn from nuclear magnetic resonance experiments and obtained a satisfactory agreement. In a later treatment, McCourt and Snider³⁵⁾ considered both $[\underline{J}]^{(2)}$ and $[\underline{W}]^{(2)} [\underline{J}]^{(2)}$. The latter is of importance when the bulk viscosity η_v and the cross coefficient ζ are considered, since $[\underline{J}]^{(2)}$ does not give a contribution to these quantities and the shear viscosity coefficient η_1 . Recent calculations for rough spherical molecules³⁶⁾ have shown that for this model the relative importance of $[\underline{J}]^{(2)}$, $[\underline{W}]^{(2)} \underline{J}$ and $[\underline{W}]^{(2)} [\underline{J}]^{(2)}$ is given by the ratio -100: +4 : -1.

In chapter 3 a calculation on the basis of the expan-

sion functions $[\underline{W}]^{(2)}$ and $[\underline{J}]^{(2)}$ is given of $\underline{\eta}$ for mixtures of diatomic diamagnetic gases. The results are specialized further to a binary mixture of a diatomic diamagnetic and a noble gas.

Measurements of viscosity in mixtures are much more interesting than those for heat conductivity due to the following two reasons:

- a. The number of expansion functions required for a satisfactory description of the Senftleben-Beenakker effect is always one less for viscosity than for heat conductivity. Hence the expression obtained for $\underline{\eta}$ is somewhat simpler than that for $\underline{\lambda}$ (it contains fewer different collision integrals).
- b. The parameter $\Theta_{\frac{1}{2}}$ for which the longitudinal effects reach half their saturation value and Θ_{\max} for which the transverse ones reach their maximum are given by the diagonal matrix elements $(J^{(0)} \underline{W} [\underline{J}]^{(2)}, \underline{W} [\underline{J}]^{(2)})$ and $(J^{(0)} [\underline{J}]^{(2)}, [\underline{J}]^{(2)})$ for heat conductivity and shear viscosity respectively.

As is pointed out more fully in chapter 2 the heat conductivity expression is connected with collisional reorientation of both \underline{W} and \underline{J} whereas the second one is linked with reorientation of \underline{J} only. Thus viscosity gives more direct information about inelastic effects than heat conductivity. In mixtures measurements of $\Theta_{\frac{1}{2}}$ and Θ_{\max} as a function of concentration lead to separate information about reorientation of \underline{J} due to molecule-molecule and molecule-atom collisions.

Chapters 4 and 5 deal with the analytic continuation for complex B/n of the theoretical expressions for heat conduc-

tivity and shear viscosity. In chapter 4 ionized gases are considered and in chapter 5 polyatomic neutral gases. As can be seen from (7) (see also figure 1) the longitudinal coefficients show a dispersion and the transverse ones an absorption type behaviour as a function of B/n . This leads to the question as to whether the two are linked by a dispersion relation. By introducing spherical coordinates one can write some of the transport coefficients as real and imaginary parts of a complex function of the real parameter B/n ²³). For instance $2\eta_2 - \eta_1$ and $-\eta_4$ and also η_3 and $-\eta_5$ form such pairs.

The problem is now to find an analytic continuation of these complex functions. In order to solve this problem it is convenient to start from equation (4). It has the formal solution:

$$\underline{\phi} = (J^{(0)} + J^{(1)})^{-1} \underline{\psi} = J^{-1} \underline{\psi} \quad (10)$$

Or, in spherical coordinates:

$$\phi_{\ell}^m = (J^{(0)} + J^{(1)})^{-1} \psi_{\ell}^m = J^{-1} \psi_{\ell}^m \quad (11)$$

The main feature of the work presented in chapters 4 and 5 is the reduction of J^{-1} to an expression containing resolvents of the type

$$(\hat{J}^{(0)} + i\alpha B/n)^{-1}; \alpha \text{ real} \quad (12)$$

Due to the dissipative nature of $\hat{J}^{(0)}$ along with $J^{(0)}$ (spectrum in the left complex half plane) an analytic extension for complex B/n in one half plane is always possible. For ionized gases the reduction to (12) is readily obtained from the rotational invariance of $J^{(0)}$. The situation is

not so simple for neutral polyatomic gases, due to the circumstance that at least two vector variables are present (W, J).

If in an ionized gas mixture charged particles of both signs are present the expressions for the transport coefficients contain resolvents with positive and negative α 's and an analytic extension in one half plane is not possible. This also happens for polyatomic neutral gases.

The best one can do in these cases is to split the transport coefficients into two parts, $L^{(+)}$, and $L^{(-)}$; each allowing a dispersion relation, but of contrary sign. Thus an overall dispersion only exists if one of the pair $L^{(+)}$, $L^{(-)}$ vanishes.

This is the case for electrons in an equilibrium background (Lorentz gas). Here transport is due only to electrons and a dispersion relation indeed holds. The same is true for transport coefficients of monatomic gases measured in rotating systems. Here the Coriolis force acts in precisely the same way as the Lorentz force in a magnetic field but no sign differences in the α 's arise in this case.

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THE INFLUENCE OF ANGULAR MOMENTUM ANISOTROPY ON THE HEAT CONDUCTIVITY OF DILUTE DIATOMIC GASES

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Synopsis

The influence of angular momentum anisotropy on the heat conductivity of a dilute gas consisting of diamagnetic linear molecules is investigated. By the use of a new technique to solve the expansion coefficients of the molecular distribution function it was possible to obtain a solution for this function which does not contain any further approximations than those implied by the choice of trial functions for this distribution function. Secondly it is clearly exhibited how angular momentum reorientation cross sections enter into the formalism when an external magnetic field is applied (Senftleben-Beenakker effect). In this way it was possible to obtain the value of one of these cross sections for CO and N₂ from the experimental results on this effect. Moreover it is pointed out how all cross sections entering into the formulae for the heat conductivity and viscosity of H₂ and D₂ can be obtained separately from the combined experimental results on both transport coefficients.

I. *Introduction.* About the influence of magnetic fields on the transport properties of dilute polyatomic gases, the Senftleben-Beenakker effect, a rapidly growing body of experimental results exists^{1) 2) 3)}. Theoretical computations based on a simple collision model proposed by Kagan and Maksimov (K. M.)^{4) 5)} have been made, but the obtained results for viscosity, heat conductivity and binary diffusion are not in mutual agreement^{6) 7)}. As a matter of fact the model contains an adjustable parameter describing the nonsphericity of the collision cross sections and this parameter has to be chosen different for the different transport phenomena. It is also possible to proceed without making model assumptions. One then obtains results that contain several kinetic cross sections that cannot be numerically evaluated without a detailed knowledge of the complicated collision mechanism of polyatomic molecules. Such a program was recently completed by McCourt and Snider^{8) 9)} for the case of heat conductivity and viscosity in a semi-quantum treatment. A classical line of approach was followed by Kagan and Maksimov in a second paper¹⁰⁾. Here they separated the

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collision operator into a monatomic part and a second part which contained the essentially polyatomic features. Assuming matrix elements formed from the second part to be small with respect to the first they employed a perturbation technique to obtain expressions for the field influence on heat conductivity and viscosity. This assumption will hold for off-diagonal matrix elements but not for the diagonal ones. The latter contain angular momentum reorientation cross sections that are in the same order of magnitude as the transport cross sections with the exception of hydrogen, deuterium and possibly HD. In the present paper the classical case is considered once more but no smallness assumptions are made except those implied by the choice of trial functions in the expansion of the molecular distribution function. By the use of a new technique to derive the expansion coefficients in the distribution function it was possible to show which assumptions correspond to the occurrence of 'single and double frequencies' in the expression for the saturation curve. Moreover, it is clearly exhibited how angular momentum reorientation enters into the formalism.

II. *Equations governing the heat conductivity in a magnetic field.* By means of the Chapman-Enskog method it is possible to generate a solution for the heat conductivity problem. For the heat conductivity tensor λ , defined by

$$\mathbf{q} = -\lambda \cdot \partial_{\mathbf{x}} T \quad (2.1)$$

where \mathbf{q} is the heat flux and T the absolute temperature in degrees Kelvin one obtains for a diamagnetic gas, consisting of linear molecules

$$\lambda = (2k^2T/m)((W^2 + M^2 - \frac{7}{2}) \mathbf{W}, \mathbf{A}). \quad (2.2)$$

Here the inner product is defined as

$$(\Phi, \Psi) = \int F^{(0)} \Phi \Psi \, d\sigma \quad (2.3)$$

where

$$F^{(0)} = (4\pi^{\frac{1}{2}})^{-1} \exp - (W^2 + M^2), \, d\sigma = dW \frac{dM}{M} \, d\psi \quad (2.4)$$

$W = (m/2kT)^{\frac{1}{2}} V$ and $M = (2IkT)^{-\frac{1}{2}} J$ are reduced quantities derived from the peculiar velocity V and angular momentum J , ψ is the angle specifying the position of the molecular axis in the plane perpendicular to J , m is the mass, I the moment of inertia of the molecules considered and k is Boltzmann's constant.

$A(W, M, \psi, B)$ is the solution of the equation

$$(\frac{7}{2} - W^2 - M^2) \mathbf{W} = J\mathbf{A} = J^{(0)} \mathbf{A} - n^{-1} (\dot{M} \cdot \partial_M + \dot{\psi} \cdot \partial_{\psi}) \mathbf{A} \quad (2.5)$$

where n is the gas density and \dot{M} is given by

$$\dot{M} = \gamma M \times B \quad (2.6)$$

γ being the gyromagnetic ratio. ψ can also be expressed in terms of ψ and M but this will not be used here.

For the linearized collision operator $J^{(0)}$ the expression used by Taxman¹¹⁾ is assumed to hold (see also ref. 12 appendix B).

Hence:

$$J^{(0)}A = \int F_1^{(0)}(A'' + A_1' - A - A_1) gb db d\epsilon d\sigma_1 \quad (2.7)$$

g , b and ϵ have their usual meaning as relative velocity, impact parameter and azimuthal angle about the direction of the initial relative velocity. The subscript 1 refers to the second molecule taking part in the collision. Double primed quantities refer to the initial state of the so called 'corresponding collision' which restores molecules in the unprimed state, whereas single primes will be used to refer to the final state in 'direct collisions' which remove molecules from the unprimed state. As is well known double primes can be replaced by single ones when inverse collisions exist, that is when $J^{(0)}$ is self-adjoint. This is the case for monatomic gases but generally not for polyatomic ones. To obtain unique solutions (2.4) has to be supplemented by orthogonalizing A to the nullity of J . Hence:

$$(A, \Phi) = 0, \Phi \in \{1, W, W^2 + M^2\}. \quad (2.8)$$

The set of equations (2.5), (2.8) applies as long as magnetization effects can be neglected, but can easily be adapted to include these.

III. *Trial functions for A.* To obtain approximate solutions of (2.5) A is usually expanded into some set of orthogonal functions, which series is then truncated after a few terms. For monatomic gases the eigenfunctions of the Maxwellian collision operator are very suitable for this purpose and inclusion of only one or two terms in the series expansion is sufficient for most purposes. For polyatomic gases, however, no exactly solvable collision model is known and hence series expansions are nearly always into products of Maxwellian eigenfunctions and some convenient orthogonal set of internal state functions. In earlier papers^{11) 13) 14)} these were nearly always restricted to expansions into internal energy variables. A few years ago, however, it was pointed out by Kagan and Afanas'ev (K.A.)¹⁵⁾ that angular momentum direction variables have to be taken into account as well; external gradients not only create an anisotropy in velocity space but also in angular momentum space as both are connected via the collision mechanism. For the existence of external field influences angular momentum anisotropy is paramount for it is just this anisotropy that is attacked by the precession of angular momentum in external fields. The situation is somewhat different from the case of ionized gases in a magnetic field where the anisotropy in velocity space is directly attacked by the Lorentz force. As the latter is a more direct process the influence on the transport coefficients is much larger.

The ideas of Kagan and Afanas'ev were worked out further by Waldmann¹⁶⁾ and Dahler c.s.¹⁷⁾¹⁸⁾¹⁹⁾ for gases consisting of rough spheres, loaded spheres and spherocylinders. From these it becomes clear that a good approximation to A can be obtained by means of the trial function originally proposed by K.A.¹⁵⁾:

$$A = \sum_{\alpha=1}^3 A^{(\alpha)} \Phi^{(\alpha)} \quad (3.1)$$

where

$$\Phi^{(1)} = \left(\frac{5}{2} - W^2\right) W, \quad \Phi^{(2)} = (1 - M^2) W, \quad \Phi^{(3)} = W \cdot M^0 M \quad (3.2)$$

Here the \cdot between the M 's has its usual meaning (see for instance ref. 12). Although the $A^{(\alpha)}$'s may still depend on ψ this can be neglected for the present purpose⁴⁾¹⁵⁾, but not when the influence of an electric field is studied²⁰⁾. When a magnetic field is present the $A^{(\alpha)}$'s are no longer scalars but instead one now has (in component notation):

$$A_k = A_{kl}^{(1)} \Phi_l^{(1)} + A_{kl}^{(2)} \Phi_l^{(2)} + A_{klmn}^{(3)} \Phi_{lmn}^{(3)} \quad (3.3)$$

where

$$\Phi_{lmn}^{(3)} = W_l M_m^0 M_n \quad (3.4)$$

As $\Phi^{(3)}$, according to (3.4), is no longer irreducible but the Kronecker-product of irreducible representations of the rotationgroup of dimensions one and two respectively it can be decomposed into three irreducible parts. By doing so one obtains:

$$A_k = \sum_{\alpha=1}^5 A_k^{(\alpha)} \Phi^{(\alpha)} \quad (3.5)$$

where $\Phi^{(1)}$, $\Phi^{(2)}$ and $\Phi^{(3)}$ are still given by (3.2) but in addition one now has:

$$\begin{aligned} \Phi_{lm}^{(4)} &= \frac{\mathbf{0}}{(W \times M)_l M_m} \\ \Phi_{lmn}^{(5)} &= \frac{\mathbf{0}}{W_l M_m M_n} \end{aligned} \quad (3.6)$$

Here again the notation of ref. 12 has been used, the combination of double bar and $\mathbf{0}$ indicating irreducibility. Note that in (3.5) subscripts have been dropped for brevity as will be done in the future when no confusion can arise. All $\Phi^{(\alpha)}$ as used in (3.5) are mutually orthogonal, their norms are given in appendix I. To define the coefficients $A_{klm}^{(4)}$ and $A_{klmn}^{(5)}$ uniquely they are supposed to be irreducible in (l, m) and (l, m, n) , respectively. Substitution now leads to the following expression for the heat conductivity tensor:

$$\lambda_{kl} = -(2k^2 T/m) \left(\frac{5}{4} A_{lk}^{(1)} + \frac{1}{2} A_{lk}^{(2)} \right) \quad (3.7)$$

IV. *Equations for the $A^{(\alpha)}$ -coefficients.* By introducing (3.5) into (2.5) and forming the inner products with each of the five $\Phi^{(\alpha)}$'s one obtains a set of

five equations from which the $A^{(\alpha)}$'s can be determined:

$$-\delta_{kr}(\frac{5}{4}\delta_{1\beta} + \frac{1}{2}\delta_{2\beta}) = \sum_{\alpha} A_k^{(\alpha)}[\Phi^{(\alpha)} + \Phi_1^{(\alpha)}, \Phi^{(\beta)}] + \frac{1}{n} \sum_{\alpha} A_k^{(\alpha)}(\dot{M} \cdot \partial_M \Phi^{(\alpha)}, \Phi^{(\beta)}). \quad (4.1)$$

The definition of the Enskog brackets in the first term at the right hand side is given in appendix II where a further evaluation in terms of kinetic collision cross sections (generalized Ω -integrals) is also given. In connection with this it should be remarked that the matrix elements of $J^{(0)}$ with respect to $\Phi^{(4)}$ and $\Phi^{(5)}$ as well as those formed from each of them with the other $\Phi^{(\alpha)}$ -functions vanish due to the rotational invariance of $J^{(0)}$ and the Wigner-Eckart theorem. The inner products $(\dot{M} \cdot \partial_M \Phi^{(\alpha)}, \Phi^{(\beta)})$ are given in appendix I. Thus one is left with the result:

$$-\frac{15}{4}\delta_{kr} = \sum_{\alpha=1}^3 t_{\alpha 1} A_{kr}^{(\alpha)} \quad (4.2a)$$

$$-\frac{3}{2}\delta_{kr} = \sum_{\alpha=1}^3 t_{\alpha 2} A_{kr}^{(\alpha)} \quad (4.2b)$$

$$0 = \sum_{\alpha=1}^3 t_{\alpha 3} A_{kr}^{(\alpha)} + \zeta A_{kl}^{(3)} \epsilon_{lrm} b_m - \frac{2}{3} \zeta A_{krm}^{(4)} b_m \quad (4.2c)$$

$$0 = t_{44} A_{krs}^{(4)} + \frac{1}{2} \zeta A_{kl}^{(3)} b_m \Delta_{mlrs} + \frac{5}{8} \zeta A_{klm}^{(4)} \epsilon_{lnw} b_w \Delta_{nmrs} - \frac{2}{3} \zeta A_{kcrs}^{(5)} b_w \quad (4.2d)$$

$$0 = t_{55} A_{krst}^{(5)} + \frac{7}{45} \zeta A_{klm}^{(4)} b_w \Delta_{wlm, rst} + \frac{14}{45} \zeta A_{klmn}^{(5)} \epsilon_{mpw} b_w \Delta_{lpnrst} \quad (4.2e)$$

Here is

$$t_{\alpha\beta} = [(\Phi^{(\alpha)} + \Phi_1^{(\alpha)}) \cdot \Phi^{(\beta)}] \quad (4.3)$$

where the dot in the Enskog bracket indicates contraction with respect to the available indices, b is the unit vector in the magnetic field direction and $\zeta = \gamma B/n$.

The Δ -tensors are isotropic tensors, which are irreducible in their first and second sets of subscripts respectively, see appendix I.

A closer inspection of (4.2c) shows that $A_{klm}^{(4)}$ enters only with one of the last two indices saturated with b_n . Hence it is not necessary to solve the whole tensor $A_{klm}^{(4)}$ from the equations (4.2) but only the saturated form $A_{kl}^{(4)} = A_{klm}^{(4)} b_m$. Saturation of (4.2d) with b_s now leads to:

$$0 = t_{44} A_{kr}^{(4)} + \frac{1}{2} \zeta A_{kl}^{(3)} (\delta_{lr} + \frac{1}{3} b_l b_r) + \frac{5}{8} \zeta A_{kl}^{(4)} \epsilon_{lrm} b_m - \frac{2}{3} \zeta A_{kr}^{(5)} \quad (4.2d')$$

where $A_{kr}^{(5)} = A_{krst}^{(5)} b_s b_t$. In the same way saturation of (4.2e) with $b_s b_t$ leads to:

$$0 = t_{55} A_{kr}^{(5)} + \frac{14}{225} \zeta A_{km}^{(4)} (8\delta_{mr} + b_m b_r) + \frac{28}{45} \zeta A_{kl}^{(5)} \epsilon_{lrw} b_w \quad (4.2e')$$

From the resulting equations $A^{(4)}$ and $A^{(5)}$ are readily eliminated, thus

leaving equations (4.2a), (4.2b) and

$$\begin{aligned}
 0 = & \sum_{\alpha=1}^3 t_{\alpha 3} A_{km}^{(\alpha)} \left\{ (5t_{44} - \frac{14}{15} t_{55}) \delta_{mr} + (\frac{25}{6} + \frac{28}{9} t_{44}/t_{55}) \zeta \varepsilon_{mrw} b_w + \right. \\
 & \left. + \frac{14}{5} \zeta^2 / t_{55} b_m b_r \right\} + \\
 & + A_{km}^{(3)} \left\{ - (\frac{8}{3} + \frac{28}{9} t_{44}/t_{55}) \zeta^2 \delta_{mr} + 5t_{44} \zeta \varepsilon_{mrw} b_w + (\frac{14}{3} + \frac{28}{9} t_{44}/t_{55}) \zeta^2 b_m b_r \right\} \quad (4.4)
 \end{aligned}$$

to determine the remaining $A^{(\alpha)}$'s.

