

Asymptotic Magnetic Behavior of Gas Transport Properties

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The nonvanishing elements of the viscosity and thermal conductivity tensors of polyatomic gases fall into two classes: those that change sign with a rotation about the magnetic field line and those that do not. It is shown that the boundedness of the linearized Waldmann–Snider collision operator and its properties under symmetry transformations imply that for linear Zeeman splitting the first class vanishes at zero and infinite field as $|B|$ and $|B|^{-1}$ and that the second class approaches its asymptotes as $|B|^{-2}$ and $|B|^{-2}$.

KEY WORDS: Kinetic theory; transport properties; Senftleben–Beenakker effect; asymptotic properties.

1. INTRODUCTION

In the last decade a very promising line of research has been concerned with the variation of transport coefficients with magnetic field strength—the Senftleben–Beenakker effect.⁽¹⁾ The interest stems from the fact that in contrast to the gross viscosity and thermal conductivity coefficients, which depend primarily on the spherical part of the molecular interaction, the magnetic shifts occur only if colliding molecules can reorient, and this in turn requires molecules interactions with some degree of anisotropy. On the whole, the shape of the magnetic dependence is predicted rather well with a kinetic theory^(2,3) employing simple trial functions,^(4–6) although some

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discrepancies are now apparent.^(7,8) However, other than a classical analog,⁽⁹⁾ the general theory has not yet been used to calculate individual cross sections, although it has had impressive success in correlating Senftleben–Beenakker cross sections with other experiments.^(7,10,11)

The assumption of a simple trial function for the molecular distribution function is equivalent to postulating a definite class of molecular models. In the case of the present theories^(4,6) this model can be interpreted as a weak-coupling model in which only one type of angular momentum anisotropy is coupled to the orientation-independent part of the velocity–angular momentum distribution. This assumption leads directly to the well-known double frequency dependence found in most experiments.^(1,10)

The degree of dependence of these phenomena on the particular molecular or kinetic model has not been established. In this paper we show that the boundedness of the original Waldmann–Snider linearized collision operator^(2,3) in a particular metric and its behavior under symmetry transformations partially determine the asymptotic behavior of the usual transport coefficients as functions of magnetic field. The next section summarizes the kinetic theory required, identifies the tensor elements comprising the transport coefficients as certain inner products of vectors in a Hilbert space, and introduces two ways of partitioning the space that leave the elements of interest unchanged. The third section then proves the boundedness of the collision operator and determines the asymptotic behavior using the theory of perturbations of linear operators.⁽¹²⁾ The physical picture of the Senftleben–Beenakker effect is that a magnetic field induces a precession of the angular momentum about the field direction and at high fields tends to average out the angular momentum components perpendicular to the field. The boundedness property merely implies that the system cannot relax infinitely quickly and at some point cannot counteract the averaging due to the precession. The symmetry properties divide the elements of the transport coefficient tensors into three types: those for which the magnetic shifts vanish identically; those which are even functions of the magnetic field strength; and those which are odd and vanish at zero and infinite field strength. This seems to be as much as can be said without further specifying the molecular model.

The possibility of putting rigorous bounds on transport property calculations is also considered briefly and it is concluded that it is not feasible for simple approximations.

2. KINETIC THEORY PRELIMINARIES

In certain cases^(2,3,13) the full quantum density matrix may be replaced by a semiclassical density matrix f . We shall adopt Snider's formulation⁽³⁾ where f is a Wigner function, a classical function of the translational degrees

of freedom but still a quantum density matrix in the internal degrees of freedom. Here we shall consider only rotation. If the mean flight time is much less than the inverse frequencies corresponding to the energy splittings of the principal quantum numbers (j for a diatomic molecule or j, k for a symmetric top), the phase of the off-diagonal elements will oscillate many times between collisions. We may then justify the further approximation that the density matrix is diagonal in the principal quantum numbers.^(2,13) This approximation allows an H -theorem,⁽¹⁴⁾ i.e., irreversibility.

For each dynamic variable an operator A is now defined that is classical in the translational degrees of freedom and quantum in the internal ones.⁽¹⁵⁾ The local average of A is then determined by

$$\begin{aligned}\bar{A} &= \text{tr} \int d^3\mathbf{p} f(\mathbf{r}, \mathbf{v}, t) A \\ &= \sum_{jkm} \int d^3\mathbf{p} \langle \psi_{jkm} | f A | \psi_{jkm} \rangle\end{aligned}\quad (1)$$

where tr is the trace operation taken over a complete set of wave functions ψ_{jkm} that span the wave function space for the internal degrees of freedom. Then $\langle \cdots \rangle$ is the inner product of this wave function space. The distribution function may now be separated into two parts: a Maxwell distribution $f^{(0)}$ normalized to yield the correct local velocity \mathbf{v}_0 , and number and energy density, and a perturbation ϕ :

$$f = f^{(0)}(I + \phi) \quad (2)$$

$f^{(0)}$ is self-adjoint in the wave function space, i.e., $f^{(0)\dagger} = f^{(0)}$, where A^\dagger is the adjoint of A . Since the distribution function or density matrix should be self-adjoint,

$$f^{(0)}\phi = \phi^\dagger f^{(0)} \quad (3)$$

This allows averages of operators vanishing at equilibrium to be written as⁽¹⁶⁾

$$\bar{A} = \text{tr} \int d^3\mathbf{p} \phi^\dagger f^{(0)} A \equiv (\phi, A) = (A, \phi)^* \quad (4)$$

