Transport Coefficients in Moderately Dense Gases

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The first virial corrections for shear viscosity \( \eta \) and thermal conductivity \( \lambda \) are calculated, starting from the Boltzmann-Landau equation of a quantum gas in binary collision approximation. The first order Chapman-Ensksog solution is used. With a very simplified collisional operator numerical values are got and compared with experiments. The result is that the kinetic equation including the interaction effects in quasi-free motion is able to explain the empirical order of magnitude of \( d\eta/dn \).

Recently attempts have been made, to calculate transport coefficients of gases for not too low densities. A summary has been given by Cohen, Ernst, and Dorfmann 1, Réhbod 2 and Kawasaki and Oppenheim 3.

There are three methods:

(i) The earliest was that of Enskog 4, starting from a modified Boltzmann equation for hard cores.

(ii) Another one starts from a formula, which expresses the transport coefficient by time-correlation functions 5.

Or: (iii) The transport properties are given by certain integrals over reduced non-equilibrium distribution functions 6. The equivalence of the last methods has been shown recently by Réhbod 2 for classical gases. (See also 7.)

In this paper we will return to a Boltzmann equation approach to transport theory. This has been very successful for low density gases. Of course, the wellknown Boltzmann equation is not capable of treating gases at moderate densities: it leads to equilibrium properties of perfect gases and to lowest-order-in-density transport coefficients. To extend the range of application with respect to the density, Boltzmann’s equation for the particle distribution function \( f(r,p,t) \) must be extended first. One attempt in doing that is Enskog’s proposal for a modified collisional change \( \Xi \). Its main advantage is that the transport coefficients can be calculated up to very high densities even near the critical region. Its disadvantages are that it can only be formulated for a hard sphere gas, and that an ad hoc modification of the final results (together with an additional fitting of an interaction parameter) is necessary to get correct results. Numerically they agree with experiments over a large range of density, but at small densities there are considerable deviations between the Enskog theory and experiment 7. Now recently methods have been developed to generalize transport equations to systems with arbitrary densities, based on ideas of Bogoluibov, Landau, Kirkwood, Cohen, Prigogine etc. For quantum gases especially in the binary collision approximation it has been shown 8 that a simply altered Boltzmann equation of the Landau-type very well describes moderately dense gases with arbitrary (but short range, of course) interaction. The point is: the influence of the interaction on a given molecule is not only described by collisions, between which the particles are free — there is, moreover, a mean interaction also during the time of mean free flight \( r \), modifying the energy \( \varepsilon_p \) of molecule with momentum \( p \).

\[
\varepsilon_p(r,t) = \frac{p^2}{2m} + \int F(p,q) f(r,q,t) dq.
\]

(1)

\[
F(p,q) = \frac{F(q,p)}{F(k)}; \quad k = \frac{1}{2} (p - q).
\]

(2)


is the real part of the two particle scattering amplitude in forward direction. If we restrict to binary collision approximation, it is independent of \( f \). The collisional operator in the transport equation is altered in containing the conservation law for the energy (1), besides momentum conservation as usual. As \( \varepsilon_p \) depends on the distribution \( f \), the collisional operator \( \sigma \) gets density dependent.

According to the idea of Landau also the streaming part of the transport equation has to be altered. The velocity of a quantum particle with dispersion relation (1) is

\[
\frac{\partial \varepsilon_p}{\partial p} = \frac{p}{m} + \int F(p, q) f(r, q, t) \, dq
\]

and its acceleration is

\[
-\frac{\partial \varepsilon_p}{\partial r} = \int F(p, q) \frac{\partial f(r, q, t)}{\partial r} \, dq \sim \text{density}.
\]

The distribution function thus must be a solution of

\[
\frac{\partial f}{\partial t} + \frac{\partial \varepsilon_p}{\partial p} \frac{\partial f}{\partial r} - \frac{\partial \varepsilon_p}{\partial p} \frac{\partial f}{\partial p} = \int \sigma(p, p_1 \rightarrow p' p'_1 ; f) (f' f'_1 - f f_1) \, dp_1 \, dp' \, dp'_1.
\]

Statistics effects have been neglected. As is shown in \(^8\), this Boltzmann–Landau equation leads to quasi-equilibrium properties of a real gas: virial equation of state, density-corrections for local energy, entropy etc., a modification of the sound velocity \( c = c(n) \) and the prediction of a physical phenomenon in gases, which is known from low temperature quantum liquids: Zero sound is likely to be expected in a moderately dense Boltzmann gas for that region of temperature, in which the repulsive component of the intermolecular force predominates. All these quasi-equilibrium effects are only due to the modified streaming part of (5), because the r. h. s. does not appear in the conservation laws, which govern quasi-equilibrium behaviour. This shows the importance of the modifications (3) and (4). Its lack in the Enskog theory would lead to wrong results for the transport coefficients, if it were not added indirectly as so-called “collisional transfer” of momentum etc. This has only be formulated for hard spheres. The Boltzmann–Landau equation (5) thus seems to be a generalization of Enskog’s theory of moderately dense gases with arbitrary interaction, provided a transport equation of Markov-type is correct at all.