From the equations (4.2) it is seen that for vanishing external field $A^{(4)}$ and $A^{(5)}$ vanish also. One now obtains

$$A_{ki}^{(\alpha)} = A^{(\alpha)} \delta_{ki}; \quad \alpha \in (1, 2, 3) \quad (4.5)$$

where the $A^{(\alpha)}$'s must be solved from

$$- (\frac{15}{4} \delta_{1\beta} + \frac{3}{2} \delta_{2\beta}) = \sum_{\alpha=1}^3 t_{\alpha\beta} A^{(\alpha)}; \quad \beta \in (1, 2, 3). \quad (4.6)$$

The Enskog brackets can be evaluated one step further by means of integration with respect to the center of mass velocity. The results are given appendix II. Introducing these into (4.6) one is left with the following set of coupled equations:

$$\begin{aligned}
 -\frac{15}{4} &= \{4\langle \gamma\gamma : \Delta\gamma\gamma \rangle + 7\langle \gamma^2 \Delta\gamma^2 \rangle\} A^{(1)} - 5\langle \gamma^2 \Delta\gamma^2 \rangle A^{(2)} + 4\langle M^0 M : \Delta\gamma\gamma \rangle A^{(3)} \\
 -\frac{3}{2} &= -5\langle \gamma^2 \Delta\gamma^2 \rangle A^{(1)} + \{3\langle \gamma^2 \Delta\gamma^2 \rangle + 4\langle (M^2 - M_1^2) \gamma : \Delta M^2 \gamma \rangle\} A^{(2)} \\
 &- \langle (M^0 M - M_1^0 M_1) : \gamma \Delta M^2 \gamma \rangle A^{(3)} \\
 0 &= 4\langle M^0 M : \Delta\gamma\gamma \rangle A^{(1)} - 4\langle (M^0 M - M_1^0 M_1) : \gamma \Delta M^2 \gamma \rangle A^{(2)} \\
 &+ \{2\langle (M^0 M + M_1^0 M_1) : \Delta M^0 M \rangle + 4\langle (M^0 M - M_1^0 M_1) : \gamma \Delta (M^0 M \cdot \gamma) \rangle\} A^{(3)} \quad (4.7)
 \end{aligned}$$

For the definition of the collision integrals $\langle FAG \rangle$ see appendix II. The part of the scheme in the left upper corner surrounded by the dashed line corresponds to the result obtained by Taxman¹¹⁾. Both experiment^{1) 2) 3)} and model calculations on loaded spheres and spherocylinders^{18) 19)} show that the influence of angular momentum anisotropy on transport coefficients is small. Hence $A^{(3)}$ is only weakly coupled to $A^{(1)}$ and $A^{(2)}$ which condition is satisfied when t_{13} and t_{23} are small as compared to the diagonal elements $t_{\alpha\alpha}$. In connection with this it should be remarked that t_{33} is of the order of t_{11} and t_{22} . In the totally elastic limit it reduces to $16/9\Omega^{(1,1)}$, $\Omega^{(1,1)}$ being one of the familiar monatomic collision integrals.

$A^{(1)}$ and $A^{(2)}$ can be solved from (4.6) and substituted into (3.7) thus giving the heat conductivity tensor for vanishing external field:

$$\lambda_{kl} = \lambda \delta_{kl}, \quad \lambda = \frac{6k^2 T}{mD} \left\{ \frac{25}{16} \left| \frac{t_{22} t_{23}}{t_{23} t_{33}} \right| + \frac{1}{4} \left| \frac{t_{11} t_{13}}{t_{13} t_{33}} \right| - \frac{5}{4} \left| \frac{t_{12} t_{13}}{t_{23} t_{33}} \right| \right\} \quad (4.8)$$

where $D = \det(t_{\alpha\beta})$. Note that (4.8) deviates from the Taxman result only in quadratic or higher order terms in t_{13} and t_{23} .

V. *The heat conductivity tensor in the presence of a magnetic field.* To obtain the heat conductivity tensor for the case of nonvanishing ζ it is convenient to subtract the field free solution from (4.2a, b) and (4.4). Writing

$$A_{kr}^{(\alpha)} = A^{(\alpha)}\delta_{kr} + Y_{kr}^{(\alpha)} \quad (5.1)$$

one obtains:

$$\begin{aligned} \sum_{\alpha=1}^3 t_{\alpha\beta} Y_{kr}^{(\alpha)} &= 0, \quad \beta \in (1, 2) \\ \sum_{\alpha=1}^3 t_{\alpha 3} Y_{km}^{(\alpha)} \{ & (5t_{44} - \frac{14}{15}\zeta^2/t_{55})\delta_{mr} + (\frac{25}{6} + \frac{28}{9}t_{44}/t_{55})\zeta\epsilon_{mrw}b_w + \frac{14}{5}\zeta^2/t_{55}b_m b_r \} \\ + Y_{km}^{(3)} \{ & -(\frac{8}{3} + \frac{28}{9}t_{44}/t_{55})\zeta^2\delta_{mr} + 5t_{44}\zeta\epsilon_{mrw}b_w + (\frac{14}{3} + \frac{28}{9}t_{44}/t_{55})\zeta^2b_m b_r \} \\ = A^{(3)} \{ & (\frac{8}{3} + \frac{28}{9}t_{44}/t_{55})\delta_{kr} - 5t_{44}\zeta\epsilon_{krw}b_w - (\frac{14}{3} + \frac{28}{9}t_{44}/t_{55})\zeta^2b_k b_r \} \quad (5.2) \end{aligned}$$

From the first two equations $Y^{(1)}$ and $Y^{(2)}$ can be solved in terms of $Y^{(3)}$. Introducing this into the third equation one is left with a closed equation for $Y^{(3)}$:

$$\begin{aligned} Y_{km}^{(3)} \left\{ \hat{t}_{33} \left(5t_{44} - \frac{14}{15} \frac{\zeta^2}{t_{55}} \right) - \left(\frac{8}{3} + \frac{28}{9} \frac{t_{44}}{t_{55}} \right) \zeta^2 \right\} \delta_{mr} + \\ + \left[\hat{t}_{33} \left(\frac{25}{6} + \frac{28}{9} \frac{t_{44}}{t_{55}} \right) + 5t_{44} \right] \zeta \epsilon_{mrw} b_w \\ + \left[\frac{14}{5} \frac{\hat{t}_{33}}{t_{55}} + \frac{14}{3} + \frac{28}{9} \frac{t_{44}}{t_{55}} \right] \zeta^2 b_m b_r \} = \\ A^{(3)} \left\{ \left[\frac{8}{3} + \frac{28}{9} \frac{t_{44}}{t_{55}} \right] \delta_{kr} - 5t_{44} \zeta \epsilon_{krw} b_w - \left[\frac{14}{3} + \frac{28}{9} \frac{t_{44}}{t_{55}} \right] \zeta^2 b_k b_r \right\} \quad (5.3) \end{aligned}$$

where

$$\hat{t}_{33} = D \left| \begin{array}{cc} t_{11} & t_{12} \\ t_{12} & t_{22} \end{array} \right| \quad (5.4)$$

which differs from t_{33} only in terms of second order in t_{13} and t_{23} . $Y_{kl}^{(3)}$ is easily solved from (5.3) by noting that the inverse of

$$a\delta_{kl} + b\epsilon_{klm}b_m + cb_k b_l \quad (5.5)$$

is given by

$$\alpha\delta_{kl} + \beta\epsilon_{klm}b_m + \gamma b_k b_l \quad (5.6)$$

with $\alpha = a/(a^2 + b^2)$; $\beta = -b/(a^2 + b^2)$, $\alpha + \gamma = (a + c)^{-1}$

The result is:

$$Y_{kl}^{(3)} = (A^{(3)}/\hat{t}_{33}) U_{kl} \quad (5.7)$$

where

$$\begin{aligned}
 U_{kl}(x) = \frac{5}{2}t_{44} \left\{ - \frac{[P(PQ-1)x^2 + Q]x^2}{(PQ-1)^2x^4 + (P^2 + Q^2 + 2)x^2 + 1} \cdot \delta_{kl} \right. \\
 \left. - \frac{[(1+P^2)x^2 + 1]x}{(PQ-1)^2x^4 + (P^2 + Q^2 + 2)x^2 + 1} \cdot \varepsilon_{klm}b_m \right. \\
 \left. + \left(\frac{[P(PQ-1)x^2 + Q]x^2}{(PQ-1)^2x^4 + (P^2 + Q^2 + 2)x^2 + 1} - \frac{x^2}{(\frac{3}{2}P + Q - \frac{11}{4})x^2 + 1} \right) b_k b_l \right\}
 \end{aligned} \quad (5.8)$$

Here is:

$$\begin{aligned}
 P = \frac{4}{3} + \frac{1}{9}t_{44}/t_{55} \quad x = \frac{2}{5}\zeta/t_{44} \\
 Q = \frac{3}{4} + \frac{5}{2}t_{44}/t_{33}
 \end{aligned} \quad (5.9)$$

By inserting (5.7) into (5.2) one now obtains $Y^{(1)}$ and $Y^{(2)}$ which can be substituted into (3.7) with the final result:

$$\Delta\lambda_{kl} = \lambda_{kl} - \lambda\delta_{kl} = \frac{6k^2T}{m} (\Delta/D)^2 U_{lk} \quad (5.10)$$

where

$$\Delta = \begin{vmatrix} t_{11} & t_{12} & \frac{5}{4} \\ t_{12} & t_{22} & \frac{1}{2} \\ t_{13} & t_{23} & 0 \end{vmatrix} \quad (5.11)$$

In the limit $x \rightarrow \infty$ U_{kl} becomes equal to

$$U_{kl}(\infty) = \frac{5}{2}t_{44} \left\{ - \frac{P}{PQ-1} \delta_{kl} + \left[\frac{P}{PQ-1} - \frac{1}{\frac{3}{2}P + Q - \frac{11}{4}} \right] b_k b_l \right\} \quad (5.12)$$

In this limit the ratio $(\Delta\lambda)_{//}/(\Delta\lambda)_{\perp}$, where $//$ and \perp refer to magnetic field direction parallel and perpendicular to $\partial_x T$ respectively, becomes

$$\frac{(\Delta\lambda)_{//}}{(\Delta\lambda)_{\perp}} = \frac{PQ-1}{P(\frac{3}{2}P + Q - \frac{11}{4})} \quad (5.13)$$

VI. *Some special cases.* a. An approximation leading to important simplifications in $U_{kl}(x)$ will be discussed first.

The coefficients t_{33} , t_{44} and t_{55} all correspond to contracted forms of the matrix element $(J^{(0)}\Phi_{klm}^{(3)}, \Phi_{pqr}^{(3)})$ where $\Phi_{klm}^{(3)}$ is defined by (3.4). In fact one has:

$$\begin{aligned}
 - (J^{(0)}\Phi_{klm}^{(3)}, \Phi_{pqr}^{(3)}) &= \frac{3}{100}t_{33}\Delta_{sklm}\Delta_{spqr} \\
 &+ \frac{1}{90}t_{44}(\varepsilon_{kls}\delta_{mt} + \varepsilon_{kms}\delta_{lt})(\delta_{su}\delta_{tv} + \delta_{sv}\delta_{tu})(\varepsilon_{pqu}\delta_{rv} + \varepsilon_{prv}\delta_{qu}) \\
 &+ \frac{1}{42}t_{55}\Delta_{klm}, pqr.
 \end{aligned} \quad (6.1)$$

If the interaction between W and M via the collision mechanism becomes vanishingly small then (6.1) becomes proportional to $\delta_{kp}\Delta_{lm,qr}$ (see also ref. 8). Thus the following approximation seems reasonable for the case of weak coupling between W and M :

$$-(J^{(0)}\Phi_{klm}^{(3)}, \Phi_{pqr}^{(3)}) \approx \frac{1}{10}t_{33}\delta_{kp}\Delta_{lm,qr} \quad (6.2)$$

which is exact for the contracted quantity $(J^{(0)}\Phi_{kkm}^{(3)}, \Phi_{ppr}^{(3)}) = (J^{(0)}\Phi_m^{(3)}, \Phi_r^{(3)})$. Comparison of (6.1) and (6.2) shows that (6.2) amounts to the approximation

$$t_{44} \approx \frac{3}{2}t_{33}, \quad t_{55} \approx \frac{7}{5}t_{33} \quad (6.3)$$

(6.3) is indeed exactly fulfilled in the totally elastic limit but it is important to note that it also holds for the contributions of the reorientation cross section $\langle (M^0M + M_1^0M_1) : \Delta M^0M \rangle$ to t_{33} , t_{44} and t_{55} in the general inelastic case. Hence this cross section may be arbitrarily large without invalidating (6.2) and (6.3).

Introducing (6.3) into (5.9) and (5.10) and replacing t_{33} by t_{33} one obtains the well-known result⁴⁾⁵⁾:

$$U_{kl}(y) = \frac{3}{10}t_{33} \left\{ \frac{-3y^2(3+4y^2)}{(1+y^2)(1+4y^2)} \delta_{kl} - \frac{(8y^2+5)y}{(1+y^2)(1+4y^2)} \varepsilon_{klm} b_m + \frac{y^2(7+4y^2)}{(1+y^2)(1+4y^2)} b_k b_l \right\} \quad (6.4)$$

where

$$y = \frac{3}{5}\zeta/t_{33} \quad (6.5)$$

Thus it is seen that the occurrence of the 'single and double frequencies' y and $2y$ is closely connected with the validity of the 'diagonal approximation' (6.2).

b. In their first paper⁴⁾ Kagan and Maksimov used the following model to obtain numerical results:

$$\langle FAG \rangle \approx \langle \{1 + \frac{3}{2}\mu(M^0M/M^2 + M_1^0M_1/M_1^2) : (\gamma^0\gamma/\gamma^2 + \gamma'^0\gamma'/\gamma'^2)\} FAG \rangle_0 \quad (6.6)$$

$$M' = M, \quad M_1' = M_1. \quad (6.7)$$

Here μ is an adjustable parameter, describing the nonsphericity of the cross section and the subscript 0 in $\langle \rangle_0$ indicates that this quantity must be computed in the elastic limit. One thus obtains:

$$\begin{aligned} t_{11} &\approx 4\langle \gamma\gamma : \Delta\gamma\gamma \rangle_0 = 4\Omega^{(2,2)} & t_{12} &= t_{13} = 0 \\ t_{22} &\approx 4\langle \gamma \cdot \Delta\gamma \rangle_0 = 4\Omega^{(1,1)} & t_{23} &\approx \frac{4}{5}\mu \left(\frac{4}{3}\Omega^{(1,1)} - \Omega^{(2,1)} \right) \\ t_{33} &\approx \frac{16}{9}\langle \gamma \cdot \Delta\gamma \rangle_0 = \frac{16}{9}\Omega^{(1,1)} \end{aligned} \quad (6.8)$$

This can be looked upon as a first approximation beyond the totally elastic

result. It can be generalized somewhat to include energetically inelastic collisions. For this purpose one assumes instead of (6.7):

$$\mathbf{M}'/M' = \mathbf{M}/M, \quad \mathbf{M}'_1/M'_1 = \mathbf{M}_1/M_1. \quad (6.9)$$

In this case t_{12} and t_{13} are no longer vanishing but one now has:

$$\begin{aligned} t_{12} &\approx -5\langle\gamma^2\Delta\gamma^2\rangle \\ t_{13} &\approx -\frac{4}{15}\mu\langle\gamma^2\Delta\gamma^2\rangle \end{aligned} \quad (6.10)$$

whereas an additional contribution to t_{33} arises as well.

VII. *Discussion.* As the saturation curve given by (6.4) is in fair agreement with experiment the approximation (6.2) may indeed be assumed to hold. Hence the only collision integral entering into the description of the saturation curve is t_{33} which shall be written as

$$\begin{aligned} t_{33} &= \sigma_a + \sigma_b; \quad \sigma_a = 2\langle(\mathbf{M}^0\mathbf{M} + \mathbf{M}_1^0\mathbf{M}_1) : \Delta\mathbf{M}^0\mathbf{M}\rangle \\ &\quad \sigma_b = 4\langle(\mathbf{M}^0\mathbf{M} - \mathbf{M}_1^0\mathbf{M}_1) : \gamma\Delta(\mathbf{M}^0\mathbf{M} \cdot \gamma)\rangle \end{aligned} \quad (7.1)$$

in the following.

It is well known that angular momentum reorientation cross sections can be quite large for polyatomic molecules²¹⁾ and therefore one is not allowed to replace t_{33} by its elastic limit. It was found by Korving⁶⁾ that agreement with experiment can be obtained for diamagnetic gases by using the parameter $(H/p)/(H/p)_\frac{1}{2}$ for the description of the saturation curve. Here H is the magnetic field strength and p the pressure. The quantity $(H/p)_\frac{1}{2}$ refers to that field strength over pressure ratio for which half of the saturation value is reached. This procedure amounts to an elimination of t_{33} and hence a good agreement may be expected. Korving then compared the experimentally obtained value of $(H/p)_\frac{1}{2}$ (and hence t_{33}) with the expression obtained in the elastic limit. He found that for N_2 and CO the elastic theoretical result was about half the experimental one. Comparison of the somewhat unreliable low density results obtained by Gorelik *et alii*³⁾ for H_2 and D_2 showed that in this case t_{33} equals its elastic limit. This should be so, for H_2 and D_2 are nearly spherically symmetric molecules and angular momentum reorientation during collisions should be rare as compared to other polyatomic gases. In connection with this accurate heat conductivity measurements of H_2 , D_2 and HD should be of great value. From (6.5) it follows that

$$(\zeta_1)_{el}/\zeta_1 = (\sigma_b)_{el}/(\sigma_a + \sigma_b) \quad (7.2)$$

where the subscript *el* refers to the elastic limit. From Korving's results⁶⁾ it follows that $(\zeta_1)_{el}/\zeta_1$ equals 0.63 for N_2 and 0.51 for CO .

Assuming σ_b to be equal to its elastic value one then finds $\sigma_a/\sigma_b \approx 0.6$ for N_2 and 0.95 for CO . Hence the reorientation cross sections are of the same order of magnitude as the transport ones. The somewhat larger value

for CO may be connected with the asymmetric character of this molecule. It should be noted, however, that the assumption $\sigma_b \approx (\sigma_b)_{el}$ may be wrong.

The case of viscosity has not been treated here but nevertheless a number of results can already be drawn from simple considerations.

For rough spheres Condiff *et alii*¹⁷⁾ found that in this case the distribution function must be approximated by M^0M and M^0MW^0W in addition to the monatomic trial function W^0W . The influence of M^0M on the magnitude of the field free viscosity coefficient is about two times as large as that of W^0WM^0M . However, in the totally elastic limit ΔM^0M vanishes whereas ΔW^0WM^0M does not. Hence it is not clear if M^0M will give the most important contribution in cases less inelastic than rough spherical molecules. This difficulty was recognized by McCourt and Snider⁹⁾, who, in a semi-quantum treatment, kept both trial functions in the expansion of the distribution function. They found that this does not complicate the final results much. The viscosity change in a magnetic field now becomes a simple sum of contributions from both trial functions, each containing a different saturation parameter ζ . Going over to the equivalent classical case the ζ -parameter corresponding to the contribution from Φ is inversely proportional to the diagonal element $(\Phi, J^{(0)}\Phi)$. Hence:

$$\zeta_1 \sim [(M^0M + M_1^0M_1) : M^0M]^{-1} \sim (\sigma_a)^{-1} \quad (7.3)$$

$$\begin{aligned} \zeta_2 \sim & [(W^0WM^0M + W_1^0W_1M_1^0M_1) : M^0MW^0W]^{-1} = \\ & = \left\{ \frac{5}{3}\sigma_a + 2\langle \gamma^0\gamma(M^0M + M_1^0M_1) : \Delta M^0M\gamma^0\gamma \rangle + \right. \\ & \left. + \frac{20}{3}\langle \gamma(M^0M - M_1^0M_1) : \Delta M^0M\gamma \rangle \right\}^{-1} \quad (7.4) \end{aligned}$$

The last of these can be simplified somewhat further for, according to (7.2):

$$\begin{aligned} \langle \gamma(M^0M - M_1^0M_1) : \Delta M^0M\gamma \rangle & \approx 3\langle \gamma \cdot (M^0M - M_1^0M_1) \cdot \\ & \cdot \Delta(M^0M \cdot \gamma) \rangle = \frac{3}{4}\sigma_b. \quad (7.5) \end{aligned}$$

Thus one is left with:

$$\zeta_2 \sim \left(\frac{5}{3}\sigma_a + 4\sigma_b + \sigma_c \right)^{-1} \quad (7.6)$$

where

$$\sigma_c = 2\langle \gamma^0\gamma(M^0M + M_1^0M_1) : \Delta M^0M\gamma^0\gamma \rangle. \quad (7.7)$$

which equals $\frac{8}{3}\Omega^{(2,2)}$ in the elastic limit. Thus in this limit

$$\zeta_2 \sim \left(\frac{2}{3}\Omega^{(1,1)} + \frac{1}{5}\Omega^{(2,2)} \right)^{-1} \quad (7.8)$$

in agreement with the elastic treatment of Knaap and Beenakker⁵⁾. For H_2 and D_2 σ_a is small as compared to σ_b and σ_c and hence ζ_1 will be much larger than ζ_2 at the same H/p -value. This explains the early saturation as compared to other gases for which σ_a is of the order of the normal transport cross sections. For these gases both contributions may overlap and hence a more careful analysis is necessary. This as well as a comparison of

the off-diagonal cross sections entering in the expressions for heat conductivity, viscosity and binary diffusion will be discussed in a later paper. For the case of H_2 and D_2 viscosity measurements at higher H/p -values may lead to information about the relative importance of the two angular momentum-dependent trial functions. The off-diagonal cross section determining the magnitude of the viscosity effect connected with M^0M is the same cross section t_{13} that enters into the heat conductivity result. Due to this and the circumstance that the modified Eucken approximation is valid in this case it is now possible to obtain the values of t_{13} and t_{23} separately when accurate heat conductivity results become available. Moreover the study of the temperature dependence of the viscosity effect on H_2 and D_2 seems promising for this leads immediately to the temperature dependence of the simple cross sections σ_a and t_{13} .

