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General expression for the matrix of saturated field effects

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A general expression for the change in transport coefficients of a dilute gas in the limit of an infinite external magnetic or electric field is derived without using a perturbation expansion of the collision operator. Previously derived properties of the saturated field effects are subsequently generalized and some implications are discussed.

In a recent review of the kinetic theory of field effects on transport phenomena in dilute polyatomic gases, expressions for the saturated field effects have been presented.[1] These expressions were a convenient tool for discussing a number of properties of field effects. They were, however, derived only up to second order in a perturbation expansion of the collision operator $\mathscr{R}$. In this Rapid Communication it will be shown that similar expressions can be derived in general within the framework of the kinetic theory of dilute gases.

Consider transport coefficients $\overleftrightarrow{L}^{\alpha\beta}$ defined by

$$\vec{J}^{\alpha} = -\sum_{\beta} \overleftrightarrow{L}^{\alpha\beta} \cdot \vec{X}^{\beta} \ , \tag{1}$$

where $\vec{X}^{\beta}$ is a macroscopic thermodynamic force and $\vec{J}^{\alpha}$ a thermodynamic flux. From the Boltzmann equation, using a first-order Enskog approximation, one can show that the coefficients $\overleftrightarrow{L}^{\alpha\beta}$ in a magnetic or electric field $\vec{B}$ or $\vec{E}$, respectively, can be written as

$$\overleftrightarrow{L}^{\alpha\beta}(\vec{B};\vec{E}) = k \langle \vec{\Psi}^{\alpha} | (\mathscr{R} + i\mathscr{L})^{-1} \vec{\Psi}^{\beta} \rangle^{*} \ , \tag{2}$$

where the $\vec{\Psi}^{\alpha}$ represent microscopic fluxes of which the irreversible macroscopic fluxes $\vec{J}^{\alpha}$ are averages, and the operator $\mathscr{L}$ represents the field-dependent part of the Liouville operator which is proportional to B or E, the strength of the field; k is Boltzmann's constant. This expression is restricted to dilute gases in the linear regime. For details of the notation and the theoretical developments leading to Eq. (2) we refer to, e.g., Ref. 1.

All velocity-dependent and angular-momentum-dependent functions are elements of a Hilbert space with inner product as in Eq. (2). For the purpose of the derivation, the basis of the Hilbert space is chosen in such a way that all basis functions are eigenfunctions of $\mathscr{L}$. The space can then be divided into two subspaces, H_0, spanned by all eigenfunctions with zero eigenvalue, and H_1, spanned by all other eigenfunctions. Note that H_0 contains not only all functions isotropic in the angular momentum, but also anisotropic-in-$\vec{J}$ functions with eigenvalue zero.

The collision operator $\mathscr{R}$ is now split into a diagonal part $\mathscr{R}_{\rm d}$, which couples only functions within each of the two subspaces, and a nondiagonal part, $\mathscr{R}_{\rm nd}$, which accounts for cross couplings:

$$\mathscr{R} = \mathscr{R}_{\rm d} + \mathscr{R}_{\rm nd} \ . \tag{3}$$

Whereas the notation is the same as in Ref. 1, the subdivision of Hilbert space and the splitting of $\mathscr{R}$ are not. In Ref. 1 H_0 contains only the functions which are isotropic in the angular momentum, while the anisotropic functions with zero eigenvalue belong to H_1. With this usual subdivision the elements of $\mathscr{R}_{\rm nd}$, reflecting the coupling between isotropic and anisotropic-in-$\vec{J}$ functions, can be treated as small perturbations and the operator $(\mathscr{R}+i\mathscr{L})^{-1}$ expanded in terms of $\mathscr{R}_{\rm nd}$.[2–5] One would like, however, to avoid such an expression and subsequent approximations. For this purpose the alternative subdivision and corresponding splitting of $\mathscr{R}$ introduced above is more appropriate.

If we then use the operator identity valid for arbitrary operators A and B,

$$(A+B)^{-1} = A^{-1} - A^{-1}B(A+B)^{-1} = A^{-1} - (A+B)^{-1}BA^{-1} = A^{-1} - A^{-1}BA^{-1} + A^{-1}B(A+B)^{-1}BA^{-1} \ , \tag{4}$$

with

$$A = \mathscr{R}_{\rm d} + i\mathscr{L}, \quad B = R_{\rm nd}, \quad A+B = \mathscr{R} + i\mathscr{L} \ , \tag{5}$$