The modified streaming part is also very plausible from the derivation of the transport equation from first principles. The S-matrix in the collisional change only occurs if one integrates the Liouville or von Neumann equation over a finite time \( t \ldots t + \Delta t \). This must necessarily change the pure motion, which only infinitesimally is described by \( \mathbf{v} \cdot \nabla \mathbf{r} \). In finite time intervals “interference” between \( H_{\text{kin}} \) and \( V \) occurs, altering the streaming part simultaneously with the collisional part. In fact both are mixed and it is somewhat artificially to separate them into a term, in which momentum change predominates \( (\varepsilon_f/\partial t) \) and another, in which position change predominates. But as long as the system is gas-like, this picture should be true, at least approximatively.

In this paper we will study the transport coefficients for shear viscosity \( \eta \) and heat conduction \( \lambda \) based on (5). As is well known, this requires (even in the low density limit) the solution of an integral equation with the collisional operator as kernel. It has been shown by Réssinos very clearly that all other methods of calculating transport coefficients also meet the very same integral equation for the linear deviation of the distribution function from (local) equilibrium. We will not check here the principal equivalence of our approach to the others. It clearly reduces to the well-known results for very dilute gases if \( n \approx 0 \). At moderate densities there are density corrections which could be calculated e. g. with perturbation methods. But in order to get a first test for the quality of (5) with respect to the density dependence of \( \eta \) and \( \lambda \), we will not write down the whole generalized theory of integration of (5), but will proceed by simplifying the collisional operator:

\[
\frac{\partial f}{\partial t} \sim \frac{f - f_0}{\tau}.
\]

It is well known for very dilute gases (see e. g. \(^10\)) that some typical features of transport theory may already be got by using such simplified collisional operator.

The accurate integration theory would lead to convolution integrals of \( F(p, q) \) with \( \sigma \), adding some more numerical trouble to the usual calculations of \( \eta \) and \( \lambda \). This cannot be done unless \( F \) is known, either by calculating the real part of the

\(^9\) L. D. Landau, Soviet Phys.—JETP 3, 920 [1957]; 5, 101 [1957].

scattering amplitude or by inverting
\[ B(T) = \left\langle \frac{\beta}{2} F(p, q) \right\rangle_0 = \left\langle \frac{\beta}{2} F(k) \right\rangle_0, \] (7)
which connects the second virial coefficient \( B \) with \( F^8 \). As long as such results are not available one would try to factorize the convolutions, which essentially means to neglect the dependence of \( F \) and \( \sigma \) from its variables. This in turn allows the simplification (6).

I. Approximate Solution of the Boltzmann–Landau Equation

If the collisions have a very strong effect, almost immediately local equilibrium is established. \( f \) is fully determined by local density, mean velocity and temperature:

\[ f_0(r, p, t) = \exp \{ \beta (\alpha + p \cdot u - \varepsilon_p (f_0)) \}, \] (8)
\[ n(r, t) = \int f_0(r, p, t) \, dp, \] (9)
\[ u(r, t) = \left\langle \frac{p}{m/f_0} \right\rangle = \left\langle \frac{3\varepsilon_p (f_0)}{3p} \right\rangle / f_0. \] (10)

Particle, momentum and energy transport in such gases only occurs by convection. We are now interested in small deviations from quasi-equilibrium. 

\[ f = f_0 + f_1 \quad \text{and} \quad f_1 \ll f_0. \]

Formally one takes care of deviations \( \xi \) from local equilibrium \( \xi = 0 \) by a factor \( 1/\xi \) before \( \partial f / \partial t \).

Putting
\[ f = f_0 + \xi f_1 + \xi^2 f_2 + \ldots \]
we get
\[ \frac{\partial f_0}{\partial t} \bigg|_{\xi = 0} = 0 \rightarrow (8). \]
\[ \frac{\partial f_0}{\partial t} + \frac{\partial \varepsilon_p (f_0)}{\partial p} \cdot \frac{\partial f_0}{\partial p} + \frac{3\varepsilon_p (f_0)}{3p} \cdot \frac{\partial f_0}{\partial p} = L(f_1). \] (11)

The linear operator \( L \) is given by
\[ L(f_1) = \int \left[ \sigma (f_0) \left( f_0^{(1)} f_1^{(2)} + f_0^{(2)} f_1^{(1)} \right) \right. \]
\[ - f_0^{(p)} f_1^{(1)}(p) - f_0^{(1)} f_1^{(p)}(p) \]
\[ + \frac{\delta \sigma}{\delta f} \cdot f_1 \left( f_0^{(1)} f_0^{(2)} - f_0^{(p)} f_0^{(p)} \right) \].