In connection with the foregoing it is interesting to note that an elastic theory such as that of ref 5 breaks down first in cases where nearly all molecular collisions are elastic.

As was mentioned already in the introduction Kagan and Maksimov recently published a paper in which they divided the collision operator into an elastic part and a second one that contained all polyatomic features. Assuming the latter to be small compared with the first they now used a perturbation method to solve equation (2.5) and the equivalent equation for viscosity.

As will be clear from the preceding discussion this smallness assumption does not apply to diagonal elements for it should amount to neglect of σ_b as compared to σ_a and σ_c . The same criticism applies to ref. 20 where the same method was used. As this paper is concerned with polar molecules σ_b may be even larger here as reorientation collisions occur frequently in polar gases²¹). A second drawback of the Kagan-Maksimov method is that the bulk viscosity cross section $\langle \gamma^2 \Delta \gamma^2 \rangle$ being of truly polyatomic nature is assumed to be small of first order as compared to the shear viscosity and heat conductivity cross sections. It is then found that magnetic field influences are of first order smallness whereas they are of second order smallness for shear viscosity and heat conductivity. This should be compared with ref. 17 where the influence of angular momentum anisotropy is found to be of minor importance for bulk viscosity whereas it is important for shear viscosity and heat conductivity. It may be possible, however, that the K.M. method can be changed in such a way that diagonal elements are not approximated but that off-diagonal ones like t_{13} and t_{23} in the present investigation are assumed to be small compared to diagonal ones.

An advantage of the spherical-harmonics expansion used by K.M. is that it clearly shows how "single and double frequencies" are connected with the m -value in the angular momentum spherical harmonics $Y_1^m(M/M)$.

The fact that K.M. do find single and double frequencies for the case of

heat conductivity will be connected with an approximation of the type (7-2) in their work.

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APPENDIX I

Straightforward computation leads to the following expressions for the inner products used in the text:

$$\begin{aligned}(\Phi_k^{(1)}, \Phi_l^{(1)}) &= \frac{5}{4} \delta_{kl} & (\Phi_{kl}^{(4)}, \Phi_{mn}^{(4)}) &= \frac{1}{16} \Delta_{kl, mn} \\ (\Phi_k^{(2)}, \Phi_l^{(2)}) &= \frac{1}{2} \delta_{kl} & (\Phi_{klm}^{(5)}, \Phi_{uvw}^{(5)}) &= \frac{1}{45} \Delta_{klm, uvw} \\ (\Phi_k^{(3)}, \Phi_l^{(3)}) &= \frac{2}{9} \delta_{kl}\end{aligned}$$

Here $\Delta_{kl, mn}$ and $\Delta_{klm, uvw}$ are isotropic tensors, defined by the fact that they are symmetric and traceless in their first and second sets of indices respectively, their nonvanishing traces being given by $\Delta_{kl, kl} = 10$ and $\Delta_{klm, klm} = 42$.

$$\begin{aligned}(\mathbf{M} \times \mathbf{B} \cdot \partial_M \Phi^{(\alpha)}, \Phi^{(\beta)}) &= -(\mathbf{M} \times \mathbf{B} \cdot \partial_M \Phi^{(\beta)}, \Phi^{(\alpha)}) \\ (\mathbf{M} \times \mathbf{B} \cdot \partial_M \Phi_k^{(3)}, \Phi_p^{(3)}) &= \frac{1}{3} \varepsilon_{kpw} B_w \\ (\mathbf{M} \times \mathbf{B} \cdot \partial_M \Phi_{kl}^{(4)}, \Phi_p^{(3)}) &= -\frac{1}{10} B_w \Delta_{wplk} \\ (\mathbf{M} \times \mathbf{B} \cdot \partial_M \Phi_{kl}^{(4)}, \Phi_{pq}^{(4)}) &= \frac{1}{12} B_w (\varepsilon_{wkm} \Delta_{mlpq} + \varepsilon_{wlm} \Delta_{mkpq}) \\ (\mathbf{M} \times \mathbf{B} \cdot \partial_M \Phi_{kl}^{(4)}, \Phi_{pqr}^{(5)}) &= \frac{1}{45} B_w \Delta_{wkl, pqr} \\ (\mathbf{M} \times \mathbf{B} \cdot \partial_M \Phi_{klm}^{(5)}, \Phi_{uvw}^{(5)}) &= \frac{1}{45} B_n \{ (\varepsilon_{nlq} \delta_{mp} + \varepsilon_{nmq} \delta_{lp}) \delta_{kr} \\ &\quad - \frac{1}{3} (\varepsilon_{klp} \delta_{mq} + \varepsilon_{kmp} \delta_{lq}) \delta_{nr} \} \Delta_{pqr, uvw}\end{aligned}$$

APPENDIX II

The Enskog brackets are defined as

$$[\Phi, \Psi] = \int F^{(0)} F_1^{(0)} \Phi(\Psi - \Psi') g b db d\varepsilon d\sigma d\sigma_1$$

Hence

$$(J^{(0)} \Phi, \Psi) = -[\Phi + \Phi_1, \Psi]$$

where Liouville's theorem has been used to change from double to single

primes, cf. ref. 11. Special cases are:

$$[\Phi_k^{(\alpha)}, \Phi_l^{(\beta)}] = \frac{1}{3}[\Phi^{(\alpha)} \cdot \Phi^{(\beta)}] d_{kl} \quad a, \beta \in (1, 2, 3)$$

$$[\Phi_{kl}^{(4)}, \Phi_{mn}^{(4)}] = \frac{1}{10}[\Phi^{(4)} \cdot \Phi^{(4)}] \Delta_{kl, mn}$$

$$[\Phi_{klm}^{(5)}, \Phi_{npq}^{(5)}] = \frac{1}{42}[\Phi^{(5)} \cdot \Phi^{(5)}] \Delta_{klm, npq}$$

After integration over the center of mass velocity one obtains, writing $t_{\alpha\beta} = [(\Phi^{(\alpha)} + \Phi_1^{(\alpha)}) \cdot \Phi^{(\beta)}]$;

$$t_{11} = 7\langle \gamma^2 \Delta \gamma^2 \rangle + 4\langle \gamma \gamma : \Delta \gamma \gamma \rangle$$

$$t_{12} = -5\langle \gamma^2 \Delta \gamma^2 \rangle$$

$$t_{13} = 4\langle M^0 M : \Delta \gamma \gamma \rangle$$

$$t_{22} = 3\langle \gamma^2 \Delta \gamma^2 \rangle + 4\langle (M^2 - M_1^2) \gamma \cdot \Delta (M^2 \gamma) \rangle$$

$$t_{23} = -4\langle (M^0 M - M_1^0 M_1) : \gamma \Delta (M^2 \gamma) \rangle$$

$$t_{33} = 2\langle (M^0 M + M_1^0 M_1) : \Delta M^0 M \rangle + 4\langle (M^0 M - M_1^0 M_1) : \gamma \Delta (M^0 M \cdot \gamma) \rangle$$

$$t_{44} = 3\langle (M^0 M + M_1^0 M_1) : \Delta M^0 M \rangle + \\ + 4\langle ((\gamma \times M)^0 M - (\gamma \times M_1)^0 M_1) : \Delta (\gamma \times M)^0 M \rangle$$

$$t_{55} = 6\langle (M^0 M + M_1^0 M_1) : \Delta M^0 M \rangle + \\ + 4\langle \gamma (M^0 M - M_1^0 M_1) : \Delta M^0 M \gamma \rangle - \frac{2}{3}t_{44} - \frac{3}{5}t_{33}$$

Here $\Delta \Phi = \Phi - \Phi'$, γ is the reduced relative velocity $\frac{1}{2}\sqrt{2}(W - W_1)$ and

$$\langle F \Delta G \rangle = \frac{1}{128\pi^{\frac{3}{2}}} (4kT/m)^{\frac{1}{2}} [\exp - (\gamma^2 + M^2 + M_1^2) F \cdot \Delta G \cdot \\ \cdot \gamma b \, db \, d\epsilon \, d\gamma \frac{dM}{M} \cdot \frac{dM_1}{M_1} \, d\psi \cdot d\psi_1]$$

As the collision operator $J^{(0)}$ is not selfadjoint $t_{\alpha\beta}$ does not generally coincide with $t_{\beta\alpha}$. However, the brackets used in this paper possess this symmetry property. This is not trivial for it has to be proved from the space reflection and time reversal invariance of the intermolecular mechanics.

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ON THE SENFTLEBEN-BEENAKKER EFFECT IN MIXTURES

I. THE MAGNETIC FIELD DEPENDENCE OF THE SHEAR VISCOSITY TENSOR IN MIXTURES OF DIAMAGNETIC GASES

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Synopsis

The theory has been developed for the magnetic field dependence of the shear viscosity tensor of a dilute gas mixture consisting of linear diamagnetic molecules (Senftleben-Beenakker effect). For binary mixtures of diamagnetic and noble gases explicit expressions have been derived, which show that these mixtures offer interesting possibilities for the measurement of angular momentum reorientation cross sections for molecule-noble gas collisions.

I. *Introduction.* During the last few years a large number of both experimental and theoretical papers concerning the influence of a magnetic field on the transport properties of dilute polyatomic gases, the Senftleben-Beenakker effect, have appeared¹⁾⁻⁶⁾. For pure gases the theory has reached a certain degree of maturity. One is now able to correlate the experimental results for the viscosity and heat conductivity of gases consisting of linear molecules to kinetic cross sections (collision integrals), which depend on the non-spherical part of the intermolecular potential^{6) 7) 8)}.

For mixtures, however, the situation is different. Some heat conductivity measurements in mixtures have been made in the thirties by Senftleben and Pietzner⁹⁾. Also some experimental data on viscosity in mixtures exist¹⁰⁾. Senftleben has tried to measure a field influence on binary diffusion¹¹⁾. It turned out, however, that such an effect must be much smaller than that on the viscosity and heat conductivity. This has recently been confirmed by Vugts *e.a.*¹²⁾. On thermal diffusion too, no effect has been found¹³⁾. Theoretical results on mixtures are scanty. Binary diffusion has been treated shortly by Kagan and Maksimov⁴⁾ and in some more detail by the author¹⁴⁾. Borman *e.a.*¹⁵⁾ considered the case of mixtures of polar gases in electric fields. The elastic collision model that was used in their publication makes their numerical results doubtful, however.

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In the present paper the case of shear viscosity in mixtures of diamagnetic gases consisting of linear molecules has been considered. Unlike heat conductivity the parameter that determines the position on the saturation curve contains pure angular momentum reorientation cross sections only. Hence, the influence of external fields on the viscosity coefficient in mixtures will lead to important information about the non-spherical interaction between different types of molecules. Especially if one of the components of a binary mixture is a noble gas the theoretical expressions are not very complicated. Experiments on mixtures consisting of molecules like HD or N₂ and a series of noble gases seem promising as they will lead to a useful addition to already known data about atom-molecule interactions from other transport properties.

II. *Basic equations for shear viscosity in mixtures.* For a dilute gas of polyatomic molecules in the presence of a magnetic field \mathbf{B} , the viscous part Π of the pressure tensor is related to the gradients of the stream velocity \mathbf{v}_0 by^{7) 16)};

$$\Pi = -2(\eta + \mathbf{U}\mu) : \overline{\partial_x \mathbf{v}_0} - (\kappa \mathbf{U} + 2\mathbf{v})(\partial_x \cdot \mathbf{v}_0). \quad (2.1)$$

Here the double bar and small circle have their usual meaning¹⁷⁾, \mathbf{U} is the second rank unit tensor. η is the coefficient of shear viscosity, which is a fourth rank tensor in the presence of an external field, κ is the bulk viscosity coefficient. The symmetric traceless second rank tensors μ and \mathbf{v} are transport coefficients describing cross effects between shear and bulk viscosity. They vanish for $\mathbf{B} = 0$ and are connected by the Onsager relation

$$\mu^\dagger(\mathbf{B}) = \mathbf{v}(-\mathbf{B}). \quad (2.2)$$

η is symmetric and traceless in its front and back pair of indices, which fact diminishes its number of independent components to five.

Expressions for the complete set of viscosity coefficients for a pure gas have been obtained by McCourt and Snider⁷⁾, who based their calculations on the semi-quantum Waldmann-Snider kinetic equation¹⁸⁾.

In the present paper an expression for η in mixtures will be derived in a classical treatment. In mixtures of gases η contains contributions from all components. If fact one has

$$\eta = kT(W^0 W, \mathbf{B}), \quad (2.3)$$

where the inner product is defined as

$$(\Phi, \Psi) = \sum_i x_i (\Phi, \Psi)_i; \quad (\Phi, \Psi)_i = \int F_i^{(0)} \Phi_i \Psi_i d\sigma_i, \quad (2.4)$$

with, for linear molecules,

$$F_i^{(0)} = (4\pi^2)^{-1} \exp - (W_i^2 + M_i^2); \quad d\sigma_i = dW_i (dM_i/M_i) d\psi_i. \quad (2.5)$$

The subscript i refers to the i^{th} component of the mixture, n_i is its number density and $x_i = n_i/n$, where n is the total number density, its concentration. $W_i = (m_i/2kT)^{1/2} V_i$ and $M_i = (2I_i kT)^{-1/2} J_i$ are reduced quantities derived from the peculiar velocity V_i and angular momentum J_i , whereas ψ_i is the angle specifying the position of the molecular axis in the plane orthogonal to J_i^2 . m_i is the mass, I_i the moment of inertia of the i^{th} component molecules, k is Boltzmann's constant and T the absolute temperature. The symmetric and traceless tensor field $B_i(W_i, M_i, \Psi_i, B)$ is the solution of the "Chapman-Enskog" equation

$$-2W_i^0 W_i = (JB)_i = (J^{(0)}B)_i - \frac{1}{n} (\dot{M}_i \cdot \partial_{M_i} + \dot{\psi}_i \cdot \partial_{\psi_i}) B_i, \quad (2.6)$$

where \dot{M}_i is given by

$$\dot{M}_i = \hat{\gamma}_i M_i \times B, \quad (2.7)$$

$\hat{\gamma}_i$ being the gyromagnetic ratio. $\dot{\psi}_i$ can also be expressed in terms of M_i and ψ_i but this is not needed here, for B_i will be assumed to be independent of ψ_i , which is appropriate for the magnetic field case, but not when electric fields are present. For the linearized collision operator the expression from ref. 8, extended to mixtures, will be used. Hence;

$$(J^{(0)}B)_i = \sum_j x_j \int F_j^{(0)} (B_i'' + B_j'' - B_i - B_j) g_{ij} b db d\epsilon d\sigma_j. \quad (2.8)$$

For the meaning of the different quantities entering into (2.8) see ref. 8. In particular double primes are used for the initial state in restituting collisions, whereas single primes refer to the final state in direct collisions. As usual B must be orthogonalized to the null space of J (the sub-space spanned by the summational invariants) to obtain unique solutions of (2.6). Thus:

$$(B, \Phi) = 0; \quad \Phi_i \in \{\delta_{ij}, \sqrt{m_i} W_i, W_i^2 + M_i^2\}. \quad (2.9)$$

To obtain approximate solutions of (2.6) and similar equations for other transport coefficients two different methods are in use at present. The first consists of changing from the L^2 -space defined by (2.4) to an l^2 -space formulation by expanding B into a suitable complete set of functions and forming inner products of (2.6) with each of them. Truncation of the expansion series after a finite number of terms leads to a finite set of linear equations which can be solved in principle. Variational principles to justify this procedure are discussed by Snider¹⁹). The second method is a perturbation method originated by Kagan and Maksimov⁴). This method, however, may lead to erroneous results due to an unjustified assumption about the polyatomic linearized collision operator⁸). It has turned out that the method can be changed into an elegant iteration procedure²⁰), at the same time leading to a better understanding of the "single and double

frequency" property^{5) 7) 8)} of the field dependent transport coefficients. In this paper the first method will be used. The proposed trial function for B_i is:

$$B_i = W_i^0 W_i : B_i^{(1)} + M_i^0 M_i : B_i^{(2)}. \quad (2.10)$$

This is adequate for the case of hydrogen isotopes and presumably also a good approximation for other gases. It has been shown by McCourt and Snider⁷⁾ how to include the next higher order function $W^0 W M^0 M$ for the case of pure cases (see also ref. 5). Their treatment can be extended to mixtures if the need arises. (2.10) satisfies (2.9) and leads to the following expression for η after insertion into (2.3):

$$\eta = \frac{1}{2} kT \sum_i x_i B_i^{(1)}. \quad (2.11)$$

Substitution of (2.10) into (2.6) and forming inner products with each of the functions $W_i^0 W_i$ and $M_i^0 M_i$ leads to the following set of equations for the expansion coefficients $B_i^{(\alpha)}$:

$$\begin{aligned} 5T = \sum_j x_j \{ & [W_i^0 W_i : W_i^0 W_i]_{ij} B_i^{(1)} + [W_i^0 W_i : W_j^0 W_j]_{ij} B_j^{(1)} \\ & + [W_i^0 W_i : M_i^0 M_i]_{ij} B_i^{(2)} + [W_i^0 W_i : M_j^0 M_j]_{ij} B_j^{(2)} \}, \end{aligned} \quad (2.12)$$

$$\begin{aligned} 0 = \sum_j x_j \{ & [M_i^0 M_i : W_i^0 W_i]_{ij} B_i^{(1)} + [M_i^0 M_i : W_j^0 W_j]_{ij} B_j^{(1)} \\ & + [M_i^0 M_i : M_i^0 M_i]_{ij} B_i^{(2)} + [M_i^0 M_i : M_j^0 M_j]_{ij} B_j^{(2)} \} - \zeta_i h : B_i^{(2)}, \end{aligned} \quad (2.13)$$

where

$$T_{klmn} = \frac{1}{2} (\delta_{km} \delta_{ln} + \delta_{kn} \delta_{lm}) - \frac{1}{3} \delta_{kl} \delta_{mn} \quad (2.14)$$

and

$$h_{klmn} = \frac{1}{4} (\delta_{km} \epsilon_{lnr} + \delta_{kn} \epsilon_{lmr} + \delta_{lm} \epsilon_{knr} + \delta_{ln} \epsilon_{kmr}) b_r. \quad (2.15)$$

with $b = B/B$, are equal to the tensors $T_1^{(4,0)}$ and $H^{(1)}$ employed by McCourt and Snider^{6) 7)}. ζ_i is given by

$$\zeta_i = \frac{8}{3} \gamma_i B/n \quad (2.16)$$

and the Enskog brackets are defined as

$$[F_h, G_k]_{ij} = \int F_i^{(0)} F_j^{(0)} F_h(G_k - G'_k) g_{ij} b db d\epsilon d\sigma_i d\sigma_j. \quad (2.17)$$

The change from the double primes to the single ones has been made via Liouville's theorem in pair space. To arrive at (2.12) and (2.13) the following relation has been used

$$[F_h, G_k]_{ij} = \frac{1}{5} [F_h : G_k]_{ij} T, \quad (2.18)$$

which holds for all functions discussed here. Moreover, the symmetry property

$$[F_h : G_k]_{ij} = [G_k : F_h]_{ij} \quad (2.19)$$

is valid for these functions. It can be proved from the space reflection and time reversal invariance of the intermolecular mechanics.

III. *Binary mixtures.* For binary mixtures one obtains from (2.12) and (2.13) the following set of four coupled equations:

$$\begin{aligned} 5x_1T &= a_1B_1^{(1)} + a_{12}B_2^{(1)} + b_1B_1^{(2)} + b_{12}B_2^{(2)} \\ 5x_2T &= a_{12}B_1^{(1)} + a_2B_2^{(1)} + b_{21}B_1^{(2)} + b_2B_2^{(2)} \\ 0 &= b_1B_1^{(1)} + b_{21}B_2^{(1)} + c_1B_1^{(2)} + c_{12}B_2^{(2)} - x_1\zeta_1 h : B_1^{(2)} \\ 0 &= b_{12}B_1^{(1)} + b_2B_2^{(1)} + c_{12}B_1^{(2)} + c_2B_2^{(2)} - x_2\zeta_2 h : B_2^{(2)} \end{aligned} \quad (3.1)$$

The coefficients at the right hand side each contain a number of Enskog brackets. Their explicit forms are given in the appendix. It is useful to note that the a 's contain pure linear momentum reorientation cross sections (the well-known Ω -integrals), whereas the c 's are made up from pure angular momentum reorientation cross sections. The b 's, however, consist of cross sections which contain both velocity and angular momenta vectors. For all diatomic gases except the hydrogen isotopes, the a 's and c 's are in the same order of magnitude, for the latter, however, the c 's are more than ten times smaller than the a 's. The b 's are considerably smaller than the a 's and c 's which fact follows from the experimental smallness of the Senftleben-Beenakker effect. This enables one to neglect quantities $b_\alpha b_\beta$ as compared to $a_\alpha a_\beta$, $a_\alpha c_\beta$ or $c_\alpha c_\beta$.