we can rewrite the right-hand side of Eq. (2) in an alternative form,

$$\begin{aligned}\langle \vec{\Psi}^{\alpha} | (\mathscr{R}+i\mathscr{L})^{-1} \vec{\Psi}^{\beta} \rangle^{*} = {} & \langle \vec{\Psi}^{\alpha} | (\mathscr{R}_{\rm d}+i\mathscr{L})^{-1} \vec{\Psi}^{\beta} \rangle^{*} - \langle \vec{\Psi}^{\alpha} | (\mathscr{R}_{\rm d}+i\mathscr{L})^{-1} \mathscr{R}_{\rm nd} (\mathscr{R}_{\rm d}+i\mathscr{L})^{-1} \vec{\Psi}^{\beta} \rangle^{*} \\ & + \langle \vec{\Psi}^{\alpha} | (\mathscr{R}_{\rm d}+i\mathscr{L})^{-1} \mathscr{R}_{\rm nd} (\mathscr{R}+i\mathscr{L})^{-1} \mathscr{R}_{\rm nd} (\mathscr{R}_{\rm d}+i\mathscr{L})^{-1} \vec{\Psi}^{\beta} \rangle^{*} \ .\end{aligned} \tag{6}$$

The second term, which is odd in $\mathscr{R}_{\rm nd}$, vanishes because it represents the inner product of two functions which are orthogonal to each other. Indeed, the microscopic fluxes $\vec{\Psi}^{\alpha}$, which are isotropic in the angular momentum, are elements of H_0, while functions $(\mathscr{R}_{\rm d}+i\mathscr{L})^{-1}\mathscr{R}_{\rm nd}(\mathscr{R}_{\rm d}+i\mathscr{L})^{-1}\vec{\Psi}^{\alpha}$ are elements of H_1. Hence

$$\langle \vec{\Psi}^{\alpha} | (\mathscr{R}+i\mathscr{L})^{-1} \vec{\Psi}^{\beta} \rangle^{*} = \langle \vec{\Psi}^{\alpha} | (\mathscr{R}_{\rm d}+i\mathscr{L})^{-1} \vec{\Psi}^{\beta} \rangle^{*} + \langle \vec{\Psi}^{\alpha} | (\mathscr{R}_{\rm d}+i\mathscr{L})^{-1} \mathscr{R}_{\rm nd} (\mathscr{R}+i\mathscr{L})^{-1} \mathscr{R}_{\rm nd} (\mathscr{R}_{\rm d}+i\mathscr{L})^{-1} \vec{\Psi}^{\beta} \rangle^{*} \ . \tag{7}$$

Since, moreover,

$$(\mathscr{R}_d + i\mathscr{L})^{-1}\vec{\Psi}^\alpha = R_d^{-1}\vec{\Psi}^\alpha - (\mathscr{R}_d + i\mathscr{L})^{-1} i\mathscr{L}\mathscr{R}_d^{-1}\vec{\Psi}^\alpha = \mathscr{R}_d^{-1}\vec{\Psi}^\alpha \ , \tag{8}$$

where we have used the fact that functions $\mathscr{R}_d^{-1}\vec{\Psi}^\alpha$ are elements of H_0, so that $\mathscr{L}\mathscr{R}_d^{-1}\vec{\Psi}^\alpha = 0$, we obtain the equality

$$\langle \vec{\Psi}^\alpha | (\mathscr{R} + i\mathscr{L})^{-1}\vec{\Psi}^\alpha \rangle^* = \langle \vec{\Psi}^\alpha | \mathscr{R}_d^{-1}\vec{\Psi}^\beta \rangle^* + \langle R\mathscr{R}_{nd}\mathscr{R}_d^{-1}\vec{\Psi}^\alpha | (\mathscr{R} + i\mathscr{L})^{-1}\mathscr{R}_{nd}\mathscr{R}_d^{-1}\vec{\Psi}^\beta \rangle^* \ . \tag{9}$$

Here we have also used the fact that $\mathscr{R}^\dagger = R\mathscr{R}R$ with $\mathscr{R}^\dagger$ the superoperator adjoint of $\mathscr{R}$ and R the angular-momentum reversal operator: $Rf(\vec{J}) = f(-\vec{J})$, $R\vec{\Psi}^\alpha = \vec{\Psi}^\alpha$. Introducing angular-momentum polarizations $\vec{\chi}^\alpha$,

$$\vec{\chi}^\alpha = \mathscr{R}_{nd}\mathscr{R}_d^{-1}\vec{\Psi}^\alpha \ , \tag{10}$$

we finally have

$$\overleftrightarrow{L}^{\alpha\beta}(\vec{B};\vec{E}) = k\langle \vec{\Psi}^\alpha | \mathscr{R}_d^{-1}\vec{\Psi}^\beta \rangle^* + k\langle R\vec{\chi}^\alpha | (\mathscr{R} + i\mathscr{L})^{-1}\vec{\chi}^\beta \rangle^* \ . \tag{11}$$