Especially the last term contributes to the density dependence of the collisional operator. The others are \( n \)-dependent via (8). In addition to the usual Chapman–Enskog theory, the integral equation (11) for \( f_1 \) has a density corrected integral kernel. Also the inhomogeneity at the l.h.s. contains density modifications. Consequently the solution \( f_1 \) of (11) is

the well-known function for \( n \to 0 \), modified by density corrections. Thus one gets the correct transport coefficients of dilute gases plus terms \( \sim n \).

Resigning possible accuracy we now employ the approximation
\[ L(f_1) \approx - f_1 / \tau. \] (6')

\( \tau \) must be of order of the time of free flight, averaged over \( p \).

\[ \tau^{-1} \int \sigma (p p_1 \to p' p_1'; f) f_0(p_1) \, dp_1 \, dp' \, dp \rightsquigarrow \]
\[ \frac{1}{\tau n} = \langle \int \sigma (p p_1 \to p' p_1'; f) \, dp' \, dp \rangle_{p, p_1'.} \] (12)
\( \tau n \) depends on density via the averaging functions \( f_0 \) and because the total cross-section

\[ G(p, q; f) = \int \sigma (p, q \to p' q'; f) \, dp' \, dq' \] (13)
does it. In binary collision approximation only the energy conservation law depends on \( f \). Triple collisions can be taken care of by the \( f \)-dependence of the partial cross section.

\[ \frac{1}{\tau n} = \langle \frac{1}{\tau n} \rangle_{n=0} \left[ 1 + \left( \frac{dG/dn}{G} \right)_{n=0} n + \ldots \right]. \]

Thus
\[ \tau n = (\tau n)_{n=0} \left[ 1 + \Delta n + \ldots \right] \] (14)
with
\[ \Delta n = - \left( \frac{d}{dn} \ln G(p, q) \right)_{n=0}. \] (15)

We will show in section II that \( \Delta n \sim -B \), thus giving corrections in the same order of magnitude as the corrections in the streaming operator.

With the simplification (6') the solution of the Boltzmann–Landau-equation is

\[ f = f_0 - \tau \left( \frac{3}{3\tau} + \frac{3\varepsilon_p (f_0)}{3p} \cdot \frac{3}{3r} - \frac{3\varepsilon_p (f_0)}{3r} \cdot \frac{3}{3p} \right) f_0. \] (16)

The \( p \)-dependence of \( f(r, p, t) \) is fully determined by (8) and (1), space and time variables enter through \( \alpha, \beta, u \). These functions now shall be chosen such that

\[ n \equiv \int f(r, p, t) \, dp \]
\[ u = \left\langle \frac{p}{m/f_0} \right\rangle = \left\langle \frac{3\varepsilon_p (f_0)}{3p} \right\rangle / f_0. \]

Consequently it should be
\[ 0 = \int f_1(p) \, dp \]
\[ = - \tau \int \left( \frac{3}{3\tau} + \frac{3\varepsilon_p (f_0)}{3p} \cdot \frac{3}{3r} - \frac{3\varepsilon_p (f_0)}{3r} \cdot \frac{3}{3p} \right) f_0(p) \, dp \]
\[ = - \tau \left( \frac{3n}{3\tau} + \text{div} n u \right). \] (19)
This is indeed so, because the continuity equation holds. Similarly one proves
\[ \int \frac{P}{m} f_1 \, dp = 0. \]  
(20)
For: if \( \beta \) is chosen as physical temperature, (20) is just the conservation law for the momentum in local equilibrium, see e. g. 8. [For the last equality sign in (18) see also 8.]