To solve the set of equations (3.1) the usual subdivision of $B_i^{(\alpha)}$ into a field free part and a second part, which contains the magnetic field dependence, will be made^{2) 5) -8)}.

Hence:

$$B_i^{(\alpha)} = B_i^{(\alpha)T} + Y_i^{(\alpha)}(B); \quad Y_i^{(\alpha)}(0) = 0. \quad (3.2)$$

In this way one obtains

$$\eta(B) = \eta_0 T + \Delta\eta(B), \quad (3.3)$$

where

$$\eta_0 = \frac{1}{2}kT \sum_i x_i B_i^{(1)}; \quad \Delta\eta(B) = \frac{1}{2}kT \sum_i x_i Y_i^{(1)}. \quad (3.4)$$

Introduction of (3.2) into (3.1) leads to the following set of equations for the $B_i^{(\alpha)}$'s:

$$\begin{pmatrix} 5x_1 \\ 5x_2 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} a_1 & a_{12} & b_1 & b_{12} \\ a_{12} & a_2 & b_{21} & b_2 \\ b_1 & b_{21} & c_1 & c_{12} \\ b_{12} & b_2 & c_{12} & c_2 \end{pmatrix} \begin{pmatrix} B_1^{(1)} \\ B_2^{(1)} \\ B_1^{(2)} \\ B_2^{(2)} \end{pmatrix} \quad (3.5)$$

Using the above mentioned smallness assumption for the b 's one obtains from this:

$$\begin{aligned} B_1^{(1)} &= 5(x_1 a_2 - x_2 a_{12})/a \\ B_2^{(1)} &= 5(x_2 a_1 - x_1 a_{12})/a \\ B_1^{(2)} &= [(b_{12} c_{12} - b_1 c_2) B_1^{(1)} + (b_2 c_{12} - b_{21} c_2) B_2^{(1)}]/c \\ B_2^{(2)} &= [(b_1 c_{12} - b_{12} c_1) B_1^{(1)} + (b_{21} c_{12} - b_2 c_1) B_2^{(1)}]/c \end{aligned} \quad (3.6)$$

where

$$a = \begin{vmatrix} a_1 & a_{12} \\ a_{12} & a_2 \end{vmatrix}; \quad c = \begin{vmatrix} c_1 & c_{12} \\ c_{12} & c_2 \end{vmatrix}. \quad (3.7)$$

The expression for η_0 obtained from this is on the level of the Wang-Chang-Uhlenbeck and de Boer theory²¹); it contains energetically inelastic collision integrals but angular momentum anisotropy does not enter. Subtraction of the equations (3.5) from the corresponding ones (3.1) leads to the following set of equations for the $Y_i^{(\alpha)}$'s

$$\begin{aligned} 0 &= a_1 Y_1^{(1)} + a_{12} Y_2^{(1)} + b_1 Y_1^{(2)} + b_{12} Y_2^{(2)} \\ 0 &= a_{12} Y_1^{(1)} + a_2 Y_2^{(1)} + b_{21} Y_1^{(2)} + b_2 Y_2^{(2)} \\ x_1 \zeta_1 B_1^{(2)} h &= c_1 Y_1^{(2)} + c_{12} Y_2^{(2)} - x_1 \zeta_1 h : Y_1^{(2)} \\ x_2 \zeta_2 B_2^{(2)} h &= c_{12} Y_1^{(2)} + c_2 Y_2^{(2)} - x_2 \zeta_2 h : Y_2^{(2)} \end{aligned} \quad (3.8)$$

where again the smallness assumption about the b 's has been invoked. The second pair of these are two strongly coupled equations for $Y_1^{(2)}$ and $Y_2^{(2)}$, for c_{12} will be of the same order of magnitude as c_1 and c_2 in general. They can be decoupled, however, at the price of introducing terms containing $h : h$. For that purpose one expresses $Y_2^{(2)}$ in terms of $Y_1^{(2)}$ by means of the third equation (3.8). Introduction of this into the last one leads to a closed equation for $Y_1^{(2)}$ and in the same way a similar equation for $Y_2^{(2)}$ can be obtained. The resulting expressions are:

$$\begin{aligned} Y_1^{(2)} - 2(\Theta_1 + \Theta_2)(c_1 c_2/c) h : Y_1^{(2)} + 4\Theta_1 \Theta_2 (c_1 c_2/c) h : h : Y_1^{(2)} &= \\ = 2(\Theta_1 B_1^{(2)} - (c_{12}/c_1) \Theta_2 B_2^{(2)})(c_1 c_2/c) h - 4\Theta_1 \Theta_2 (c_1 c_2/c) h : h &= \\ Y_2^{(2)} - 2(\Theta_1 + \Theta_2)(c_1 c_2/c) h : Y_2^{(2)} + 4\Theta_1 \Theta_2 (c_1 c_2/c) h : h : Y_2^{(2)} &= \\ = 2(\Theta_2 B_2^{(2)} - (c_{12}/c_2) \Theta_1 B_1^{(2)})(c_1 c_2/c) h - 4\Theta_1 \Theta_2 (c_1 c_2/c) h : h, & \end{aligned} \quad (3.9)$$

where

$$\Theta_i = x_i \zeta_i / (2c_i). \quad (3.10)$$

It is seen that the coefficients at the left hand side are the same in both equations. This enables one to derive an equation for arbitrary linear combinations of both $Y_\alpha^{(2)}$'s. This is an important result for the quantity

entering into the expression for $\Delta\eta$ is

$$Z = x_1 Y_1^{(1)} + x_2 Y_2^{(1)}, \quad (3.11)$$

which indeed can be written as such a linear combination.

In this way one obtains:

$$\begin{aligned} Z - 2(\theta_1 + \theta_2)(c_1 c_2 / c) h : Z + 4\theta_1 \theta_2 (c_1 c_2 / c) h : h : Z = \\ = 2[\theta_1 \cdot \frac{1}{5} c_1 (B_1^{(2)})^2 + \theta_2 \cdot \frac{1}{5} c_2 (B_2^{(2)})^2] h \\ - 4\theta_1 \theta_2 (c_1 c_2 / c) [\frac{1}{5} c_1 (B_1^{(2)})^2 + \frac{2}{5} c_{12} B_1^{(2)} B_2^{(2)} + \frac{1}{5} c_2 (B_2^{(2)})^2] h : h. \end{aligned} \quad (3.12)$$

A striking difference with similar equations for a pure gas is the occurrence of the terms proportional to $h : h$. These terms are due to the coupling via c_{12} of the last two equations (3.8). When c_{12} vanishes they disappear again, although this is not immediately apparent from (3.12). They also disappear if one of the ζ_i 's vanishes as is the case if one of the components is a noble gas. It may be anticipated that for ternary mixtures terms proportional to $h^3 \equiv h : h : h$ will turn up. The solution of (3.12) is a straight-forward task. For that purpose one expands Z into a series in h :

$$Z = \sum_{k \geq 1} Z_k h^k. \quad (3.13)$$

This series can be truncated after four terms due to the closure relation

$$h^5 = -\frac{5}{4} h^3 - \frac{1}{4} h. \quad (3.14)$$

Substitution into (3.12), use of (3.14) and equation of like powers of h then leads to four equations from which the expansion coefficients can be determined. As the result is a complicated function of θ_1 , θ_2 and other parameters this will not be discussed here. Instead the simpler case of mixtures with noble gases will be discussed in the next section.

IV. *Binary mixtures with noble gases.* For binary mixtures of which the second component is a noble gas the quantities ζ_2 , b_{12} , b_2 , c_{12} and c_2 vanish. Hence, $B_2^{(2)} = 0$ and

$$B_1^{(2)} = -(b_1 B_1^{(1)} + b_{21} B_2^{(1)}) / c. \quad (4.1)$$

Due to this (3.12) simplifies into

$$Z - 2\theta_1 h : Z = 2\theta_1 \cdot \frac{1}{5} c_1 (B_1^{(2)})^2 h, \quad (4.2)$$

with the well-known solution

$$Z = \frac{1}{5} c_1 (B_1^{(2)})^2 F(\theta_1, h), \quad (4.3)$$

where

$$F(\theta_1, h) = \frac{2\theta_1}{(1 + \theta_1^2)(1 + 4\theta_1^2)} [(1 + 5\theta_1^2)(h + 2\theta_1 h^2) + 4\theta_1^2(h^3 + 2\theta_1 h^4)]. \quad (4.4)$$

For the relative change of the viscosity coefficient in a magnetic field one finally obtains:

$$\Delta\eta/\eta_0 = \frac{(b_1 B_1^{(1)} + b_{21} B_2^{(1)})^2}{5c_1(x_1 B_1^{(1)} + x_2 B_2^{(1)})} F(\Theta_1, h) \equiv KF(\Theta_1, h). \quad (4.5)$$

To proceed further it is useful to take the magnetic field along the x axis as this reduces the number of nonzero components of $\Delta\eta$ significantly²²). From this point onwards the analysis of McCourt and Snider⁷⁾ applies, $\Delta\eta/\eta_0$ corresponding to their $(\Delta\eta/\eta_0)^{02}$, K to ψ' and Θ_1 to ζ' . For completeness sake the resulting expressions for the five viscosity coefficients η_1 to η_5 , as defined in ref. 22, are given below:

$$\begin{aligned} \eta_1 &= \eta_0 \\ \eta_2 &= \eta_0 \left(1 - \frac{1}{2}K \frac{4\Theta_1^2}{1 + 4\Theta_1^2} \right) \\ \eta_3 &= \eta_0 \left(1 - K \frac{\Theta_1^2}{1 + \Theta_1^2} \right) \\ \eta_4 &= +\eta_0 K \frac{2\Theta_1}{1 + 4\Theta_1^2} \\ \eta_5 &= -\eta_0 K \frac{\Theta_1}{1 + \Theta_1^2}. \end{aligned} \quad (4.6)$$

In capillary tube experiments with the field perpendicular to the capillary the actually measured quantity is²³⁾

$$\Delta\eta/\eta_0 = \frac{1}{2}(2\eta_2 - \eta_1 + \eta_3 - 2\eta_0)/\eta_0, \quad (4.7)$$

which is given by

$$\Delta\eta/\eta_0 = -\frac{1}{2}K \left[\frac{\Theta_1^2}{1 + \Theta_1^2} + \frac{4\Theta_1^2}{1 + 4\Theta_1^2} \right]. \quad (4.8)$$

The question might arise if in more general mixtures of diatomic gases the viscosity coefficient η_1 still equals η_0 . This is indeed the case, for Z will again be given by an expression of the type (3.13). As $\eta_1 - \eta_0$ corresponds to Z_{1111} (in component notation) and $h_{1111}^k = 0$ this quantity will vanish in the approximation (2.10).

V. *Discussion.* a. As will be clear from the preceding, binary mixtures with noble gases are the simplest to deal with from the theoretical point of view. In that case the field dependence of the shear viscosity tensor is the same as for pure gases, only the coefficients K and Θ_1 , that determine the magnitude of the effect and the position on the saturation curve, are

different. One now has

$$\begin{aligned} \Theta_1 &= \frac{\hat{\gamma}B}{6n} \frac{1}{x_1 \langle M_1^0 M_1 + M_2^0 M_2 \rangle : \Delta M_1^0 M_1 \rangle_1 + x_2 \langle M_1^0 M_1 : \Delta M_1^0 M_1 \rangle_{12}} \\ &= \frac{\hat{\gamma}B}{6n(x_1 \sigma_1 + x_2 \sigma_{12})}. \end{aligned} \quad (5.1)$$

For the definition of the bracket expressions, see the appendix.

σ_1 and σ_{12} are pure angular momentum reorientation cross sections, σ_1 for collisions between two molecules, σ_2 for molecule-atom collisions. The experimental determination of $\Theta_{1,\eta}$, the Θ_1 -value for which the effect reaches half its saturation value or of $\Theta_{\max,\eta}$, the Θ_1 -value for which the transverse coefficients η_4 and η_5 reach their maximum, leads to the value of $\sigma = x_1 \sigma_1 + x_2 \sigma_{12}$.

From its concentration dependence one is able to obtain the value of σ_{12} separately.

The expression for K is not so simple. It reads:

$$K = \frac{8x_1[(x_1 \langle \gamma^0 \gamma : \Delta M_1^0 M_1 \rangle_1 + x_2 (m_2/m_{12}) \langle \gamma^0 \gamma : \Delta M_1^0 M_1 \rangle_{12}) B_1^{(1)} + x_2 (m_1/m_{12}) \langle \gamma^0 \gamma : \Delta M_1 M_1 \rangle_{12} B_2^{(1)}]^2}{5\sigma(x_1 B_1^{(1)} + x_2 B_2^{(1)})}. \quad (5.2)$$

The $B_i^{(1)}$'s are functions of concentrations and Ω -integrals and can be evaluated in the standard way²⁴, σ can be obtained as discussed above and $\langle \gamma^0 \gamma : \Delta M_1^0 M_1 \rangle_1$ can be obtained from pure gas measurements. Thus it is possible to obtain $\langle \gamma^0 \gamma : \Delta M_1^0 M_1 \rangle_{12}$ which is determined by the anisotropic molecule-noble gas interaction. Measurement on mixtures of molecules like HD or N₂ and noble gases will thus lead to a useful addition to already known data about atom-molecule collisions from other transport phenomena.

b. If in a binary mixture of two diatomic gases the parameters Θ_1 and Θ_2 are widely separated ($\Theta_1 \gg \Theta_2$), (3.12) can be approximated by

$$Z - 2\Theta_1(c_1 c_2 / c h) : Z = 2\Theta_1 \frac{1}{2} c_1 (B_1^{(1)})^2 h \quad (5.3)$$

for moderate fields, which again leads to an expression of the type (4.5). However, in this case the parameters b_{12} , b_2 , c_{12} and c_2 no longer vanish and hence Θ and K have a more complicated structure than in the noble gas case. This is more or less the situation for mixtures of paramagnetic and diamagnetic gases, although a paramagnetic gas like oxygen needs a more careful description*). Due to their large magnetic moment the ratio

*) See refs. 2 and 5. The mixture concept used in these papers for the description of the three different spin states in oxygen will break down as soon as transitions between these states occur. The author is indebted to Dr. F. R. McCourt for an interesting discussion on this point.

of Larmor and collision frequencies is already large for the paramagnetic gas while it is still small for the diamagnetic one and hence a partial saturation is reached, which will be described by an equation akin to (5.3). For higher fields the diamagnetic gas will be saturated as well and hence one expects a saturation curve that consists of two different contributions. For the transverse effect one will expect two extrema, one corresponding to the paramagnetic and one to the diamagnetic gas.

c. The treatment given here for linear molecules can easily be extended to general polyatomic gases; only the internal-state phase volumes will change⁴). It is not yet known at present if in addition to M^0M more anisotropic internal-state functions must be taken into account in the expansions for the B_i 's in this case. Provided this is not necessary experiments on mixtures of symmetric top molecules and noble gases are promising. For a number of these molecules reorientation cross sections have been measured by means of nonresonant absorption techniques²⁵). The cross sections obtained from these experiments are $\langle \mu_1 + \mu_2 \cdot \Delta \mu_1 \rangle_1$ and $\langle \mu_1 \cdot \Delta \mu_1 \rangle_{12}$, μ being the effective electric dipole moment. For mixtures of CH_3Cl or CHF_3 and gases like He or H_2 both quantities differ appreciably²⁵). It would be very interesting to supplement these data with the corresponding values of

$$\langle (M_1^0 M_1 + M_2^0 M_2) : \Delta M_1^0 M_1 \rangle_1 \text{ and } \langle M_1^0 M_1 : \Delta M_1^0 M_1 \rangle_{12}$$

obtained from $\Theta_{1,\eta}$ or $\Theta_{\text{max},\eta}$. Moreover, a comparison of these with the corresponding values for molecules like CF_4 may lead to information about the difference in the interactions between nonpolar and polar polyatomic molecules.

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APPENDIX

In this appendix the further evaluation of the Enskog brackets will be discussed. For that purpose the following quantities are introduced:

$$\begin{aligned} m_{ij} &= m_i + m_j; \mathcal{G} = \mathcal{G}_{ij} = (m_i/m_{ij})^{\frac{1}{2}} W_i + (m_j/m_{ij})^{\frac{1}{2}} W_j \\ \mu_{ij} &= m_i m_j / m_{ij}; \gamma = \gamma_{ji} = (m_i/m_{ij})^{\frac{1}{2}} W_j - (m_j/m_{ij})^{\frac{1}{2}} W_i \end{aligned} \quad (\text{A.1})$$

As \mathcal{G} is proportional to the center of mass velocity, it does not change upon collisions and an integration over this variable can be performed. Thus one

obtains

$$[F_h, G_k]_{ij} = (8/\pi^3) \langle \int (\exp -\mathcal{G}^2) F_h \Delta G_k d\mathcal{G} \rangle_{ij}, \quad (\text{A.2})$$

where

$$\langle K_h \Delta L_k \rangle_{ij} = (128\pi^3)^{-1} (2kT/\mu_{ij})^{\frac{1}{2}} \int [\exp -(\gamma^2 + M_i^2 + M_j^2)] K_h \Delta L_k d\omega_{ij} \quad (\text{A.3})$$

with

$$\Delta L_k = L_k - L'_k \quad (\text{A.4})$$

and

$$d\omega_{ij} = \gamma_{ij} b db d\epsilon d\gamma (dM_i/M_i)(dM_j/M_j) d\psi_i d\psi_j \quad (\text{A.5})$$

The Enskog brackets used in this paper become

$$\begin{aligned} [W_i^0 W_i : W_i^0 W_i]_{ij} &= 8(m_j/m_{ij})^2 \langle \gamma^0 \gamma : \Delta \gamma^0 \gamma \rangle_{ij} + 80/3(m_i m_j / m_{ij}^2) \langle \gamma \cdot \Delta \gamma \rangle_{ij} \\ [W_j^0 W_j : W_i^0 W_i]_{ij} &= 8(m_i m_j / m_{ij}^2) \langle \gamma^0 \gamma : \Delta \gamma^0 \gamma \rangle_{ij} - 80/3(m_i m_j / m_{ij}^2) \langle \gamma \cdot \Delta \gamma \rangle_{ij} \\ [M_i^0 M_i : W_i^0 W_i]_{ij} &= 8(m_j/m_{ij}) \langle \gamma^0 \gamma : \Delta M_i^0 M_i \rangle_{ij} \\ [M_j^0 M_j : W_i^0 W_i]_{ij} &= 8(m_j/m_{ij}) \langle \gamma^0 \gamma : \Delta M_j^0 M_j \rangle_{ij} \\ [M_i^0 M_i : M_i^0 M_i]_{ij} &= 8 \langle M_i^0 M_i : \Delta M_i^0 M_i \rangle_{ij} \\ [M_j^0 M_j : M_i^0 M_i]_{ij} &= 8 \langle M_j^0 M_j : \Delta M_i^0 M_i \rangle_{ij} \end{aligned} \quad (\text{A.6})$$

In connection with this, note the symmetry property (2.19).

The quantities displayed in equation (3.1) are:

$$\begin{aligned} a_1 &= x_1^2 [W_1^0 W_1 : (W_1^0 W_1 + W_2^0 W_2)]_1 + x_1 x_2 [W_1^0 W_1 : W_1^0 W_1]_{12} \\ a_{12} &= x_1 x_2 [W_1^0 W_1 : W_2^0 W_2]_{12} \\ a_2 &= x_2^2 [W_1^0 W_1 : (W_1^0 W_1 + W_2^0 W_2)]_2 + x_1 x_2 [W_2^0 W_2 : W_1^0 W_1]_{12} \\ b_1 &= x_1^2 [W_1^0 W_1 : (M_1^0 M_1 + M_2^0 M_2)]_1 + x_1 x_2 [W_1^0 W_1 : M_1^0 M_1]_{12} \\ b_{12} &= x_1 x_2 [W_1^0 W_1 : M_2^0 M_2]_{12} \\ b_{21} &= x_1 x_2 [W_2^0 W_2 : M_1^0 M_1]_{12} \\ b_2 &= x_1 x_2 [W_2^0 W_2 : M_2^0 M_2]_{12} + x_2^2 [W_2^0 W_2 : (M_1^0 M_1 + M_2^0 M_2)]_2 \\ c_1 &= x_1^2 [M_1^0 M_1 : (M_1^0 M_1 + M_2^0 M_2)]_1 + x_1 x_2 [M_1^0 M_1 : M_1^0 M_1]_{12} \\ c_{12} &= x_1 x_2 [M_1^0 M_1 : M_2^0 M_2]_{12} \\ c_2 &= x_1 x_2 [M_2^0 M_2 : M_2^0 M_2]_{12} + x_2^2 [M_2^0 M_2 : (M_1^0 M_1 + M_2^0 M_2)]_2 \end{aligned} \quad (\text{A.7})$$

In case that the second gas is a noble gas there is no M_2 and hence b_{12} , b_2 , c_{12} and c_2 vanish. In that case (A.3) simplifies somewhat for now one can immediately perform the integration over $(dM_2/M_2) d\psi_2$ for (1, 2) collision integrals and over both sets of internal state variables for (2, 2)

collisions. It should be noted that the bulk viscosity cross section $\langle \gamma^2 \cdot \Delta \gamma^2 \rangle_2$ vanishes as well.