The zero-field coefficient may now be written as

$$\overleftrightarrow{L}^{\alpha\beta}(0) = k\langle \vec{\Psi}^\alpha | \mathscr{R}_d^{-1}\vec{\Psi}^\beta \rangle^* + k\langle R\vec{\chi}^\alpha | \mathscr{R}^{-1}\vec{\chi}^\beta \rangle^* \ , \tag{12}$$

and the change in transport coefficient due to external fields as

$$\Delta\overleftrightarrow{L}^{\alpha\beta}(\vec{B};\vec{E}) = k\langle R\vec{\chi}^\alpha | (\mathscr{R} + i\mathscr{L})^{-1}\vec{\chi}^\beta \rangle^* - k\langle R\vec{\chi}^\alpha | \mathscr{R}^{-1}\vec{\chi}^\beta \rangle^* \ . \tag{13}$$

Equation (13) gives an exact alternative expression for the change in transport coefficients in external fields, which may be compared to the one which follows directly (without further transformations) from Eq. (2):

$$\Delta\overleftrightarrow{L}^{\alpha\beta}(\vec{B};\vec{E}) = k\langle \vec{\Psi}^\alpha | (\mathscr{R} + i\mathscr{L})^{-1}\vec{\Psi}^\beta \rangle^* - k\langle \vec{\Psi}^\alpha | \mathscr{R}^{-1}\vec{\Psi}^\beta \rangle^* \ . \tag{14}$$

The only difference between the transformed expression (13) and the original expression (14) is that the first contains the polarizations $\vec{\chi}^\alpha \in H_1$, instead of the microscopic fluxes $\vec{\Psi}^\alpha \in H_0$.[6]

It is precisely this feature which will enable us to derive a simple expression for the matrix of saturated field effects, i.e., for the infinite field limit

$$\Delta\overleftrightarrow{L}^{\alpha\beta}(\infty) = \lim_{B;E\to\infty} \langle R\vec{\chi}^\alpha | (\mathscr{R} + i\mathscr{L})^{-1}\vec{\chi}^\beta \rangle^* - k\langle R\vec{\chi}^\alpha | \mathscr{R}^{-1}\vec{\chi}^\beta \rangle^* \ . \tag{15}$$

In order to evaluate this limit we divide the collision operator in the following way,

$$\mathscr{R} = \mathscr{R}_s + \mathscr{R}_{ns} \ , \tag{16}$$

where $\mathscr{R}_s$ is the secular part of $\mathscr{R}$ which commutes with $\mathscr{L}$,

$$\mathscr{R}_s\mathscr{L} = \mathscr{L}\mathscr{R}_s \ , \tag{17}$$

while $\mathscr{R}_{ns}$ is the nonsecular part and does not commute with $\mathscr{L}$.[7] We then have

$$\begin{aligned}\lim_{B;E\to\infty} \langle R\vec{\chi}^\alpha | (\mathscr{R} + i\mathscr{L})^{-1}\vec{\chi}^\beta \rangle &= \lim_{B;E\to\infty} \langle R\vec{\chi}^\alpha | [1 + (\mathscr{R}_s + i\mathscr{L})^{-1}\mathscr{R}_{ns}]^{-1}(\mathscr{R}_s + i\mathscr{L})^{-1}\vec{\chi}^\beta \rangle \\ &= \lim_{B;E\to\infty} \langle R[1 + (\mathscr{R}_s + i\mathscr{L})^{-1}\mathscr{R}_{ns}]^{-1}\vec{\chi}^\alpha | (\mathscr{R}_s + i\mathscr{L})^{-1}\vec{\chi}^\beta \rangle \ .\end{aligned} \tag{18}$$

Since $\vec{\chi}^\alpha$ lies in H_1, the function $(\mathscr{R}_s + i\mathscr{L})^{-1}\vec{\chi}^\alpha$ is a state vector in H_1 of which all components vanish in the limit $B;E \to \infty$. Consequently,

$$\lim_{B;E\to\infty} \langle R[1 + (\mathscr{R}_s + i\mathscr{L})^{-1}\mathscr{R}_{ns}]^{-1}\vec{\chi}^\alpha | (\mathscr{R}_s + i\mathscr{L})^{-1}\vec{\chi}^\beta \rangle = 0 \ , \tag{19}$$

and the matrix of saturated field effects becomes

$$\Delta\overleftrightarrow{L}^{\alpha\beta}(\infty) = -k\langle R\vec{\chi}^\alpha | \mathscr{R}^{-1}\vec{\chi}^\beta \rangle^* \ . \tag{20}$$