With the solution (16) of the Boltzmann–Landau equation all interesting quantities can be calculated. At first we consider the stress tensor
\[ \sigma_{\mu \nu} = \frac{\partial \tilde{S}_p}{\partial \tilde{p}_\mu} \int f(p) \, dp, \quad \nu \neq \mu. \]
If \( f = f_0 \), there would not be any non-diagonal elements; the pressure is isotropic in quasi-equilibrium. Thus
\[ \sigma_{\mu \nu} = \frac{\partial u_\mu}{\partial x_\nu} + \frac{\partial u_\nu}{\partial x_\mu} \]
thus showing directly the symmetry of the stress tensor. If one furthermore defines the constant of proportionality as shear viscosity \( \eta \), the density corrections of \( \eta \) are included in the result.

\[ \langle G \rangle_{n=0} = \left\langle \left[ \tilde{\sigma} \left( p, p_1; p' p_1' \right) \delta(p + p_1 - p' - p_1') \delta \left( \frac{p^2}{2m} + \ldots \right) \right] \right\rangle_{\text{free Maxw. distrib.}} \]

The connection between the usual total cross section and \( \tilde{\sigma} \) is
\[ \left( \frac{n}{2} \right)^2 \left\langle \tilde{\sigma} \left( |k|, \omega'; K \right) \right\rangle_{\text{free}} = \frac{k}{m} \alpha_{\text{tot}}(k). \]  
(27)
As \( G(p, q; f = 0) \sim \alpha_{\text{tot}}(p - q) \) only depends on the relative momentum \( k \), \( (\tau n)_{n=0} \) is independent from \( u \). The result is the wellknown formula \( l_0 \approx 1/n \alpha_{\text{tot}}. \) The \( K \)-independence of \( G \), the imaginary part of the forward scattering amplitude corresponds to that of \( F \), the real part. Now the next order of density:
\[ \frac{d}{dn} \langle G(p, q) \rangle_{n=0} = \int dp \, dq \, G(p, q; f = 0) \left( \frac{d}{dn} w(p) \, w(q) \right)_{n=0} + \int dp \, dq \, w_0(p) \, w_0(q) \left( \frac{d}{dn} G(p, q; f) \right)_{n=0} \]
with the normalized momentum distribution:
\[ w_0(p) = \frac{\exp \{ - \beta (p - m u - \varepsilon p(f)) \}}{\int \exp \{ - \beta (p - m u - \varepsilon p(f)) \} \, dp}_{n=0} = \frac{\exp \{ - (\beta/2m) (p - m u)^2 \}}{\int \exp \{ - (\beta/2m) (p - m u)^2 \} \, dp}. \]  
(29)
The first term in (28) is easily to be calculated with the methods, shown in the appendix of 8. The result is

\[ -2 \beta \{ G(p, q; f = 0) F(q, \tilde{s}) - G(\tilde{p}, \tilde{q}; f = 0) F(\tilde{s}, \tilde{t}) \} . \tag{30} \]

The dash indicates the mean value with the free Maxwellian distribution (29). As \( G(f = 0) \) and \( F \) only depend on the relative momenta, this result does not depend on \( u \). If we assume \( G \) and/or \( F \) approximately to be independent from \( p - q \), the correlated mean value factorizes and this contribution to \( A_c \) vanishes. It is of order of \( C \) (third virial coefficient), see 8.

The second term in (28) is the average of \( \frac{d}{dn} G(K + k, K - k; f) \), weighed with the free distributions

\[ \exp \left\{ -\beta k^2/m \right\} \frac{\exp \left\{ - (\beta/4 m) (K - 2 m u)^2 \right\}}{\int \exp \left\{ - (\beta/4 m) (K - 2 m u)^2 \right\} dK} \]

Transforming the \( K \)-average around \( u = 0 \) and indicating again such averaging procedure by a dash, we have

\[ \frac{\int \delta(E_k - E_{k'})}{dK} \left\langle \frac{d}{dn} \delta(E_k - E_{k'}) \right\rangle n = 0 \]

where

\[ E_k \equiv n \frac{k^2}{m} + n \int [F(k, q - K/2 - mu) + F(-k, q - K/2 - mu)] w_0(q) dq \]

\[ = \frac{k^2}{m} + n \left( F(k, q - K/2) + F(-k, q - K/2) \right) . \]

Originally the averaging over \( K \) should be performed outside the energy conservation law. But in lowest order in the density only terms linear in \( n F \) are taken care of in the conservation law. This allows the averaging procedure under the \( \delta \)-function. As consequence we see that \( E_k \) only depends from \( |k| \).

\[ \delta(E_k - E_{k'}) = \delta \left( \left( k - k' \right) \frac{dE_k}{dk} \right) \]

\[ = \delta(k - k') \frac{m}{2k} \left( 1 - \frac{m}{k} \frac{d}{dk} F(k, q - K/2) \right) . \]

Now the derivation with respect to \( n \) can be performed.

\[ \frac{d}{dn} G(k, q; f = 0) \frac{m^2}{2} \frac{d}{dk} F(k, q - K/2) \]

\[ = -2 \left( \frac{d}{dk} \left( k \frac{d}{dk} F(k, q - K/2) \right) \right) \]

\[ = 2 \left( F(k, q - K/2) \left\langle \frac{k}{k} \frac{d}{dk} \delta_{v(t)}(k) \right\rangle \right) \tag{31} \]

\[ = 2 \left( F(k, q - K/2) \left\langle \frac{k}{k} \frac{d}{dk} \delta_{v(t)}(k) \right\rangle \right) \]