In the limit that nearly all collisions are energetically elastic which is the case for H_2 and D_2 one may replace $\langle \gamma^0 \gamma : \Delta \gamma^0 \gamma \rangle_{ij}$ by $\Omega_{ij}^{(2,2)}$ and $\langle \gamma \cdot \Delta \gamma \rangle_{ij}$ by $\Omega_{ij}^{(1,1)}$, their elastic limits. For other gases this should also be a fair approximation.

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DISPERSION RELATIONS AND SUM RULES
FOR THE TRANSPORT COEFFICIENTS
OF DILUTE IONIZED GASES IN A MAGNETIC FIELD

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Synopsis

In the presence of a homogeneous magnetic field \mathbf{B} the thermal conductivity and shear viscosity tensors of ionized gases are anisotropic. The thermal conductivity tensor contains three independent components, one independent of \mathbf{B} , one even and one odd in \mathbf{B} . The shear viscosity tensor contains five independent components, one field independent, two even and two odd in \mathbf{B} . For pure gases, the transport coefficients which are even in \mathbf{B} can be written as the real part of complex functions of the parameter $\zeta = eB/nM$, while the coefficients odd in \mathbf{B} are the imaginary parts of these functions. Here e is the charge, M the mass and n the density of the gas under consideration.

Using the Chapman-Enskog equations it is then shown that these functions possess an analytic extension in one complex half plane and fall off as $1/|\zeta|$ for large $|\zeta|$; these facts enable one to obtain dispersion relations, connecting the transport coefficients odd in \mathbf{B} to those even in \mathbf{B} . For mixtures the situation is more complicated. Dispersion relations hold only if all charges have the same sign. However, a number of sum rules hold under more general conditions.

1. *Introduction.* In the presence of a homogeneous external magnetic field \mathbf{B} transport phenomena may become anisotropic^{1,2,3}). In heat conducting systems the heat flux \mathbf{q} is no longer parallel to the temperature gradient $\partial_{\mathbf{x}}T$. In general there will be a heat flux perpendicular to both \mathbf{B} and $\partial_{\mathbf{x}}T$; the Righi-Leduc effect. A similar effect in electric conductivity is the Hall-effect, whereas recently such a phenomenon has been found in the viscous flow of dilute diatomic gases (transverse Senftleben-Beenakker effect⁴).

Theoretical expressions describing such transverse phenomena have been known since long for the case of ionized gases in a magnetic field^{1-3,5}) and have recently been obtained for the Senftleben-Beenakker effect as well⁶). A classification of the different possible phenomena from the point of view of irreversible thermodynamics has also been given^{3,7}).

A common feature of the expressions for ionized gases and the Senftleben-

Beenakker effect is that the transport coefficients connected with longitudinal phenomena show a dispersive behaviour as a function of B/n , where n is the gas density, whereas those connected with transverse effects have an absorption behaviour. By longitudinal is meant a flow in the plane of B and the external gradient for vectorial phenomena, whereas the flow perpendicular to this plane is called transverse; this can be suitably generalized to higher rank tensorial transport coefficients (e.g. the shear viscosity coefficient). In fact the parameter entering into the formulae is the ratio of the precession frequency (proportional to B) and the collision frequency (proportional to n). The transverse transport coefficients show a maximum for the value $(B/n)_{\max}$ of B/n for which both frequencies are equal. The longitudinal coefficients tend to a saturation value for large B/n . The value $(B/n)_{\frac{1}{2}}$ for which the change from their field-free value is half that for the saturation value is roughly equal to $(B/n)_{\max}$ and corresponds to a point of inflection on the saturation curve.

In a real gas a number of collision frequencies are present, all corresponding to different eigenvalues of the linearized collision operator and many of them may lead to contributions to the transport coefficients. Thus one may expect that the overall dispersion and absorption curves will consist of many contributions, each one containing a different relaxation time. In most cases only a few of these are important, but it is difficult to obtain the values of the corresponding relaxation times from the experimental curves if they are not widely separated.

In an ionized gas the precession frequency is the orbital frequency of the charged particles spiralling around the field axis (Larmor frequency). In this case the relaxation times of interest are those connected with the collisional change in linear momentum. This is different for the Senftleben-Beenakker effect. Here the precession frequency is that of the internal angular momentum which precesses around the field axis, due to the presence of a magnetic moment of para- or dia-magnetic origine. The relaxation times are now related to collisional changes in both linear and angular momentum.

Many dispersive and absorptive physical phenomena are connected by dispersion relations, the Kramers-Kronig relations being a well-known example. The purpose of the present paper is to investigate the possible existence of a dispersion relation between transverse and longitudinal transport coefficients for a dilute ionized gas, for which the starting point will be the Chapman-Enskog equation. Although it is well-known that a treatment based on the Boltzmann equation is not valid for a fully ionized gas, as, due to the long range forces, collective phenomena dominate, it is applicable to weakly ionized gases, where the main interaction is that between charged particles and neutrals. The case of a small amount of electrons in an equilibrium back ground (Lorentz mixture) is an example of such a system. In more strongly ionized gases the Boltzmann equation can still

have some validity, due to Debye screening of the Coulomb potential.

It turns out that for a pure gas a dispersion relation can indeed be established. For mixtures a dispersion relation only holds if the charges of the components of the mixture all have the same sign. Also a number of sum rules can be derived, which hold under more general conditions. The derivation of these results relies heavily on the rotational invariance of the linearized collision operator. Due to this the Lorentz force flow operator can be diagonalized by introducing spherical coordinates. Thus the analytic properties of the solution of the Chapman-Enskog equations as a function of B/n are reduced to those of the resolvent operator of the linearized collision operator and one is able to use some results from the theory of semi-groups to obtain dispersion relations and sum rules. As the Coriolis force has the same structure as the Lorentz force the theory developed in this paper also applies to the transport coefficients of gases in rotating systems.

2. *Expressions for the heat conductivity and viscosity tensors of pure gases in a magnetic field.* In a homogeneous magnetic field \mathbf{B} the viscous part Π of the pressure tensor is related to the gradient of the stream velocity v_0 by

$$\Pi = -2\eta(\mathbf{B}) : \overline{\partial_x v_0}, \quad (2.1)$$

the double bar and small circle having their usual meaning¹). $\eta(\mathbf{B})$ is the coefficient of shear viscosity. It is a fourth rank tensor, symmetric and traceless in its front and back pairs of indices. Because of this there are only five independent components, three of which are even and two odd in \mathbf{B} . As the gas will be assumed to be dilute and collisions between particles to be elastic there will be no bulk viscosity and also no cross effects between shear and bulk viscosity. The heat conductivity tensor $\lambda(\mathbf{B})$ which relates the heat flux \mathbf{q} to the temperature gradient $\partial_x T$ is defined by

$$\mathbf{q} = -\lambda(\mathbf{B}) \cdot \partial_x T. \quad (2.2)$$

It contains three independent components, two are even and one is odd in \mathbf{B} .

According to the Chapman-Enskog method η and λ for a pure gas are given by

$$\begin{aligned} \eta &= kT(W^0 W, \mathbf{B}), \\ \lambda &= k((W^2 - \frac{1}{2}) V, \mathbf{A}), \end{aligned} \quad (2.3)$$

where k is Boltzmann's constant, M the mass of the particles and $W = (M/2kT)^{1/2} V$, a reduced quantity derived from the peculiar velocity V . The inner product is defined as

$$(\Phi, \Psi) = \pi^{-1} \int e^{-W^2} \Phi \Psi dW = \int F^{(0)} \Phi \Psi dW. \quad (2.4)$$

It defines the real Hilbert space \mathcal{H}_r .

The symmetric and traceless tensor field $\mathbf{B}(\mathbf{B})$ and the vector field $\mathbf{A}(\mathbf{B})$

are solutions of the "Chapman-Enskog" equations

$$\begin{aligned} -2W^0W &= J(\mathbf{B}) \mathbf{B}(\mathbf{B}), \\ (\frac{5}{2} - W^2) V &= J(\mathbf{B}) \mathbf{A}(\mathbf{B}), \end{aligned} \quad (2.5)$$

where

$$J(\mathbf{B}) = J^{(0)} + J^{(1)}(\mathbf{B}), \quad (2.6)$$

$J^{(0)}$ being the linearized Boltzmann collision operator given by

$$J^{(0)}\Phi = \int F_1^{(0)}(\Phi' + \Phi'_1 - \Phi - \Phi_1) gb db d\varepsilon dW_1. \quad (2.7)$$

Notation is conventional^{1,2}), except for the fact that reduced quantities have been used. The operator $J^{(1)}(\mathbf{B})$ is derived from the Lorentz force term. It can be written as

$$J^{(1)}(\mathbf{B}) = \frac{e}{nM} \mathbf{B} \cdot \mathbf{W} \times \partial_{\mathbf{W}}, \quad (2.8)$$

where e is the charge of the particles and n the gas density. To obtain unique solutions of (2.5), \mathbf{A} and \mathbf{B} must be orthogonalized to the summational invariants 1, \mathbf{W} and W^2 . It will be understood that these functions are not contained in \mathcal{H}_r and hence the eqs. (2.5) are operator equations on this space having unique solutions.

Of course the Boltzmann equation is not applicable to a pure gas of charged particles due to the presence of Coulomb forces. Thus the present discussion refers to a gas on which a force of the Lorentz type acts but where the intermolecular forces are of sufficiently short range. This is the case for a rotating pure gas as the Coriolis force has the same structure as the Lorentz force. Again $J^{(1)}$ is of the type (2.8) with $(e/nM) \mathbf{B}$ replaced by $(2/n) \boldsymbol{\omega}$, $\boldsymbol{\omega}$ being the rotation vector.

The present formalism also applies to the Lorentz gas, a low concentration of electrons in an equilibrium background. Here transport is due solely to the electrons and the back-ground gas enters only via the collision operator (2.7) for which case Φ_1 and Φ'_1 vanish. It will be assumed in the following that $J^{(0)}$ and $J^{(1)}(\mathbf{B})$ have a common domain \mathcal{D}_r , dense in \mathcal{H}_r and that the functions at the left in (2.5) are contained in this set.

As is well-known, $J^{(0)}$ is negative definite

$$(J^{(0)}\Phi, \Phi) \leq 0, \quad \forall \Phi \in \mathcal{D}_r. \quad (2.9)$$

Moreover it is self-adjoint

$$J^{(0)} = J^{*(0)}. \quad (2.10)$$

From Gauss's theorem it follows that

$$J^{(1)} = -J^{*(1)}, \quad (2.11)$$

and hence (2.9) also holds with $J^{(0)}$ replaced by J .

For the present purpose it is advantageous to use complex notation. Thus \mathcal{H}_c will be a complex Hilbert space generated by the inner product

$$(\Phi, \Psi) = \pi^{-\frac{1}{2}} \int e^{-W^2} \Phi \bar{\Psi} dW, \quad (2.12)$$

the bar denoting complex conjugation.

Following Kagan and Maksimov⁶⁾ spherical coordinates will be employed. This enables one to represent longitudinal and transverse coefficients as real and imaginary parts of complex functions of the real parameter $\zeta = eB/(nM)$.

The transformation from Cartesian to spherical coordinates is accomplished by means of the transformation formulae given in table I where vectors and traceless symmetric tensors of rank two are related to spherical irreducible tensors of first and second rank, respectively.

TABLE I

| Transformation formulae between the Cartesian and spherical components of vectors and second rank symmetric traceless tensors; | | | |
|---|--|--|--|
| $\mathbf{A} = \{A_k\} = \{A_1^m\}, \quad \mathbf{A} = \{A_{kl}\} = \{A_2^m\}, \quad A_{kl} = A_{lk}; \quad \text{tr } A_{kl} = 0$ | | | |
| $A_1 = \sqrt{\frac{2\pi}{3}} (A_1^{-1} - A_1^1)$ | | $A_1^1 = -\sqrt{\frac{3}{8\pi}} (A_1 + iA_2)$ | |
| $A_2 = i\sqrt{\frac{2\pi}{3}} (A_1^{-1} + A_1^1)$ | | $A_1^0 = \sqrt{\frac{3}{4\pi}} A_3$ | |
| $A_3 = \sqrt{\frac{4\pi}{3}} A_1^0$ | | $A_1^{-1} = \sqrt{\frac{3}{8\pi}} (A_1 - iA_2)$ | |
| $A_{11} = -\frac{2}{3}\sqrt{\frac{\pi}{5}} A_2^0 + \sqrt{\frac{2\pi}{15}} (A_2^{-2} + A_2^2)$ | | $A_2^2 = \sqrt{\frac{15}{8\pi}} \{\frac{1}{2}(A_{11} - A_{22}) + iA_{12}\}$ | |
| $A_{22} = -\frac{2}{3}\sqrt{\frac{\pi}{5}} A_2^0 - \sqrt{\frac{2\pi}{15}} (A_2^{-2} + A_2^2)$ | | $A_2^1 = \sqrt{\frac{15}{8\pi}} (A_{13} - iA_{23})$ | |
| $A_{12} = i\sqrt{\frac{2\pi}{15}} (A_2^{-2} - A_2^2)$ | | $A_2^0 = \frac{3}{4}\sqrt{\frac{5}{\pi}} A_{33}$ | |
| $A_{13} = -\sqrt{\frac{2\pi}{15}} (A_2^{-1} - A_2^1)$ | | $A_2^{-1} = -\sqrt{\frac{15}{8\pi}} (A_{13} + iA_{23})$ | |
| $A_{23} = i\sqrt{\frac{2\pi}{15}} (A_2^{-1} + A_2^1)$ | | $A_2^{-2} = \sqrt{\frac{15}{8\pi}} \{\frac{1}{2}(A_{11} - A_{22}) - iA_{12}\}$ | |

The eqs. (2.5) can now be written as

$$\Psi_l^m = J(\mathbf{B}) \Phi_l^m(\mathbf{B}) \quad (2.13)$$

with

$$\begin{aligned} \Psi_1^m &= (\frac{5}{2} - W^2) V Y_1^m(W/W), & \Phi_1^m &= A^m, \\ \Psi_2^m &= -2W^2 Y_2^m(W/W), & \Phi_2^m &= B^m, \end{aligned} \quad (2.14)$$

the Y_l^m being spherical harmonics. P_l^m will denote the projection on the subspace $\mathcal{H}_l^m \subset \mathcal{H}_c$ spanned by Y_l^m . It will be recognized that the operator $J = (1/i) W \times \partial_W$ is formally identical with the angular momentum operator of quantum mechanics in reduced units. Taking B along the z axis one can write

$$J^{(1)}(B) = i\zeta J_z, \quad \zeta = eB/(nM). \quad (2.15)$$

One thus obtains

$$\Psi_l^m = (J^{(0)} + i\zeta J_z) \Phi_l^m(\zeta). \quad (2.16)$$

The property (2.9) on \mathcal{D}_r leads to the following property on \mathcal{D}_c , the corresponding domain on \mathcal{H}_c ,

$$\text{Re}(J^{(0)}\Phi, \Phi) \leq 0, \quad \forall \Phi \in \mathcal{D}_c, \quad (2.17)$$

which again is also true for $J^{(0)}$ replaced by J . J_z has the spectral decomposition:

$$J_z = \sum_{l=0}^{\infty} \sum_{m=-l}^l m P_l^m. \quad (2.18)$$

If one neglects the influence of B on the collision mechanism $J^{(0)}$ is rotational invariant and hence

$$P_l^m J^{(0)} P_l^{m'} = J_l^{(0)} \delta_{ll'} \delta_{mm'}; \quad J_l^{(0)} = P_l^m J^{(0)} P_l^m; \quad (2.19)$$

$J_l^{(0)}$ does not depend on m , which fact is easily seen from the Wigner-Eckart theorem.

From (2.18) and (2.19) it is clear that J commutes with P_l^m and thus the \mathcal{H}_l^m are invariant subspaces of J . This, together with the relation $\Psi_l^m = P_l^m \Psi_l^m$, leads to a splitting of (2.16) into separate equations on each of the subspaces \mathcal{H}_l^m :

$$\Psi_l^m = (J_l^{(0)} + im\zeta) \Phi_l^m(\zeta). \quad (2.20)$$

After introduction of the spherical components of W^0W and B into (2.3) one obtains

$$\begin{aligned} \eta_1(\zeta) &= L_2^0(\zeta), \\ \eta_2(\zeta) &= \frac{1}{2}L_2^0(\zeta) + \frac{1}{4}(L_2^2(\zeta) + L_2^{-2}(\zeta)), \\ \eta_3(\zeta) &= \frac{1}{2}(L_2^1(\zeta) + L_2^{-1}(\zeta)), \\ \eta_4(\zeta) &= i \frac{1}{2}(L_2^2(\zeta) - L_2^{-2}(\zeta)), \\ \eta_5(\zeta) &= i \frac{1}{2}(L_2^1(\zeta) - L_2^{-1}(\zeta)), \end{aligned} \quad (2.21)$$

where

$$L_2^m(\zeta) = -\frac{4\pi}{15} kT(\Psi_2^m, \Phi_2^m(\zeta)). \quad (2.22)$$

The viscosity coefficients η_1 to η_5 are those given by Hooyman, de Groot and Mazur^{3,7}). Since in their paper the field is along the x axis, one has to perform a cyclic permutation of coordinates before the identification can be made. For \mathbf{B} along the z axis the heat conductivity tensor takes the form³)

$$\lambda = \begin{pmatrix} \lambda_1 & \lambda_2 & 0 \\ -\lambda_2 & \lambda_1 & 0 \\ 0 & 0 & \lambda_3 \end{pmatrix} \quad (2.23)$$

where now

$$\begin{aligned} \lambda_1(\zeta) &= \frac{1}{2}(L_1^1(\zeta) + L_1^{-1}(\zeta)), \\ \lambda_2(\zeta) &= i \frac{1}{2}(L_1^1(\zeta) - L_1^{-1}(\zeta)), \\ \lambda_3(\zeta) &= L_1^0(\zeta), \end{aligned} \quad (2.24)$$

with

$$L_1^m(\zeta) = -\frac{4\pi}{3} k(\Psi_1^m, \Phi_1^m(\zeta)). \quad (2.25)$$

The formal solution of (2.20) is

$$\Phi_1^m(\zeta) = (J^{(0)} + im\zeta)^{-1} \Psi_1^m, \quad (2.26)$$

and hence

$$(\Psi_1^m, \Phi_1^m(\zeta)) = (\Psi_1^m, (J^{(0)} + im\zeta)^{-1} \Psi_1^m) = (\Psi_1, (J^{(0)} + im\zeta)^{-1} \Psi_1), \quad (2.27)$$

where the absence of the m in the Ψ_1 at the right expresses the fact that (2.27) does not depend on the m value in Ψ_1^m ; this is due to the rotational invariance of $J^{(0)}$.

Thus

$$L_1^m(\zeta) = L_1(m\zeta). \quad (2.28)$$

From this it is clear that $L_1^0(\zeta)$ and hence η_1 and λ_3 are independent of ζ . It is also seen that λ_1 , λ_3 and η_1 , η_2 and η_3 are even in ζ whereas λ_2 , η_4 and η_5 are odd in this variable. For $\zeta = 0$ $L_1^m(\zeta) = L_1^0(\zeta)$ and hence in this case $\eta_1 = \eta_2 = \eta_3$, $\lambda_1 = \lambda_3$ whereas η_4 , η_5 and λ_2 vanish. As $J^{(0)}$ is self-adjoint, one has

$$((J^{(0)} + im\zeta)^{-1})^* = (J^{(0)} - im\zeta)^{-1},$$

and one obtains

$$\bar{L}_1^m(\zeta) = L_1^m(-\zeta) = L_1(-m\zeta) = L_1^{-m}(\zeta). \quad (2.29)$$

Thus

$$\begin{aligned}
 \lambda_1(\zeta) &= \operatorname{Re} L_1^1(\zeta) &= \operatorname{Re} L_1(\zeta) \\
 -\lambda_2(\zeta) &= \operatorname{Im} L_1^1(\zeta) &= \operatorname{Im} L_1(\zeta) \\
 2\eta_2(\zeta) - \eta_1 &= \operatorname{Re} L_2^2(\zeta) &= \operatorname{Re} L_2(2\zeta) \\
 -\eta_4(\zeta) &= \operatorname{Im} L_2^2(\zeta) &= \operatorname{Im} L_2(2\zeta) \\
 \eta_3(\zeta) &= \operatorname{Re} L_2^1(\zeta) &= \operatorname{Re} L_2(\zeta) \\
 -\eta_5(\zeta) &= \operatorname{Im} L_2^1(\zeta) &= \operatorname{Im} L_2(\zeta)
 \end{aligned} \tag{2.30}$$

The existence of a dispersion relation depends on the possibility of analytic continuation of $L_l^m(\zeta)$ in the complex ζ plane. This will be investigated further in the next section.