Apart from its general validity this expression has several advantages. First of all the positive semidefinitiveness of $\mathscr{R}$ can now directly be applied. Secondly, the analogy with the expression for a transport coefficient in the field-free case is evident. It is, in particular, the positive semidefinite character of $\mathscr{R}$ which leads directly to an inequality for the saturation value of the field effects. Indeed, as a direct consequence of this property of $\mathscr{R}$, one has not only that the matrix of transport coefficients must be positive definite [cf. Eq. (2)],

$$\sum_{\alpha,\beta} \vec{\eta}_\alpha \cdot \overleftrightarrow{L}^{\alpha\beta} \cdot \vec{\eta}_\beta \geq 0 \ , \tag{21}$$

but also that the matrix of saturated field effects [cf. Eq. (20)] must be either negative semidefinite for $\vec{\chi}$'s which are all even in the angular momentum, or positive definite for $\vec{\chi}$'s which are all odd,

$$\sum_{\alpha,\beta} \vec{\eta}_\alpha \cdot \Delta\overleftrightarrow{L}^{\alpha\beta}(\infty) \cdot \vec{\eta}_\beta \begin{cases} \leq 0, & \text{if } R\vec{\chi}^\alpha = \vec{\chi}^\alpha \ , \\ \geq 0, & \text{if } R\vec{\chi}^\alpha = -\vec{\chi}^\alpha \ . \end{cases} \tag{22}$$

In the equalities (21) and (22) the η's are arbitrary real vectors. It should be noted that while the inequality (21) can also be derived from the macroscopic argument that entropy production must be positive definite, there seems to be no macroscopic argument which can be invoked to derive the inequalities (22).

In analogy to the usual inequalities for transport coefficients,[8] it follows from (22) for the change in transport coefficients, that

$$\Delta L^{\alpha\alpha}_{\mu\mu}(\infty) \begin{cases} \leq 0, & \text{if } R\vec{\chi}^\alpha = \vec{\chi}^\alpha \ , \\ \geq 0, & \text{if } R\chi^\alpha = -\chi^\alpha \ , \end{cases} \tag{23}$$

and furthermore that, for both even and odd $\vec{X}$'s,

$$[\Delta L^{\alpha\beta}_{\mu\mu}(\infty)]^2 \leq \Delta L^{\alpha\alpha}_{\mu\mu}(\infty)\Delta L^{\beta\beta}_{\mu\mu}(\infty) \quad , \tag{24}$$

where $\Delta L^{\alpha\alpha}_{\mu\mu}$ denotes a diagonal element of the (diagonal) tensor $\Delta\overleftrightarrow{L}^{\alpha\alpha}$, etc. This useful inequality was previously established[1] on the basis of the above-mentioned perturbation expansion to second order and use of the spherical approximation.[7] As we have shown here, this inequality is an exact result if Boltzmann kinetic theory applies and does not depend on the relative smallness of $\mathscr{R}_{\rm nd}$.[9]

A final remark is in order. It seems plausible that the validity of the result (24) is not restricted to the dilute gas regime. One might therefore expect that it could also be established on the basis of a more general theory.

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[4]G. E. J. Eggermont, H. Vestner, and H. F. P. Knaap, Physica A 82, 23 (1976).

[5]W. E. Köhler, H. F. P. Knaap, G. E. J. Eggermont, and G. W. 't Hooft, Z. Naturforsch. 33A, 761 (1978).

[6]Note that the subdivision of Hilbert space into H_0 and H_1 and the corresponding splitting of $\mathscr{R}$ into $\mathscr{R}_{\rm nd}$ and $\mathscr{R}_{\rm d}$ adopted here, and therefore also the relation (10) defining the polarizations $\vec{X}^\alpha$ in terms of the microscopic fluxes $\vec{\Psi}^\alpha$, are invariant for rotations around the field axis, but not for arbitrary rotations. One finds the correct transformation properties of the matrix of saturated field effects, as given by Eq. (20), as a consequence.

[7]Usually the matrix elements of $\mathscr{R}_{\rm ns}$ are neglected when calculating the field dependence of transport coefficients. This is called the *spherical approximation;* see, e.g., W. E. Köhler, Z. Naturforsch. 29A, 1705 (1974). The present results, however, do not depend on this approximation.

[8]S. R. de Groot and P. Mazur, *Nonequilibrium Thermodynamics* (North-Holland, Amsterdam, 1962; Dover, New York, in press).

[9]For both Eqs. (13) and (20) the main difference with previously reported first-order approximations lies in the operators: The exact expressions derived here contain the full collision operator $\mathscr{R}$ and not, as the approximate ones of Ref. 1, the "diagonal" operator $\mathscr{R}_{\rm d}$. The old expressions can be obtained from the new ones by splitting R in the usual way, expanding $\mathscr{R}^{-1}$ in powers of $\mathscr{R}_{\rm nd}$, and retaining only the first term $\mathscr{R}_{\rm d}^{-1}$.