Term (30) and term (31) together yield \( A_c \) after division by (27). If the cross section only slowly depends from \( k \) and the correlated averages may be factorized, the approximate result is

\[ A_c = -2 \left\langle \frac{m}{k^2} \beta \right\rangle F(k, q - \frac{K}{2}) \quad \tag{32} \]

Again some knowledge of \( F \) would be needed. Without details we only can conclude [with (7)]

\[ A_c \sim -B . \quad \tag{33} \]

This fairly agrees with some experimental results at 20 °C.

Take the experimental law \( \eta = \eta_0(1 + n \delta) \). Then \( \delta \) is determined from 7, p. 2.227/8. The virial coefficient is taken from 11, § 3.6 according to the Lennard–Jones \((6-12)\) potential, which agrees very good with experimental values of \( B(T) \). It is \( B = \theta_0 B^*(T^*) \); the parameters are given, \( B^*(T^*) \) is tabulated in 11, p. 1114.

<table>
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<th>Gas</th>
<th>( \delta )</th>
<th>( \delta )</th>
<th>( \epsilon/\sigma )</th>
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III. Coefficient of Viscosity

Now we'll determine the density dependence of \( \eta \) on account of streaming effects, which add to (33). To do this we use the expression (21) for the non-diagonal elements of the pressure tensor together with the solution (16) of the Boltzmann–Landau equation, accomplished by (17), (18). It is

\[
f_1 = -\tau f_0 \left( \frac{3}{3t} + \frac{3}{3p} \cdot \frac{3}{3r} - \frac{3}{3p} \cdot \frac{3}{3r} \right) \left( \beta \alpha + \beta \cdot \mathbf{u} - \beta \cdot p \cdot \mathbf{f}_0 \right).
\]

(34)

Using

\[
\left( \frac{3}{3p} - u_\mu \right) f_0 = -\pi T \frac{3}{3p} f_0
\]

(35)
in the first part of (21), integration by part and watching \( \mathbf{v} = \phi \mathbf{f}_0 \) we have

\[
\frac{1}{-\tau n \times T} P_{\nu \mu} = \left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \left( \frac{3}{3t} + \frac{3}{3p} \cdot \frac{3}{3r} - \frac{3}{3p} \cdot \frac{3}{3r} \right) \left( \beta \alpha + \beta \cdot \mathbf{u} - \beta \cdot p \cdot \mathbf{f}_0 \right) \right) + \Pi_{\nu \mu}.
\]

\( \Pi_{\nu \mu} \) is the second part in (21) and will now be shown to vanish. Integration by part, using (35), and omitting all terms \( \sim F \) because \( \Pi_{\nu \mu} \) explicitly is proportional to \( F \):

\[
\Pi_{\nu \mu} \sim \left( \langle p_\nu - m u_\nu \rangle \langle p_\mu - m u_\mu \rangle F(p, q) \left[ \frac{3}{3t} + \frac{3}{3p} \cdot \frac{3}{3r} \right] \right) \left[ \beta \alpha + \beta \cdot \mathbf{q} \cdot \mathbf{u} - \beta \cdot \frac{1}{2 m} q^2 \right].
\]

For the same reason \( w_0 \) from (29) has to be used for the averaging procedure. We now transform in momentum space to \( \mathbf{u} = 0 \); that does not influence \( F \) because (2).

\[
\Pi_{\nu \mu} \sim \left( \langle p_\nu - m u_\nu \rangle F(p, q) \left[ \frac{3}{3t} + \frac{3}{3p} \cdot \frac{3}{3r} \right] \right) \left[ \beta \alpha + \beta \cdot \mathbf{q} \cdot \mathbf{u} - \beta \cdot \frac{1}{2 m} q^2 \right].
\]

(36)

Evidently this average in the isotropic free Maxwell distribution vanishes because odd moments are taken as \( \nu = 0 \). In the remaining expression for \( P_{\nu \mu} \) most of the terms vanish by similar arguments.

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3p} \frac{3}{3u} \right) = 0,
\]

evidently,

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} + \frac{3}{3p} + \frac{3}{3r} \right) = 0,
\]

nominally,

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \right) = 0,
\]

evidently,

and

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \right) = 0,
\]

similar to \( \Pi_{\nu \mu} \).