3. *The derivation of the dispersion relations.* To prove the existence of the dispersion relations use will be made of the theory of semi-groups of operators. Standard treatises on this subject are refs. 8 and 9. However, the ten pages of appendix 1 of ref. 10 contain nearly all the material that is needed here.

A closed linear operator A in a Hilbert space \mathcal{H} with domain $\mathcal{D}(A)$ dense in \mathcal{H} generates a contraction semi-group of class C_0 if it is dissipative, that is, if

$$\operatorname{Re}(Ax, x) \leq 0; \quad \forall x \in \mathcal{D}(A). \tag{3.1}$$

This means that there exists a semi-group of bounded operators $T(t, A)$ on \mathcal{H} with the properties

$$\begin{aligned}
 T(0, A) &= 1; & T(t_1 + t_2, A) &= T(t_1, A) T(t_2, A), & t_1, t_2 > 0; \\
 \|T(t, A)\| &\leq 1, & \forall t > 0; \\
 \lim_{t \rightarrow 0} T(t, A) x &= x, & \forall x \in \mathcal{H}.
 \end{aligned} \tag{3.2}$$

$T(t, A) x$ is continuous in $t > 0$ for all $x \in \mathcal{H}$ and for any $x \in \mathcal{D}(A)$ the derivative of $T(t, A)$ exists in the strong sense and is given by

$$\frac{d}{dt} T(t, A) x = T(t, A) Ax = AT(t, A) x, \quad t > 0. \tag{3.3}$$

Due to (3.1) the whole open complex half plane to the right of the imaginary axis is contained in the resolvent set $\rho(A)$ of A and the resolvent $R(\lambda, A) = (\lambda - A)^{-1}$ is holomorphic in λ on $\rho(A)$. Moreover, the following relation between resolvent and the elements of the semi-group exists:

$$R(\lambda, A) x = \int_0^{\infty} e^{-\lambda t} T(t, A) x dt, \quad \operatorname{Re} \lambda > 0, \quad \forall x \in \mathcal{H}. \tag{3.4}$$

From this one derives the following estimate:

$$|(x, R(\lambda, A) y)| \leq \frac{1}{|\lambda|} \left\{ |(x, y)| + \frac{1}{\operatorname{Re} \lambda} \|x\| \cdot \|Ay\| \right\},$$

$$\operatorname{Re} \lambda > 0, \quad \forall x \in \mathcal{H}, \quad \forall y \in \mathcal{D}(A). \quad (3.5)$$

These results will now be applied to the case at hand.

A discussion of the linearized Boltzmann equation from the point of view of semi-group theory has been given by Scharf¹¹). In his paper, matters such as self-adjointness and dissipativity of the collision operator are discussed quite fully. In the present paper it has been assumed that $J^{(0)}$ is self-adjoint and dissipative (see 2.10) and (2.17)). Due to this its spectrum is restricted to the negative real axis. In addition it will be assumed that (apart from the five-fold degenerate eigenvalue zero for the summational invariants) it does not extend to the right of $-\delta$ with δ positive. Physically this means that all relaxation times are finite and mathematically it guarantees the existence of the solutions of the Chapman-Enskog equations. A further result is that along with $J^{(0)}$ also $J_\delta^{(0)} = J^{(0)} + \delta$ is a dissipative operator. One obviously has:

$$R(\lambda, J^{(0)}) = R(\lambda + \delta, J_\delta^{(0)}); \quad T(t, J^{(0)}) = e^{-\delta t} T(t, J_\delta^{(0)}). \quad (3.6)$$

Thus, it is clear that $R(\lambda, J^{(0)})$ is holomorphic for all λ with $\operatorname{Re} \lambda > -\delta$ and hence the imaginary axis is included in the resolvent set.

Applying these results to (2.27) one obtains (the coefficient in front of the inner product, which is not relevant for the present discussion, will be omitted from now on):

$$L_l^m(\zeta) \equiv (\Psi_l, (J^{(0)} + im\zeta)^{-1} \Psi_l) = -(\Psi_l, R(\delta - im\zeta, J_{i\delta}^{(0)}) \Psi_l), \quad (3.7)$$

where $J_{i\delta}^{(0)} = J_l^{(0)} + \delta$ and the resolvent at the right hand side is defined on the subspace \mathcal{H}_l . It follows from (3.7) that $L_l^m(\zeta)$ has an analytic continuation in the upper half plane for $m > 0$ and in the lower one for $m < 0$. In order to avoid confusion z will be used instead of ζ , whenever this variable assumes values away from the real axis. Thus ζ is always real.

Assuming Ψ_l^m to be in the domain of $J_l^{(0)}$ one obtains the following bound from (3.5):

$$|L_l^m(z)| \leq \frac{1}{|mz + \delta|} \left\{ \|\Psi_l\|^2 + \frac{1}{m \operatorname{Im} z + \delta} \|\Psi_l\| \cdot \|J_{i\delta}^{(0)} \Psi_l\| \right\}, \quad m \operatorname{Im} z > 0. \quad (3.8)$$

From this one obtains

$$\lim_{z \rightarrow \infty} L_l^m(\zeta) = 0, \quad m \neq 0 \quad (3.9)$$

and

$$|L_l^m(z)| \leq C_l^m / |z| \quad \text{for} \quad |z| \rightarrow \infty; \quad m \neq 0; \quad C_l^m > 0. \quad (3.10)$$

Eq. (3.9) shows that in the high field limit the only surviving component of the heat flux is the one along the field direction and it equals its field-free value. For viscosity a similar conclusion can be drawn. Due to (3.10) and the fact that $L_l^m(\zeta)$ is analytic in the upper half plane for positive m , the following dispersion relation holds^{3, 12}):

$$\operatorname{Re} L_l^m(\zeta) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} \frac{\operatorname{Im} L_l^m(\zeta')}{\zeta' - \zeta} d\zeta', \quad m > 0. \quad (3.11)$$

As $\operatorname{Im} L_l^m(\zeta)$ is odd in ζ , this can be transformed into :

$$\operatorname{Re} L_l^m(\zeta) = \frac{2}{\pi} \mathcal{P} \int_0^{\infty} \frac{\zeta' \operatorname{Im} L_l^m(\zeta')}{\zeta'^2 - \zeta^2} d\zeta', \quad m > 0. \quad (3.12)$$

Thus it is seen that the quantities $\lambda_1(\zeta)$, $2\eta_2(\zeta) - \eta_1$ and $\eta_3(\zeta)$ are connected to $-\lambda_2(\zeta)$, $-\eta_4(\zeta)$ and $-\eta_5(\zeta)$, respectively, by means of a dispersion relation of the type (3.12). The results obtained here apply to the two cases mentioned earlier; the Lorentz mixture and the rotating pure gas.

4. *Mixtures.* The transport coefficients for mixtures can again be written as inner products

$$L_l^m = (\Phi_l^m, \Psi_l^m), \quad (4.1)$$

where now

$$(\Phi, \Psi) = \sum_{j=1}^N x_j (\Phi, \Psi)_j = \sum_{j=1}^N x_j \int dW_j F_j^{(0)} \Phi_j(W_j) \bar{\Psi}(W_j), \quad (4.2)$$

$$F_j^{(0)} = \pi^{-1} \exp -W_j^2.$$

The concentration of the component j is denoted by x_j and the summation is over all N components of the mixture. In (4.1) the Ψ_{lj}^m 's are of the type (2.14) and Ψ_l^m is the solution of the Chapman-Enskog equation

$$\Psi_l^m = J \Phi_l^m. \quad (4.3)$$

Or,

$$\Psi_{lj}^m = (J \Phi_l^m)_j = (J^{(0)} \Phi_l^m)_j + i \frac{e_j B}{M_j n} J_{zj} \Phi_{lj}^m, \quad (4.4)$$

where $J^{(0)}$ is the collision operator:

$$(J^{(0)} \Phi)_j = \sum_{h=1}^N x_h \int F_h^{(0)} (\Phi_j + \Phi_h - \Phi_j - \Phi_h) g_{jh} b db d\epsilon dW_h. \quad (4.5)$$

Due to rotational invariance one can again replace J_{zj} by m in (4.4). Thus

one can write

$$\Psi_l^m(\zeta) = (J^{(0)} + i\alpha m\zeta) \Phi_l^m(\zeta), \quad (4.6)$$

where $\zeta = B/n$ and α is a diagonal matrix in N -dimensional vector space with components $\alpha_{jh} = (e_j/M_j) \delta_{jh}$. Thus also in mixtures transport along the field direction is not altered by the field.

The results of the previous section can immediately be applied to the case of a rotating gas mixture. A simple scale transformation transforms α into the unit matrix. Thus

$$J \rightarrow \hat{J}^{(0)} + im\zeta, \quad (4.7)$$

$\hat{J}^{(0)}$ remains dissipative along with $J^{(0)}$ and hence (4.7) which has an inverse of the resolvent type can be discussed by means of the formalism of section III.

In general one cannot obtain (4.7) for ionized gas mixtures due to differences in the signs of the α_i 's. Thus J^{-1} is not of the resolvent type and an analytic continuation is in general not possible. For this reason a projection upon the components will be introduced. On these subspaces one again deals with resolvents. Let P_j be the projection operator which projects upon the j th component subspace:

$$(P_j\Phi, \Psi) = x_j(\Phi, \Psi)_j. \quad (4.8)$$

Then one can split J according to

$$J = J^{(d)} + J^{(nd)}, \quad (4.9)$$

where

$$\begin{aligned} J^{(d)} &= \sum_j J_j^{(d)} = \sum_j P_j J P_j = \sum_j P_j (J^{(0)} + i\alpha_j m\zeta) P_j = \\ &= \sum_j (J_j^{(0,d)} + i\alpha_j m\zeta P_j); \end{aligned} \quad (4.10)$$

$$J^{(nd)} = \sum_j \sum_{h \neq j} J_{jh}^{(nd)} = \sum_j \sum_{h \neq j} P_j J P_h = \sum_j \sum_{h \neq j} P_j J^{(0)} P_h.$$

Thus:

$$\begin{aligned} J_j^{(0,d)}\Phi_j &= x_j \int F_{j1}^{(0)}(\Phi_j' + \Phi_{j1} - \Phi_j - \Phi_{j1}) g_{j1} b db d\epsilon dW_{j1} + \\ &+ \sum_{h \neq j} x_h \int F_h^{(0)}(\Phi_j' - \Phi_j) g_{jh} b db d\epsilon dW_h; \\ J_{jh}^{(nd)}\Phi_h &= x_h \int F_h^{(0)}(\Phi_h' - \Phi_h) g_{jh} b db d\epsilon dW_h. \end{aligned} \quad (4.11)$$

Here $j1$ refers to the collision partner in collisions between like molecules. One now obtains:

$$J^{-1} = (J^{(d)} + J^{(nd)})^{-1} = J^{-1(d)} \sum_{n=0}^{\infty} (-J^{(nd)} J^{-1(d)})^n, \quad (4.12)$$

where

$$J^{-1(d)} = \sum_j J_j^{-1(d)} = \sum_j P_j (J_j^{(0)} + i\alpha_j m \zeta)^{-1} P_j. \quad (4.13)$$

Thus J^{-1} can be written in terms of products of operators of the resolvent type. It will be clear that the expansion (4.10) only converges if $J^{(nd)}$ is smaller than $J^{(d)}$.

From (4.1), (4.3) and (4.12) one obtains

$$L_l^m(\zeta) = (J^{-1} \Psi_l^m, \Psi_l^m) = \sum_n {}^n L_l^m(\zeta) \quad (4.14)$$

with

$${}^n L_l^m(\zeta) = (J^{-1(d)} (-J^{1(nd)} J^{(d)})^n \Psi_l^m, \Psi_l^m). \quad (4.15)$$

The two lowest order ${}^n L_l^m$'s are:

$${}^0 L_l^m(\zeta) = \sum_j x_j ((J_j^{(0,d)} + i\alpha_j m \zeta)^{-1} \Psi_{lj}^m, \Psi_{lj}^m)_j; \quad (4.16)$$

$${}^1 L_l^m(\zeta) = - \sum_j \sum_{h \neq j} x_j ((J_j^{(0,d)} + i\alpha_j m \zeta)^{-1} J_{jh}^{(nd)} (J_h^{(0,d)} + i\alpha_h m \zeta)^{-1} \Psi_{lh}^m, \Psi_{lj}^m)_j.$$

The expressions for ${}^n L_l^m(\zeta)$ for $n \geq 1$ contain products of resolvents. In order to discuss the ζ -dependence of these expressions, it is convenient to treat them using partial fractions. This can be done directly for the operators but one can also introduce the spectral decomposition

$$J_j^{(0)} = \int_{-\infty}^{-\delta_j} \lambda dE_{j\lambda}, \quad (4.17)$$

after which a separation can be performed. Thus, for ${}^1 L_l^m(\zeta)$:

$${}^1 L_l^m(\zeta) = - \sum_j \sum_{h \neq j} x_j \int_{\lambda} \int_{\mu} (\lambda + i\alpha_j m \zeta)^{-1} (\mu + i\alpha_h m \zeta)^{-1} \cdot (dE_{j\lambda} J_{jh}^{(nd)} dE_h \Psi_{lh}^m, \Psi_{lj}^m)_j, \quad (4.18)$$

and now the factor $(\lambda + i\alpha_j m \zeta)^{-1} (\mu + i\alpha_h m \zeta)^{-1}$ can directly be split.

In this way all ${}^n L_l^m(\zeta)$ can be broken up into expressions which contain ζ only via operators of the type $(J_j^{(0)} + i\alpha_j m \zeta)^{-p}$ where p is a positive integer.

One is now in the position to derive a number of sum rules. In the following m will always be assumed to be nonzero.

From $\lim_{\zeta \rightarrow \infty} (J_j^{(0)} + i\alpha_j m \zeta)^{-p} = 0$ for $\alpha_j \neq 0$ it is seen that in this limit the sums in the expressions for the various ${}^n L_l^m(\zeta)$ are only over the neutral components ($\alpha_j = 0$). As the remaining expression is real the transverse components of the transport coefficients vanish in this limit. Let

$$P_{\infty} = \sum_{\substack{j=1 \\ \alpha_j=0}}^N P_j \quad (4.19)$$

be the projector which projects upon the neutral components subspace.

Then one can write

$$\begin{aligned}
 L_l^m(\infty) &= \lim_{\zeta \rightarrow \infty} L_l^m(\zeta) = ((J^{(0,d)} + P_\infty J^{(n,d)})^{-1} P_\infty \Psi_l^m, \Psi_l^m) = \\
 &= \sum_{n=0}^{\infty} (J^{-1(0,d)} (-P_\infty J^{(n,d)} J^{-1(0,d)})^n P_\infty \Psi_l^m, \Psi_l^m). \quad (4.20)
 \end{aligned}$$

The P_∞ in front of Ψ_l^m restricts the sum in the inner product (4.2) to a sum over the neutrals only. As $J^{-1(0,d)}$ commutes with $P_\infty J^{(n,d)}$ is always sandwiched between two of these operators and hence all sums are over the neutral components only. Thus (4.20) constitutes the generalization of (3.9) to mixtures. Note that, although the sums are only over neutrals, $L_l^m(\infty)$ still contains the interaction between neutral and charged particles via the $J^{(0,d)}$'s.

If there are no neutral components in the mixture $P_\infty = 0$ and hence

$$L_l^m(\infty) = 0, \quad \alpha_j \neq 0, \forall j. \quad (4.21)$$

If $P_\infty = 0$ some additional sum rules hold:

As

$$\lim_{\zeta \rightarrow \infty} \zeta (J_j^{(0)} + i\alpha_j m \zeta)^{-1} = \frac{1}{i\alpha_j m}$$

one obtains

$$\lim_{\zeta \rightarrow \infty} i m \zeta^0 L_l^m(\zeta) = \sum_j \frac{x_j}{\alpha_j} \|\Psi_l^m\|_j^2; \quad \alpha_j \neq 0, \forall j.$$

Also

$$\lim_{\zeta \rightarrow \infty} m \zeta^n L_l^m(\zeta) = 0; \quad n \geq 1, \quad \alpha_j \neq 0, \forall j$$

and hence

$$\lim_{\zeta \rightarrow \infty} i m \zeta L_l^m(\zeta) = \sum_j \frac{x_j}{\alpha_j} \|\Psi_l^m\|_j^2; \quad \alpha_j \neq 0, \forall j. \quad (4.22)$$

In (4.22) the right hand side no longer contains molecular interactions, only quantities as masses, charges, concentrations and kT are involved. It should be observed that (4.22) contains two sum rules; one for the longitudinal and one for the transverse transport coefficient. Another relation is obtained from the limits

$$\begin{aligned}
 \lim_{\zeta \rightarrow \infty} \zeta^2 [(J_j^{(0)} + i\alpha_j m \zeta)^{-1} - (i\alpha_j m \zeta)^{-1}] &= \frac{J_j^{(0)}}{(\alpha_j m)^2}; \\
 \lim_{\zeta \rightarrow \infty} -\zeta^2 (J_j^{(0)} + i\alpha_j m \zeta)^{-1} J_{jh}^{(nd)} (J_h^{(0)} + i\alpha_h m \zeta)^{-1} &= -\frac{1}{\alpha_j \alpha_h m^2} J_{jh}^{(nd)}; \\
 \lim_{\zeta \rightarrow \infty} \zeta^2 J^{-1(d)} (J^{(nd)} J^{-1(d)})^n &= 0, \quad n > 1.
 \end{aligned}$$

From this one finds:

$$\begin{aligned} \lim_{\zeta \rightarrow \infty} \left\{ (m\zeta)^2 L_i^m(\zeta) + im\zeta \sum_j \frac{x_j}{\alpha_j} \|\Psi_i^m\|_j^2 \right\} &= \\ &= \lim_{\zeta \rightarrow \infty} \left\{ (m\zeta)^2 L_i^m(\zeta) - m\zeta \lim_{\zeta' \rightarrow \infty} m\zeta' L_i^m(\zeta') \right\} = \\ &= \sum_j \frac{x_j}{\alpha_j} \left(\frac{J_j^{(0)}}{\alpha_j} \Psi_j^{mi} + \sum_{h \neq j} \frac{J_{jh}^{(nd)}}{\alpha_n} \Psi_{ih}^m, \Psi_{ij}^m \right)_j; \quad \alpha_j \neq 0, \forall j. \end{aligned} \quad (4.23)$$

Although the right hand side depends on the molecular interactions this dependence is rather simple since the inner products only contain a few collision integrals $\Omega_{jh}^{(l,s)}$. (For the definition of the Ω -integrals see ref. 1). As

$$\int_{-\infty}^{+\infty} d\zeta (J_j^{(0)} + i\alpha_j m\zeta)^{-1} = -\frac{\pi}{m|\alpha_j|}; \quad \alpha_j \neq 0,$$

one obtains

$$\int_{-\infty}^{+\infty} d(m\zeta) {}^0L_i^m(\zeta) = -\pi \sum_j \frac{x_j}{|\alpha_j|} \|\Psi_i^m\|_j^2; \quad \alpha_j \neq 0, \forall j. \quad (4.24)$$

The integrals over the higher order ${}^nL_i^m$'s do not vanish in general. However, they do vanish if all α_j 's have the same sign as can be shown from partial fractions (This restricts its practical value to the Lorentz mixture and to rotating gases). In that case

$$\int_{-\infty}^{+\infty} d(m\zeta) L_i^m(\zeta) = -\pi \sum_j \frac{x_j}{|\alpha_j|} \|\Psi_i^m\|_j^2; \quad \alpha_j \neq 0, \forall j, \quad (4.25)$$

$\forall \alpha_j$ same sign.

Finally there remains the question as to whether or not a dispersion relation exists. It will be clear that no such relation exists if α_j 's of different sign occur. If, however, all nonzero α_j 's have the same sign, analytic continuation is possible in one half plane. It may happen, however, that certain α_j 's are zero. In that case a dispersion relation of the type (3.13) or (3.14) holds for

$$\Delta L_i^m(\zeta) = L_i^m(\zeta) - L_i^m(\infty) \quad (\text{all nonzero } \alpha_j \text{'s of the same sign}). \quad (4.26)$$

All results obtained above are exact consequences of the Chapman-Enskog equation provided the expansion (4.12) is valid. This expansion was needed to reduce the ζ -dependence to that via resolvents. It is likely, however, that one can circumvent the series expansion by manipulating the

set of N linear eqs. (4.3) in a different way without introducing infinite series. Thus the validity of the expansion would not be required.