Furthermore

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right) = 0
\]

because \( \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \) vanishes too. Thus

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right) = 0
\]

At last

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right) = -n \beta \mathbf{u} \cdot \left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right) = 0.
\]

The remaining contributions are

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right) = -n \beta \mathbf{u} \cdot \left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right) = 0.
\]

It is shown by similar arguments as above, that the factor before \( \frac{3}{3p} \frac{3}{3u} \) vanishes too. Thus

\[
\frac{1}{-\tau n \times T} P_{\nu \mu} = \beta \sum \frac{3}{3p} \frac{3}{3u} \left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right)
\]

(37)

and

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right) = 0.
\]

(38)

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right) = -n \beta \mathbf{u} \cdot \left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right) = 0.
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\[
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(39)

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\]

(40)

and

\[
\left( \langle p_\nu - m u_\nu \rangle \frac{3}{3p} \frac{3}{3u} \frac{3}{3u} \frac{3}{3u} \right) = 0.
\]

(41)
Here has been used that \( n \int F(p, q) w_0(q) dq \) depends on \( |p| \) only (after transformation to \( \mathbf{u} = 0 \)). We thus found
\[
P_{\mu \nu} = -\eta \left( \frac{\partial u_\mu}{\partial x_\mu} + \frac{\partial u_\nu}{\partial x_\nu} \right) = P_{\mu \nu} \quad (\nu \neq \mu) \quad (37)
\]
with the constant of proportionality
\[
\eta = A \left< \frac{1}{2} \frac{1}{k_B T} + \beta \frac{1}{k_B T} \right> \quad (38)
\]
\[
A_\nu = \beta \left< \frac{1}{2} \frac{1}{k_B T} \right> \quad (39)
\]
The pressure tensor is symmetric as stated before. The viscosity \( \eta \) will be shown as independent of \( \nu, \mu \), therefore being a pure number. In the low density limit \( n A_\nu \to 0 \) the statement (23) is proved. We only need to calculate now the first virial correction \( A_\nu \) of the viscosity, which arises from the modification of the streaming operator in the Boltzmann–Landau-equation. The free Maxwellian average (39) can be reduced to the virial coefficient and its derivatives. Introducing relative and total momentum and taking care of (2) gives
\[
A_\nu = \beta \left< \left( K_\nu + k_\nu \right) \left( \frac{1}{2} K_\mu + k_\mu \right) \frac{32}{3} \frac{1}{k_B T} \frac{1}{k_B T} F(|k|) \right>_0
\]
\[
= \beta \frac{3}{4} \left< k_\nu k_\mu \frac{32}{3} \frac{1}{k_B T} \frac{1}{k_B T} F(|k|) \right>_0.
\]
Now integrate by parts:
\[
A_\nu = \beta \frac{3}{4} \left< F - \frac{2}{m} \frac{1}{3} k^2 F \cdot 2 + \left( \frac{2}{m} \frac{1}{3} k^2 \right) k_\nu k_\mu F \right>_0
\]
One easily proves the formulae
\[
\left< \left( k_\nu \right)^2 \left( k_\mu \right)^2 \right>_0 = \frac{1}{15} \quad (\nu \neq \mu), \quad (40)
\]
\[
\left< \frac{\beta}{2} F \frac{k^2}{m} \right>_0 = \frac{B}{2} \left( B + \frac{3}{5} T B' \right), \quad (41)
\]
\[
\left< \frac{\beta}{2} F \left( k^2 \frac{k^2}{m} \right)^2 \right>_0 = \frac{35}{4} \frac{B}{B + 7 T B' + T^2 B''}, \quad (42)
\]
following from (7). This leads to the result
\[
A_\nu = \frac{2}{15} \left( 2 T B' + T^2 B'' \right) = \frac{2}{15} \frac{d}{dT} \left( T^2 B' \right) \quad (43)
\]
As \( A_\nu \) contains derivatives of \( B \), it tests higher moments of \( F(k) \). It therefore is a sensitive test of the intermolecular forces. For the (too simple) van der Waals model for \( B \) we get
\[
A_\nu = \frac{1}{15} \left( \text{van der Waals} \right) = 0. \quad (44)
\]
E. g. neither a weak interacting \( B = a/\sqrt{T} \) nor a classical hard core gas \( B = \text{const} \) give a streaming correction to the virial coefficient of the viscosity. But with the empirical \( B(T) \), being represented
excellently by the Lennard–Jones-model (ref. 11, § 3.6) we get the following results.

| Gas  | \( \frac{A_\nu}{B} \) | \| \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \| | \ |
results not until he fitted the hard sphere parameter $\sigma$ at the empirical plot; but if one fits in (44), (45), the absolute value of the first virial correction is right per constructionem. All that could be checked is the dependence from temperature. But there are no experimental results available.