In a mixture of electrons, neutrals and ions of arbitrary sign some approximate results can be obtained. This is due to the large mass difference between electrons and other particles. Thus $\alpha_j m \zeta$ is already very large for the electrons when it is still small for the other components of the mixture and one may for not too high fields put $\alpha_j = 0$ for all components except the electrons. Thus one gets an approximate dispersion relation and approximate sum rules. A second corollary of the large mass difference between electrons and the other components is that the $J_{jh}^{(nd)}$'s between electrons and other particles are very small. This may again lead to useful approximations.

It will be clear that all sum rules obtained in this section immediately hold for the Lorentz gas, as in that case the conditions on the α_j are trivially fulfilled.

5. *Discussion.* a. The semi-group of operators $T(t, J^{(0)})$, introduced in section III, has a clear physical meaning. In fact $T(t, J^{(0)})$ corresponds to what is known as the Green function of the problem. From (3.3) it is seen that

$$f(t) = T(t, J^{(0)}) f(0) \quad (5.1)$$

is the solution of the equation

$$\partial_t f(t) = J^{(0)} f(t), \quad (5.2)$$

that is, of the linearized Boltzmann equation for a spatially homogeneous system. When a magnetic field is present (5.2) becomes

$$\partial_t f(t) = J(\mathbf{B}) f(t) \quad (5.3)$$

or, breaking up (5.3) into separate equations on the subspaces \mathcal{H}_l^m :

$$\begin{aligned} \partial_t f_l^m(t) &= (J_l^{(0)} + im\zeta) f_l^m(t); \\ f_l^m(t) &= T_l^m(t, J_l^{(0)} + im\zeta) f_l^m(0) = \\ &= e^{im\zeta t} T(t, J_l^{(0)}) f_l^m(0). \end{aligned} \quad (5.4)$$

One can write the quantities $L_l^m(\zeta)$ (see (3.4) and (3.7)) as

$$\begin{aligned} L_l^m(\zeta) &= - \int_0^\infty (\Psi_l^m(0), \Psi_l^m(\zeta, t)) dt = \\ &= - \int_0^\infty e^{im\zeta t} (\Psi_l^m(0), \Psi_l^m(0, t)) dt \end{aligned} \quad (5.5)$$

with $\Psi_l^m(0) = \Psi_l^m$ and $\Psi_l^m(\zeta, t)$ given according to the second equation (5.4). Eq. (5.5) can be interpreted as the correlation function expression for the transport coefficient in the dilute gas limit at frequency $m\zeta$. As $F_l(t) =$

$= (\Psi_l^m(0), \Psi_l^m(0, t))$ does not depend on m , due to rotational invariance, one can write

$$L_l^m(\zeta) = L_l(m\zeta) = - \int_0^{\infty} e^{im\zeta t} F_l(t) dt. \quad (5.6)$$

Thus it is seen that one is able to obtain the autocorrelation functions $F(t)$ for a pure dilute ionized gas from the field dependence of the transport coefficients. At higher densities this will no longer be the case since then vector quantities other than the velocities of the particles are involved and the rotational invariance arguments used in this paper no longer apply. Similar complications arise for the Senftleben-Beenakker effect. The fact that $F_l(t)$ in (5.6) is an autocorrelation function immediately implies the existence of a dispersion relation for $L_l^m(\zeta)$. However, to arrive at (5.6) within the framework of the present theory one needs the same properties of $J^{(0)}$ that lead to a dispersion relation directly.

b. The basic property (2.17) of the Boltzmann collision operator is the mathematical expression for the positive definiteness of the entropy production. Thus any well-behaving collision operator should possess this property. This is for instance the case for the Fokker-Planck collision operator. However, the existence of a continuous spectrum ranging up to zero¹³⁾ may lead to difficulties for the analytic continuation in this case.

c. In table II the various cases are summarized for which the transport coefficients show an absorptive or dispersive behaviour. In all cases the appropriate Chapman-Enskog equation contains the external parameter ζ

TABLE II

| A review of the various cases where transport coefficients show an absorptive or dispersive behaviour as a function of an external parameter (magnetic field or, in rotating systems, rotation frequency). The existence of dispersion relations or sum rules is indicated | | |
|--|----------------------|---|
| system | dispersion relations | sum rules not containing molecular interactions |
| Lorentz mixture | yes | yes |
| rotating gas (Coriolis force) | yes | yes |
| ionized gas mixture, all components charged but charges not of the same sign | no | yes |
| ionized gas mixture, charged components of the same sign, at least one neutral component present | yes | no |
| ionized gas mixture, charged components with different sign, at least one neutral component present | no | no |
| polyatomic neutral gases | no | no |

via $J = J^{(0)} + \zeta J^{(1)}$, where $J^{(1)}$ is antisymmetric. This, together with the dissipativity of $J^{(0)}$ is sufficient to lead to absorptive or dispersive behaviour. It is well known that for linear passive systems the linearity and passivity lead to a causal behaviour of the system under the influence of an external force¹⁴). A causality condition, however, leads to dispersion relations for the Fourier transform of the linear response. In the present paper dispersion relations were found for some special cases and one might ask if there is a causality condition connected with this. This is not likely, since related cases do not possess dispersion relations. Also, although the system is passive, due to the dissipativity of $J^{(0)}$, the dependence of the thermodynamic fluxes on the external field is not linear. However, dissipativity of $J^{(0)}$ and antisymmetry of $J^{(1)}$ do lead to absorptive and dispersive behaviour.

In macroscopic theory the first condition is connected with the passivity of the system. Thus there remains the interesting question whether or not there is a macroscopic condition which leads to dispersive or absorptive behaviour of the transport coefficients of passive systems which depend on an external parameter. Even this does not seem likely for it is known that the Senftleben-Beenakker effect for the longitudinal transport coefficients may have both positive and negative sign. Thus these transport coefficients (which are positive) may, in extreme cases, first grow larger but for higher field values may drop again to lower values or vice versa. Thus the saturation curve does no longer show a simple behaviour. The only remaining feature is that the transport coefficient tends to a finite limit for high field values. For further discussions about the Senftleben-Beenakker effect, see ref. 15.

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MAGNETIC DISPERSION RELATIONS IN THE SENFLEBEN-BEENAKKER EFFECT

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Synopsis

Longitudinal and transverse components of the transport coefficients of dilute polyatomic gases in a magnetic field can be considered as real and imaginary parts respectively of complex functions of a variable ζ proportional to the field. It is shown that such functions can be generally split into two parts, corresponding to different signs of the index m_2 labelling the components of the spherical tensors built up from the angular momentum. Each of the two parts obeys separate dispersion relations with respect to ζ . Although no exact dispersion relations hold for the components of the transport coefficients as a whole, such relations are shown to hold in those approximations where the rank of irreducible tensors built up from the reduced velocity vector entering into the expansion of the distribution function does not exceed the absolute value of the index m denoting the spherical tensor components of the transport coefficients. Some experimental consequences are discussed.

1. *Introduction.* As is well known, the transport properties of a dilute polyatomic gas change upon the application of an external field (the Senfleben-Beenakker effects^{1, 2}). These effects can be obtained by solving the appropriate Chapman-Enskog equation and this can be achieved in two ways: either by means of a variational procedure³) based on a truncated expansion of the perturbation, ϕ , of the distribution function from local equilibrium or by means of an iterative procedure⁴) based on a splitting of the collision (super)operator into unperturbed and perturbing parts.

The two procedures are equivalent in the field-free case if the splitting of the collision operator in the iterative procedure is such that the unperturbed operator is that part diagonal with respect to the set of tensors chosen for

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the variational procedure. This same remark holds true in the presence of a magnetic field provided the set of expansion tensors employed is made up of eigenfunctions of the field (super)operator. For linear molecules and spherical tops this is exactly the case if spherical tensors are employed. Diamagnetic molecules in general, however, have a rotational magnetic moment not necessarily along the axis of rotation, *i.e.*, the rotational g -tensor can be anisotropic. Only the case where the g -tensor is isotropic will be considered here. It should be observed that the expansion of the distribution function in terms of irreducible Cartesian tensors is especially appropriate for the variational procedure, while the expansion in irreducible spherical tensors is more convenient for the iteration method (when a field is present). For this reason, the preceding discussion of equivalence of these procedures should not be applied without due consideration.

A special advantage offered by the spherical tensor expansion is that it facilitates an investigation of the analyticity properties of the transport coefficients in the external-field variable. Indeed, the longitudinal (even-in-field) components of the transport coefficients are given by the real part of a complex function whose imaginary part gives the transverse (odd-in-field) components⁴).

If the phenomenological equations for the heat flux vector \mathbf{q} and the pressure tensor Π are written as

$$\mathbf{q} = -\lambda(\mathbf{B}) \cdot \nabla T$$

and

$$\Pi = -2\eta(\mathbf{B}) : \mathbf{S}$$

where $\lambda(\mathbf{B})$ and $\eta(\mathbf{B})$ are the thermal conductivity and shear viscosity tensors as functions of the magnetic field \mathbf{B} while ∇T and \mathbf{S} are the temperature and (symmetric traceless) velocity gradients, then the following quantities are found to be related:

| real part | imaginary part |
|--------------------|-----------------------|
| λ_{\perp} | λ_{tr} |
| $2\eta_2 - \eta_1$ | η_4 |
| η_3 | η_5 |

The above components of the viscosity tensor are obtained through the scheme given by de Groot and Mazur⁵), whereas λ_{\perp} and λ_{tr} are defined through the scheme

$$\begin{pmatrix} \lambda_{\perp} & \lambda_{\text{tr}} & 0 \\ -\lambda_{\text{tr}} & \lambda_{\perp} & 0 \\ 0 & 0 & \lambda_{\parallel} \end{pmatrix}$$

which applies for \mathbf{B} along the z axis.

Because of this, it is of interest to investigate the analyticity properties of these complex functions of the real variable $\zeta = g_{\text{rot}}\mu_N B/\hbar n$ when ζ is extended into the complex plane. It will be shown below by an iterative procedure akin to that introduced by Kagan and Maksimov⁴) under what conditions the continued functions are analytic in a half-plane so that dispersion relations can be found connecting the longitudinal and transverse components of the transport coefficients.

A similar treatment for the case of weakly ionized gases is also in progress⁶).

2. *Partial dispersion relations.* The "second order" Chapman-Enskog equation can be written formally as

$$\psi = \mathcal{I}\phi = (\mathcal{I}_0 + i\zeta \tilde{\mathcal{I}}_1) \phi \quad (1)$$

where ψ is the inhomogeneous term appropriate to the problem under consideration, ϕ is such that the perturbation ϕ is formed by completely contracting ϕ with the corresponding macroscopic gradient, \mathcal{I}_0 is the collision superoperator and $\tilde{\mathcal{I}}_1$ is a self-adjoint superoperator* which is due to the applied magnetic field. The precise form of \mathcal{I}_0 is unimportant for the present discussion, the only properties required being its isotropy (rotational invariance) and its dissipative nature (in particular, it is *not* required to be self-adjoint). The form of $\tilde{\mathcal{I}}_1$ is, however, crucial to the problem and is

$$\tilde{\mathcal{I}}_1 = [\mathbf{J} \cdot \hat{\mathbf{B}}, \quad]_- \quad (2)$$

If the direction of the magnetic induction \mathbf{B} is taken to be that of the (positive) z axis, then the form (2) above is conducive to an expansion of the perturbation ϕ in terms of spherical tensor harmonics $\mathcal{Y}_{l_2}^{m_2}(\hat{\mathbf{J}})$ (because of the preferred direction associated with \mathbf{B}) where $\hat{\mathbf{J}}$ is related to \mathbf{J} by $\hat{\mathbf{J}} = [j(j+1)]^{-1/2} \mathbf{J}$. The spherical components of \mathbf{J} are the usual ones J_0 , J_+ and J_- and lead to the result that

$$[J_0, \mathcal{Y}_{l_2}^{m_2}(\hat{\mathbf{J}})]_- = m_2 \mathcal{Y}_{l_2}^{m_2}(\hat{\mathbf{J}}) \quad (3)$$

This result suggests the expansion of $\tilde{\mathcal{I}}_1$ in terms of projection superoperators $\mathcal{P}_{l_2}^{m_2}$ which project out the irreducible subspaces defined by $\mathcal{Y}_{l_2}^{m_2}(\hat{\mathbf{J}})$, i.e.,

$$\tilde{\mathcal{I}}_1 = \sum_{l_2, m_2} m_2 \mathcal{P}_{l_2}^{m_2} \quad (4)$$

Now, turning to the transport coefficients, it is obvious that a transport coefficient $L(\zeta)$ can be written in terms of the formal solution of eq. (1)

$$\phi = \mathcal{I}^{-1}(\zeta) \psi \quad (5)$$

* $\tilde{\mathcal{I}}_1$ is self-adjoint in the natural metric $(A, B) = \text{tr} \int f^{(0)} A^\dagger B \, d\mathbf{p}$.

as

$$L(\zeta) = (\psi, \mathcal{J}^{-1}(\zeta) \psi). \quad (6)$$

The inverse superoperator $\mathcal{J}^{-1}(\zeta)$ appearing in eq. (5) exists and is bounded on the subspace orthogonal to the summational invariants provided the resolvent set of $\mathcal{J}(\zeta)$ includes the whole imaginary axis. Such a condition is assumed to be valid throughout this paper.

A splitting of the collision superoperator into „diagonal” and „non-diagonal” parts can now be performed by utilizing the projection superoperators $\mathcal{P}_{l_2}^{m_2}$. The „diagonal” part, $\mathcal{J}_0^{(d)}$, is given as

$$\mathcal{J}_0^{(d)} = \sum_{l_2, m_2} \mathcal{P}_{l_2}^{m_2} \mathcal{J}_0 \mathcal{P}_{l_2}^{m_2} \quad (7)$$

the remainder of \mathcal{J}_0 , viz., $\mathcal{J}_0^{(nd)}$, being completely off-diagonal with respect to the $\mathcal{Y}_{l_2}^{m_2}(\hat{J})$ spherical harmonics.

With this splitting, $\mathcal{J}^{-1}(\zeta)$ can be written as

$$\mathcal{J}^{-1}(\zeta) = (\mathcal{J}^{(d)}(\zeta) - \mathcal{J}^{(nd)})^{-1} \quad (8)$$

and this can be developed formally in a series expansion, viz.,

$$\mathcal{J}^{-1}(\zeta) = \mathcal{J}^{(d)-1}(\zeta) \sum_{n=0}^{\infty} [\mathcal{J}^{(nd)} \mathcal{J}^{(d)-1}(\zeta)]^n. \quad (9)$$

This series expansion is assumed to converge in the present work. In cases where only a finite number of expansion tensors is considered, the expansion will certainly converge if $\mathcal{J}^{(nd)}$ is small enough (this appears to be the case as seen from experiment^{1, 2}).

Substitution of the expansion (9) into the equation defining $L(\zeta)$ gives

$$L(\zeta) = \sum_n (\psi, \mathcal{J}^{(d)-1}(\zeta) [\mathcal{J}^{(nd)} \mathcal{J}^{(d)-1}(\zeta)]^n \psi), \quad (10)$$

where $\mathcal{J}^{(d)-1}(\zeta)$ behaves essentially like $\mathcal{J}^{(d)}(\zeta)$ in that it can be decomposed as

$$\mathcal{J}^{(d)-1}(\zeta) = \sum_{l_2, m_2} \mathcal{P}_{l_2}^{m_2} (\mathcal{J}_0^{(d)} + im_2\zeta)^{-1} \mathcal{P}_{l_2}^{m_2} = \sum_{l_2, m_2} \mathcal{R}_{l_2}^{m_2}(-\mathcal{J}_0^{(d)}, im_2\zeta) \quad (11)$$

where $\mathcal{R}_{l_2}^{m_2}(-\mathcal{J}_0^{(d)}, im_2\zeta)$ is a resolvent (super)operator. Thus, when $\mathcal{J}^{(d)-1}(\zeta)$ acts on ψ (which is in the manifold defined by \mathcal{P}_0^0 -because ψ is independent of the angles of J) it can be replaced by $\mathcal{J}_0^{(d)-1}$.

The zeroth order term in expression (10) is then just

$$L^{(0)}(\zeta) = (\psi, \mathcal{J}_0^{(d)-1} \psi) = L^{(0)}(\infty). \quad (12)$$

The first order term vanishes identically while the second order term is

$$L^{(2)}(\zeta) = \sum_{l_2, m_2} (\psi, \mathcal{J}_0^{(d)-1} \mathcal{J}^{(nd)} \mathcal{P}_{l_2}^{m_2} (\mathcal{J}_0^{(d)} + im_2\zeta)^{-1} \mathcal{P}_{l_2}^{m_2} \mathcal{J}^{(nd)} \mathcal{J}_0^{(d)-1} \psi). \quad (13)$$

As m_2 can take positive and negative values (and 0), there is a natural splitting of $\Delta L^{(2)}(\zeta) \equiv L^{(2)}(\zeta) - L^{(2)}(\infty)$ into two parts $\Delta L_+^{(2)}(\zeta)$ and $\Delta L_-^{(2)}(\zeta)$ containing, respectively, the positive and negative values of m_2 . Thus, writing the transport coefficient in its spherical representation, each component $\Delta L_l^{m(2)}(\zeta)$ can be written (to second order) as

$$\Delta L_l^{m(2)}(\zeta) = \Delta L_{l+}^{m(2)}(\zeta) + \Delta L_{l-}^{m(2)}(\zeta). \quad (14)$$

Now, the superoperator \mathcal{F}_0 (and therefore $\mathcal{F}_0^{(d)}$) is assumed to be dissipative in the strict sense, that is to say, its spectrum is wholly contained in the half-plane defined by $\text{Re } \lambda \leq -\delta$. This amounts to the physical assumption that only finite relaxation times are present. As a consequence, \mathcal{F} will also be strictly dissipative, which result has already been used in the foregoing. $\mathcal{F}_0^{(d)-1}$ exists and is bounded and, if m_2 is positive, the same is true for $(\mathcal{F}_0^{(d)} + im_2\zeta)^{-1}$ in the whole of the upper half-plane of ζ (with ζ considered as a complex variable). Therefore $\Delta L_{l+}^{m(2)}(\zeta)$ is regular in the upper half-plane and can be thought of as an analytic function, holomorphic in the whole upper half-plane of ζ ; a similar conclusion holds for $\Delta L_{l-}^{m(2)}(\zeta)$ in the lower half-plane. Consequently, the representation (14) splits the analytic function $\Delta L_{l-}^{m(2)}(\zeta)$ into two parts, $\Delta L_{l+}^{m(2)}(\zeta)$ and $\Delta L_{l-}^{m(2)}(\zeta)$, holomorphic, respectively, in the upper and lower half-planes of ζ .*

Moreover, in the present instance, much more can be said: $\Delta L_{l-}^{m(2)}(\zeta)$ tends to zero, at least as fast as $|\zeta|^{-1}$ when $|\zeta| \rightarrow \infty$ in the upper half-plane. This follows again from the dissipative nature of $\mathcal{F}_0^{(d)}$ since, quite generally, the norm of the resolvent of a dissipative operator vanishes, at least as fast as $(\text{Re } \lambda + \delta)^{-1}$, in the right half-plane of the spectral variable λ , and the norm of the resolvent of $\mathcal{F}^{(d)}$ (for $\lambda = -im_2\zeta$) can be used in order to obtain an upper bound for $\Delta L_{l+}^{m(2)}(\zeta)$. This has the important consequence that $\Delta L_{l+}^{m(2)}(\zeta)$ obeys the dispersion relation

$$\text{Re } \Delta L_{l+}^{m(2)}(\zeta) = \frac{1}{\pi} \mathcal{P} \int_{-\infty}^{+\infty} d\zeta' \frac{\mathcal{I}m \Delta L_{l+}^{m(2)}(\zeta')}{\zeta' - \zeta}$$

which, since $\mathcal{I}m \Delta L_{l+}^{m(2)}(\zeta)$ is odd in ζ , can be written also as

$$\text{Re } \Delta L_{l+}^{m(2)}(\zeta) = \frac{2}{\pi} \mathcal{P} \int_0^{\infty} d\zeta' \frac{\zeta' \mathcal{I}m \Delta L_{l+}^{m(2)}(\zeta')}{\zeta'^2 - \zeta^2}. \quad (15)$$

* This conclusion is hardly surprising. In fact, the class of analytic functions which can be split in this way is very large: it comprises not only all meromorphic functions (Mittag-Leffler theorem) but also functions possessing essential singularities, provided they are finite in number and isolated⁷). For such functions, it is sufficient to take the principal parts of the Laurent series at the singularities below and above the real axis, the remainder being holomorphic everywhere, *i.e.*, an entire function.

Analogously, $\Delta L_{l-}^{m(2)}(\zeta)$ tends to zero at least as fast as $|\zeta|^{-1}$ when in the lower half-plane and obeys the opposite dispersion relation

$$\Re \Delta L_{l-}^{m(2)}(\zeta) = -\frac{2}{\pi} \mathcal{P} \int_0^{\infty} d\zeta' \frac{\zeta' \Im \Delta L_{l-}^{m(2)}(\zeta')}{\zeta'^2 - \zeta^2}. \quad (16)$$

Expression (15) has precisely the form of the well-known Kramers-Kronig relations for the complex susceptibility⁵).

So far, only the second iteration has been discussed. It is clear, however, that the same can be repeated in higher orders after separating the mixed terms which contain m_2 's of different sign, into sums of pure terms. This is always possible, using partial fractions, even though the fractions to be split have the nature of (super)operators (higher order powers such as $(\zeta - a)^{-p}$ ($p > 1$ and integral) cause no problems). Thus, the splitting of $\Delta L_l^m(\zeta)$ into two parts, each of which is holomorphic in only one of the two half-planes can be made to all orders, the corresponding dispersion relations holding to all orders. This is also true for the whole sum so that the superscripts (2) appearing in eqs. (15) and (16) can be dropped. It has been shown then, that each component $\Delta L_l^m(\zeta)$ of a transport coefficient can be split into two (complex) parts, obeying the dispersion relations (15) and (16). This result is very general, but not very strong, since what is really desired are overall dispersion relations for the measured quantities, *i.e.* for the components of the transport coefficients themselves. These can be obtained when one of the two parts $\Delta L_{l+}^m(\zeta)$ or $\Delta L_{l-}^m(\zeta)$ can be neglected with respect to the other. The circumstances under which this is possible are investigated in the following section.

3. *Overall dispersion relations.* It is useful to return to an examination of the second order expansion for $L_l^m(\zeta)$ and investigate the relation between the „quantum number” m_2 characterizing the angular momentum expansion term and the „quantum number” m characterizing the components of the transport coefficient. In order to do this, the nature of the departure from local equilibrium has to be more thoroughly considered. The function ϕ (a quantum mechanical operator) depends, in the general case, not only on \mathbf{J} but also on the reduced velocity \mathbf{W} . Furthermore ψ is, as has already been stated, independent of the directions of \mathbf{J} but it does depend on the directions of \mathbf{W} . If the component $L_l^m(\zeta)$ is sought, the index l can be seen to label the rank of \mathbf{W} in ψ . For example, the three pairs of components $(\lambda_{\perp}, \lambda_{\text{tr}})$, $(2\eta_2 - \eta_1, \eta_4)$ and (η_3, η_5) correspond, in the spherical tensor notation, to $l = 1, |m| = 1$; $l = 2, |m| = 2$; and $l = 2, |m| = 1$, respectively.

In order to treat also the \mathbf{W} dependence, projection operators $\mathbb{P}_{l_i}^{m_i}$ which project onto the manifolds defined by the spherical harmonics in \mathbf{W} are introduced and the expansion (9) modified by using, in place of $\mathcal{J}_0^{(d)}$, the

superoperator

$$\mathcal{F}_0^{(dd)} = \sum_{l_1 m_1 l_2 m_2} \mathbf{P}_{l_1}^{m_1} \mathcal{P}_{l_2}^{m_2} \mathcal{F}_0 \mathbf{P}_{l_1}^{m_1} \mathcal{P}_{l_2}^{m_2} \quad (17)$$

diagonal with respect to the manifolds defined by both the W - and J -spherical harmonics. Its complement is called $\mathcal{F}_0^{(n\ddot{d}d)}$, and so on.

An expression of the type (13) can now be written, more explicitly, as

$$\begin{aligned} L_l^{m(2)}(\zeta) &= (\psi_l^m, \mathcal{F}_0^{(dd)-1} \mathcal{F}_0^{(n\ddot{d}d)} (\mathcal{F}_0^{(dd)} + i\zeta \tilde{\mathcal{F}}_1)^{-1} \mathcal{F}_0^{(n\ddot{d}d)} \mathcal{F}_0^{(dd)-1} \psi_l^m) = \\ &= \sum'_{l_1 m_1 l_2 m_2} (\psi_l^m, \mathcal{F}_0^{(dd)-1} \mathbf{P}_{l_1}^m \mathcal{P}_{l_2}^0 \mathcal{F}_0 \mathbf{P}_{l_1}^{m_1} \mathcal{P}_{l_2}^{m_2} (\mathcal{F}_0^{(dd)} + i\zeta m_2)^{-1} \times \\ &\quad \times \mathbf{P}_{l_1}^{m_1} \mathcal{P}_{l_2}^{m_2} \mathcal{F}_0 \mathbf{P}_{l_1}^m \mathcal{P}_{l_2}^0 \mathcal{F}_0^{(dd)-1} \psi_l^m), \end{aligned} \quad (18)$$

where the prime on the summation indicates that the numbers l_1, l_2, m_1, m_2 cannot take simultaneously the values $l, 0, m, 0$. This has allowed the replacement of $\mathcal{F}_0^{(n\ddot{d}d)}$ by \mathcal{F}_0 in the last part of eq. (18). It is at this point convenient to change from the (implicit) representation with $l_1 m_1 l_2 m_2$ to a (be it again implicit) representation with $l m l_1 l_2$ to correspond to the form of $L_l^m(\zeta)$ appearing in eq. (18). The projection superoperators $\mathbf{P}_{l_1}^{m_1} \mathcal{P}_{l_2}^{m_2}$ must, in this transformation, be replaced by an expression given by

$$\mathbf{P}_{l_1}^{m_1} \mathcal{P}_{l_2}^{m_2} = \sum_l (l_1 m_1 l_2 m_2 | l m) \mathcal{Q}_{l l_1 l_2}^{m_1 m_2} \quad (19)$$

where $(l_1 m_1 l_2 m_2 | l m)$ is a Clebsch-Gordan coefficient and

$$\mathcal{Q}_{l l_1 l_2}^{m_1 m_2} = \sum_{\alpha l'} (l_1 m_1 l_2 m_2 | l' m_3) | l m_3 l_1 l_2 \alpha \rangle \langle l' m_3 l_1 l_2 \alpha |. \quad (20)$$

Here m_3 is required by the Clebsch-Gordan coefficient to be equal to $m_1 + m_2$ and the index α denotes all other variables required in a full decomposition of ϕ (for example, associated Laguerre polynomials in W^2 and Wang Chang-Uhlenbeck polynomials in J^2). Alternatively, $\mathbf{P}_{l_1}^{m_1} \mathcal{P}_{l_2}^{m_2}$ can be replaced by*

$$\mathbf{P}_{l_1}^{m_1} \mathcal{P}_{l_2}^{m_2} = \sum_l (l_1 m_1 l_2 m_2 | l m_3) \mathcal{Q}_{l l_1 l_2}^{m_1 m_2 \ddagger} \quad (21)$$

the double-dagger (\ddagger) denoting the adjoint in the natural metric. In this way eq. (18) becomes

$$\begin{aligned} L_l^{m(2)}(\zeta) &= \sum'_{l_1 m_1 l_2 m_2} \sum_{l' m'} (l_1 m_1 l_2 m_2 | l' m_3) (l_1 m_1 l_2 m_2 | l' m_3) \times \\ &\quad \times (\psi_l^m, \mathcal{F}_0^{(dd)-1} \mathbf{P}_{l_1}^m \mathcal{P}_{l_2}^0 \mathcal{F}_0 \mathcal{Q}_{l' l_1 l_2}^{m_1 m_2} (\mathcal{F}_0^{(dd)} + i m_2 \zeta)^{-1} \mathcal{Q}_{l' l_1 l_2}^{m_1 m_2 \ddagger} \mathcal{F}_0 \mathbf{P}_{l_1}^m \mathcal{P}_{l_2}^0 \mathcal{F}_0^{-1} \psi_l^m) \end{aligned} \quad (22)$$

But, as \mathcal{F}_0 is isotropic, $\mathbf{P}_{l_1}^m \mathcal{P}_{l_2}^0 \mathcal{F}_0 \mathcal{Q}_{l' l_1 l_2}^{m_1 m_2}$ vanishes unless $l' = l$ and $m_1 + m_2 = m$; similarly, $\mathcal{Q}_{l' l_1 l_2}^{m_1 m_2 \ddagger} \mathcal{F}_0 \mathbf{P}_{l_1}^m \mathcal{P}_{l_2}^0$ vanishes unless $l' = l$ and $m_1 + m_2 = m$.

* This is because the combined projection $\mathbf{P}_{l_1}^{m_1} \mathcal{P}_{l_2}^{m_2}$ is, of course, self-adjoint.

Hence, eq. (22) reduces to

$$L_l^{m(2)}(\zeta) = \sum'_{l_1 l_2, m_1 + m_2 = m} (l_1 m_1 l_2 m_2 | l m)^2 (\psi_l^m, \mathcal{F}_0^{(dd)-1} P_l^m \mathcal{P}_0^0 \mathcal{F}_0 \mathcal{Q}_{ll_1 l_2}^{m_1 m_2} \times \\ \times (\mathcal{F}_0^{(dd)} + i m_2 \zeta)^{-1} \mathcal{Q}_{ll_1 l_2}^{m_1 m_2 \dagger} \mathcal{F}_0 P_l^m \mathcal{P}_0^0 \mathcal{F}_0^{(dd)-1} \psi_l^m). \quad (23)$$

Because of the presence of the Clebsch-Gordan coefficient, if m is chosen positive, $\Delta L_{l-}^{m(2)}(\zeta)$ will be considerably smaller than $\Delta L_{l+}^{m(2)}(\zeta)$. The cases where it vanishes altogether are of interest since then a dispersion relation of the form (15) will hold for $\Delta L_l^{m(2)}(\zeta)$ as a whole. The Clebsch-Gordan coefficient is non-vanishing only if $m_2 = m - m_1$, which, since m_1 varies from $-l_1$ to $+l_1$, implies that

$$-l_1 + m \leq m_2 \leq l_1 + m \quad (24)$$

and m_2 will always be positive, thereby causing the vanishing of $\Delta L_{l-}^{m(2)}(\zeta)$ if $l_1 \leq m$ for $m > 0$. In other words, a dispersion relation between even and odd components of a transport coefficient corresponding to a certain m exists insofar as in the expansion of ϕ the rank l_1 of the expansion tensors in the reduced velocity W does not exceed m . Thus, for example, if in a calculation of the shear viscosity only the term $[J]^{(2)}$ (corresponding to $l_1 = 0$) is considered⁸), dispersion relations will be found for both the pairs $(2\eta - \eta_1, \eta_4)$ and (η_3, η_5) ; if, on the other hand, the terms $[J]^{(2)}[W]^{(2)9)}$ or $J[W]^{(2)10)}$ (corresponding to $l_1 = 2$) are included (space inversion considerations force $l_1 - l$ to be even), only the dispersion relation for the pair $(2\eta_2 - \eta_1, \eta_4)$ will remain. As far as the thermal conductivity is concerned, all calculations to date^{3, 9-12)} have involved only terms of rank 1 in W : for all such terms, a dispersion relation between λ_{\perp} and λ_{tr} holds.

It should be mentioned here that the second order approximation in the iteration procedure is on the same level as the so-called diagonal and spherical approximations employed normally in the variational procedure*. The explicit calculations performed in various special cases^{3-4), 8-12)} are in agreement with the present conclusions.

The foregoing considerations have been undertaken in second order, but are in fact valid to any order. The general term will contain factors of the form

$$P_{l_1'}^{m_1'} \mathcal{P}_{l_2'}^{m_2'} \mathcal{F}_0 P_{l_1}^{m_1} \mathcal{P}_{l_2}^{m_2} = \sum_{l'} (l_1 m_1 l_2 m_2 | l m_1 + m_2) (l_1' m_1' l_2' m_2' | l' m_1' + m_2') \times \\ \times \mathcal{Q}_{l_1' l_2'}^{m_1' m_2'} \mathcal{F}_0 \mathcal{Q}_{ll_1 l_2}^{m_1 m_2} \quad (25)$$

and, since \mathcal{F}_0 is isotropic, l' must equal l and, furthermore, $m_1' + m_2' = m_1 + m_2$: thus the total m propagates throughout the whole term (the other factors, being completely diagonal in m_1 and m_2 , do not create any

* See the appendix where a diagrammatic representation is discussed.

difficulties). Hence, the expression (25) contains, in particular, the Clebsch-Gordan coefficient $(l_1 m_1 l_2 m_2 | l m)$, where m labels the particular component ψ_l^m , and the preceding discussion carries over. As long as only tensors whose rank l_1 in the reduced velocity W does not exceed $|m|$ are considered, a dispersion relation of the form (15) holds to all orders and for the sum of the iterative expansion. This can be seen, for example, in the exact calculation of the thermal conductivity when the only anisotropic term considered¹²⁾ is $W[J]^{(2)}$.

The presence of dispersion relations for the pairs $(2\eta_2 - \eta_1, \eta_4)$ and (η_3, η_5) when only the $[J]^{(2)}$ expansion term is used for the viscosity trial function and the loss of the dispersion relation for the pair (η_3, η_5) when a $[W]^{(2)}$ dependence is added, allows an opportunity for determining experimentally in a sensitive way how important the various terms in the expansion are. It is quite probable that the $[J]^{(2)}$ term is the most important one in the viscosity expansion; for example, the change in the viscosity of H_2 in the field occurs at a $(B/n)_\frac{1}{2}$ value corresponding to an inelastic time scale^{13,14)}. For this reason, a comparison of the curve for η_3 obtained experimentally with that obtained through the dispersion relation (15) from the experimentally measured curve of η_5 will be a check on the size of the higher terms.

In the present work no comparison has been made with the original perturbation method of Kagan and Maksimov. A discussion of this matter can however be found in ref. 15.

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APPENDIX

A diagrammatic representation. A typical term occurring in the iteration procedure can be represented in the l_2, m_2 plane as follows: l_2 labels concentric circles of integral radii and m_2 labels horizontal straight lines of integral ordinate. The points of intersection characterize the various components

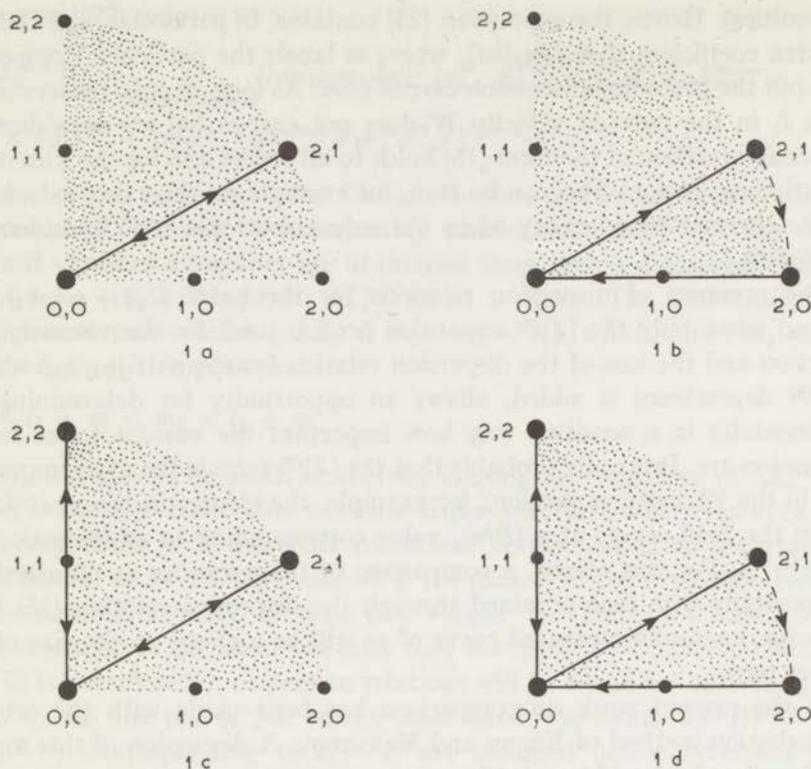


Fig. 1. Diagrammatic representation of some terms important for the thermal conductivity problem ($l_1 = 1, l_2 = 2$).

1a: second order iteration.

1b: diagonal approximation.

1c: spherical approximation.

1d: a non-diagonal diagram containing 1b as a subdiagram. Full lines indicate l_2 -changing transitions, dashed arcs l_2 -conserving transitions.

of the vector spherical harmonics in \hat{J} . Transitions from one point to another correspond to the (super)operator $\mathcal{J}_0^{(nd)}$, all diagrams starting from the origin and ending there (since ψ lies in the irreducible subspace projected out by \mathcal{P}_0^0). The number of lines occurring in the diagram gives the order of the term; hence, the second order diagram is just a segment travelled twice (fig. 1a). The "diagonal approximation" employed in the usual variational treatments³ allows only two lines from the center, the rest being restricted to certain arcs of the circle of radius l_2 connecting a number of allowed points ($m - l_1 \leq m_2 \leq m + l_1$) (fig. 1b).

On the other hand, the "spherical approximation" forbids motion along the arcs (fig. 1c). The combination of the two approximations corresponds therefore to a second order iteration. Fig. 1d shows a more general type of diagram.

This kind of diagrammatic representation is only useful when l_1 is essenti-

ally fixed, and therefore is especially suitable for the case of the thermal conductivity where l_1 can be restricted to be 1. The diagrams occurring in fig. 1 are all of interest for the thermal conductivity problem.

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SAMENVATTING.

In dit proefschrift worden enige aspecten beschreven van de invloed van een magneetveld \underline{B} op transportverschijnselen in verdunde meeratomige en gefoniseerde gassen. Zoals bekend leidt het aanleggen van een homogeen statisch magneetveld niet alleen tot een verandering in de longitudinale transportverschijnselen (even in \underline{B}), maar leidt dit ook tot het optreden van transversale effecten (oneven in \underline{B}).

Hoofdstuk 2 bevat een berekening van de warmtegeleidingstensor $\underline{\lambda}(\underline{B})$ voor een verdund twee-atomig gas. De in vroegere artikelen gemaakte aanname van kleine anisotropie in de intermoleculaire wisselwerking is hier vermeden. Als resultaat van deze, meer algemene, berekening blijken zowel de vorm van de verzadigingskrommen voor de diverse componenten van $\underline{\lambda}$ als functie van de parameter B/n (n is de gasdichtheid), als de verhouding van de verzadigingswaarden voor de twee longitudinale componenten van $\underline{\lambda}$, zich te wijzigen. De optredende correcties zijn bijvoorbeeld van belang voor een gas bestaande uit zogenaamde 'ruwe bollen'.

In het tweede hoofdstuk wordt een berekening gegeven van de viscositeitstensor $\underline{\eta}(\underline{B})$ voor mengsels van twee-atomige gassen en edelgassen. Metingen van $\underline{\eta}(\underline{B})$ voor een dergelijk mengsel als functie van de concentraties van de componenten kunnen belangrijke informatie verschaffen over het anisotrope deel der wisselwerking tussen moleculen en edelgasatomen.

Een nadere beschouwing van zowel de experimentele als de theoretische krommen voor de afhankelijkheid van de transportcoëfficiënten van B/n laat zien, dat de krommen voor de longitudinale coëfficiënten het karakter van een

dispersiekromme hebben, terwijl die voor de transversale coëfficiënten een verloop karakteristiek voor een absorptiekromme vertonen. Dit doet de vraag rijzen of longitudinale en transversale transportcoëfficiënten verbonden zijn door middel van een dispersierelatie, of, nog algemener, er aan deze laatste een causaliteitsprincipe ten grondslag ligt. Hierop wordt nader ingegaan in de hoofdstukken 4 en 5, voor respectievelijk gefoniseerde en meeratomige gassen. Het blijkt dat dispersierelaties in het algemeen niet gelden. Echter bestaan deze wel voor de transportcoëfficiënten van het Lorentzgas en voor gassen in roterende systemen. In het laatste geval komt de rotatievector $\underline{\omega}$ in de plaats van het magneetveld \underline{B} (Corioliskracht in plaats van Lorentzkracht).

Teneinde te voldoen aan de wens van de Faculteit der Wiskunde en Natuurwetenschappen volgt hier een kort overzicht van mijn studie.

Na het met goed gevolg afleggen van het eindexamen H.B.S.-B aan de Rijks H.B.S. te Alkmaar in 1958 begon ik met de studie in de wis- en natuurkunde aan de Universiteit van Amsterdam. In 1962 behaalde ik het candidaatsexamen wis- en natuurkunde met bijvak sterrenkunde. In 1965 volgde het doctoraalexamen experimentele natuurkunde met bijvakken wiskunde en mechanica. Sinds 1963 ben ik verbonden aan het F.O.M.-Instituut voor Atoom- en Molecuulfysica; aanvankelijk als wetenschappelijk assistent, na het doctoraalexamen als wetenschappelijk medewerker in gewoon verband. Onder leiding van Professor dr J. Kistemaker verrichtte ik hier de voor het doctoraalexamen noodzakelijke experimentele werkzaamheden.

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