To sum up our results: The transport theory of Chapman and Enskog applied to the Boltzmann–Landau-equation in binary collision approximation seems to deliver a method for calculating the density dependence of the transport coefficients, here especially of the shear viscosity. The magnitude of the virial correction of $\eta$ can be explained. The method seems to be a natural extension of the Enskog theory for dense gases at moderate densities, but without its severe disadvantages: (5) holds for rather arbitrary intermolecular forces and not only for hard spheres; no ad hoc modification is needed to correct the results; no fitting is needed. But in contrast, the disadvantage of the theory presented here is—besides the large numerical efforts of a more exact solution, but which is met in other methods— that one needs some more knowledge about the real part of the forward scattering amplitude, $F$, and $\sigma$, which possibly goes beyond $B$, $B'$,... Thus a predominating task is to get that knowledge first!

IV. Coefficient of Thermal Conductivity

Now the heat flow vector $\mathbf{Q}$ shall be determined from (22). If we consider a physical situation, in which

$$\mathbf{u}(r, t) \equiv 0,$$

no energy transport by convection occurs: $\mathbf{Q}_0 = 0$. The energy transport by conduction is $\sim f_1 \sim \tau$:

$$\mathbf{Q} = \int \varepsilon_p (f_0) \frac{\partial \varepsilon_p (f_0)}{\partial \mathbf{p}} f_1 (p) \, d\mathbf{p} + \int \varepsilon_p (f_0) f_0 (p) \frac{\partial F (p, q) f_1 (q)}{\partial \mathbf{p}} \, d\mathbf{q} + \int F (p, q) f_1 (q) \frac{\partial \varepsilon_p (f_0)}{\partial \mathbf{p}} f_0 (p) \, d\mathbf{p}$$

$$= \int \varepsilon_p (f_0) \frac{\partial \varepsilon_p (f_0)}{\partial \mathbf{p}} f_1 (p) \, d\mathbf{p} - \int F (p, q) \varepsilon_p (f_0) \frac{\partial f_0 (p)}{\partial \mathbf{p}} f_1 (q) \, d\mathbf{p} \, d\mathbf{q}.$$

The weight function for averaging is (8) with $u = 0$. Thus $\varepsilon_p$ as well as the $p$- (or $q$-) average of $F (p, q)$ only depend on $|p|$ (or $|q|$). Consequently some terms vanish by symmetry arguments, what can be checked easily:

$$\left\langle \left( \varepsilon_p \frac{\partial \varepsilon_p}{\partial \mathbf{p}} + \beta n F (p, q) \varepsilon_q \frac{\partial \varepsilon_q}{\partial \mathbf{q}} \right) \frac{\partial}{\partial \mathbf{t}} \left( \beta \alpha - \beta \varepsilon_p \right) \right\rangle = 0.$$

Because

$$\left( \frac{\partial \varepsilon_p}{\partial \mathbf{p}} - \frac{\partial \varepsilon_p}{\partial \mathbf{r}} - \frac{\partial \varepsilon_p}{\partial \mathbf{p}} \right) \left( \beta \alpha - \beta \varepsilon_p \right) = \frac{\partial \varepsilon_p}{\partial \mathbf{r}} \left( \beta \alpha - \beta \varepsilon_p \right) = \frac{\partial \varepsilon_p}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{r}} \beta \alpha - \frac{\partial \varepsilon_p}{\partial \mathbf{r}} \frac{\partial}{\partial \mathbf{r}} \beta \varepsilon_p,$$

we have (again using symmetry arguments)

$$\frac{1}{\tau n} \mathbf{Q} = \left\langle \left( \varepsilon_p \frac{\partial \varepsilon_p}{\partial \mathbf{p}} + \beta n F (p, q) \varepsilon_q \frac{\partial \varepsilon_q}{\partial \mathbf{q}} \right) \frac{\partial}{\partial \mathbf{r}} \left( \beta \alpha - \beta \varepsilon_p \right) \right\rangle = 0.$$
This proves (24), the zero order thermal conductivity in the approximation (6). We are now interested in the virial corrections \( \sim (nF) \): \[
\lambda = \frac{5}{2} \frac{T n \mathbf{x} \cdot \mathbf{x}}{m} (1 + n A_i). \tag{51}
\]

Then it is \[
A_i^\lambda = - \frac{2}{15} m \beta^2 \left[ \frac{d}{dn} \left( \left( \epsilon_p \frac{\partial}{\partial \mathbf{p}} + \beta n F(p, q) \epsilon_q \frac{\partial}{\partial \mathbf{q}} \right) \cdot \frac{\partial}{\partial \mathbf{q}} \left( \frac{1}{2} + n B - n T B' - \beta \epsilon_p \right) \right) \right]_{n=0},
\]
\[
+ \left( F(p, q) \cdot \left( \frac{1}{2} - \beta \frac{p^2}{2 m} \right) + 2 \frac{\partial}{\partial \mathbf{p}} \frac{\partial}{\partial \mathbf{q}} F(p, q) \right)
\] \[
+ \left( \frac{\partial}{\partial \mathbf{p}} \frac{\partial}{\partial \mathbf{q}} \left( \frac{1}{2} - \beta \frac{p^2}{2 m} \right) \right) \right]_{n=0},
\]
\[
\right) \right].
\]

In the last term one has to watch that besides the \( n \)-dependence of \( \epsilon_p \) also the weight functions depend on the density.

\[
A_i^\lambda = - (B - T B') = \frac{2}{15} \beta^2 \left[ \beta \left( \frac{F(p, q) \cdot \left( \frac{1}{2} - \beta \frac{p^2}{2 m} \right)}{2 m} \right) \right.
\]
\[
+ \left( F(p, q) \cdot \left( \frac{1}{2} - \beta \frac{p^2}{2 m} \right) + 2 \frac{\partial}{\partial \mathbf{p}} \frac{\partial}{\partial \mathbf{q}} F(p, q) \right)
\] \[
+ \left( \frac{\partial}{\partial \mathbf{p}} \frac{\partial}{\partial \mathbf{q}} \left( \frac{1}{2} - \beta \frac{p^2}{2 m} \right) \right) \right]_{n=0},
\]
\[
\right). \tag{52}
\]

Using relative and total momentum, we have \( \beta^2 K^2 / m = e_K, \beta^2 K^2 / m = e_k, \beta^2 P \cdot q / m = e_K - e_k, \beta^2 K \cdot k / m = 4 / 3 e_K e_k. \)

The last equality holds in the average over \( K \) or \( k \) resp. Odd powers of \( K \cdot k \) vanish in the average.

Using \( \langle e_K \rangle = 3 / 2, \langle e_K^2 \rangle = 15 / 4, \langle e_k^2 \rangle = 105 / 8 \)

one finds after some straightforward calculations

\[
-15 (A_i^\lambda - B - T B') = - \frac{45}{4} F_0 + \frac{65}{2} F_1 + F_2 + 2 F_3. \tag{53}
\]

Here \( F_j = \left( \frac{1}{2} \beta F(k) (\beta k^2 / m)^j \right) \)

has been given in (7), (41), (42) for \( j = 0, 1, 2. \)

As \( Q \) is given by a higher moment of the velocity \( \frac{\partial}{\partial \mathbf{p}} \) as \( P_m \), a higher moment of \( F(k) \), i.e. \( B'' \) is needed for \( A_i^\lambda. \)

One easily proves

\[
F_3 = \frac{9}{2} F_2 + \frac{3}{2} T \frac{\partial}{\partial T} F_2. \tag{54}
\]

Rearrangement in (52) thus gives the final result

\[
A_i^\lambda = - \frac{1}{15} (125 B + 105 T B' + 26 T^2 B'' + 2 T^3 B''''). \tag{55}
\]

Using the LENNARD-JONES-virial coefficient as tabulated in (11) we find

\[
\begin{array}{c|c|c|c|c|c}
\text{Gas} & A & \text{Ne} & \text{N}_2 & \text{O}_2 \\
\hline
A_i^\lambda / B & 3.4 & -10 & 25 & 3.9 \\
\end{array}
\]

As \( B<0 \) at room temperature (except Ne), we have \( A_i^\lambda < 0. \) Thus again the density dependence of the streaming operator tends to diminish the collisional effect of \( d\lambda / dn. \) Experimental values of \( A_i^\lambda / \lambda \) at room temperature may be estimated from a few tables or graphs. They are some \( 6-7 \%/\text{atm} \) in contrast to \( 0.6-0.8 \%/\text{atm} \) for \( A_i^\lambda / \eta. \)

Thus \( \eta \approx 10 \) times \( \eta \) experimentally. Our simplification of \( \frac{\partial}{\partial t} \) gives the same \( A_i^\lambda \) for viscosity as well as thermal conductivity. But the streaming part shows this factor (more precise: \( \approx 25 \)) in the order of magnitude of \( A_i^\lambda / \eta. \)

As \( A_i^\lambda \) is the Boltzmann-Landau-equation (5) seems to be able to describe the measured density dependence of the transport coefficients. To get results which are comparable to (at the moment only scarcely available) accurate measured data, one has to integrate more or less numerical the solution \( f_1 \) of equ. (11).