where \mathbf{p} is the momentum. The inner product (\cdots, \cdots) may be used to define a vector or Hilbert space of operators in which are imbedded the permissible distribution functions and operators corresponding to dynamic variables with finite thermodynamic averages.⁽¹⁶⁾ This space of operators, spanned, say, by the set $\{u_i\}_{i=1}^\infty$, is equivalent to the Schmidt class $\sigma(c)$ ⁽¹⁷⁾ the set of completely continuous operators $\{w_i\}_{i=1}^\infty$, if the correspondence $w = (f^{(0)})^{1/2}u$ is made.⁽¹⁶⁾ Let us call this space \mathcal{H} . By an extension of the Chapman–Enskog

method, it is found that through terms linear in gradients of density, temperature, and velocity, ϕ in the field-free case is determined by

$$\mathcal{L}\phi = -g \quad (5)$$

\mathcal{L} is a "superoperator"³ which is dissipative,⁽¹⁶⁾ i.e., $\text{Re}(u, \mathcal{L}u) \leq 0, \forall u$, and whose effect on ϕ is

$$\begin{aligned} \mathcal{L}\phi = & (2\pi)^4 \hbar^2 \text{tr}_1 \int d^3\mathbf{p}_1 f_1^{(0)} \left\{ \int d^3\mathbf{p}' \int d^3\mathbf{p}'_1 t_{v_r}^{v_r'}(\phi' + \phi_1) \right. \\ & \left. \times \delta(E) \delta(\mathbf{p}_{cM}) t_{v_r}^{v_r'} + \frac{1}{2\pi i} [t_{v_r}^{v_r'}(\phi + \phi_1) - (\phi + \phi_1)t_{v_r}^{v_r'}] \right\} \quad (6) \end{aligned}$$

ϕ' is shorthand for $\phi_{j'm'm'}(\mathbf{p}')$; the subscript 1 denotes the variable of another molecule colliding with the one being followed; $\delta(E)$ and $\delta(\mathbf{p}_{cM})$ are Dirac delta function operators inserted to conserve energy and center-of-mass momentum; $t_{v_r}^{v_r'}$ is the translational momentum matrix element of the transition operator t ; and v_r and v_r' are the relative velocities before and after collision. We write g as a self-adjoint operator that to first order describes the rate of change of ϕ due to the net drift from neighboring regions of phase space. In the presence of a temperature gradient⁽⁴⁾ g takes the form where

$$\begin{aligned} g = & \left(\frac{2kT}{m} \right)^{1/2} \left\{ W^2 - \frac{5}{2} + \frac{1}{kT} [H_{\text{int}} - (H_{\text{int}}, I)] \right\} W \cdot \Delta \ln T \\ \equiv & g_\alpha^T \frac{\partial}{\partial x_\alpha} \ln T \quad (6a) \end{aligned}$$

where

$$\mathbf{W} \equiv (m/2kT)^{1/2} (\mathbf{v} - \mathbf{v}_0) \quad (6b)$$

m is the molecular mass, T is the temperature, H_{int} is the rotational Hamiltonian, and \mathbf{v} is the velocity. The repeated Greek index summation convention is used. When shear flow is present⁽⁴⁾

$$g = 2(W_\alpha W_\beta - \frac{1}{3} W^2 \delta_{\alpha\beta}) S_{\alpha\beta} \equiv g_{\alpha\beta}^s S_{\beta\alpha} \quad (7a)$$

$$S_{xy} \equiv \frac{1}{2} \left(\frac{\partial v_{0x}}{\partial y} + \frac{\partial v_{0y}}{\partial x} \right) - \frac{\delta_{xy}}{3} \frac{\partial v_{0\alpha}}{\partial x_\alpha} \quad (7b)$$

δ_{ij} is the Kronecker delta. In a magnetic field Eq. (5) must be replaced by⁽⁵⁾

$$\mathcal{I}_c \phi = (\mathcal{L} + \mathcal{I}_M) \phi = -g \quad (8a)$$

$$\mathcal{I}_M \phi \equiv (i/\hbar)[H_F, \phi]_- \quad (8b)$$

where \mathcal{I}_M describes the precession about the field axis, $[\]_-$ is the commutator, and H_F , the Hamiltonian for the interaction of the field and the

magnetic moment, is necessarily Hermitian. Here ζ is a parameter chosen to be proportional to the magnetic field strength.

The i th component of the heat flux is given by

$$q_i = -k^{-1}(\phi, g_i^T) = -\lambda_{ia} \partial T / \partial x_a \quad (9)$$

$$\lambda_{ij} = -k^{-1}(\mathcal{J}_\zeta^{-1} g_j^T, g_i^T), \quad i, j = x, y, z \quad (10)$$

Similarly, the shear part of the pressure tensor is given by

$$\Pi = \eta : S \quad (11)$$

$$\eta_{ij,kl} = -(2kT)^{-1}(\mathcal{J}_\zeta^{-1} g_{kl}^S, g_{ij}^S) \quad (12)$$

Thus each of the components of the thermal conductivity and shear viscosity tensors may be expressed as an inner product of vectors in \mathcal{H} .

At zero field strength $\mathcal{J}_0 = \mathcal{L}$ is spherically symmetric and from the symmetry under rotational transformations it is not difficult to show that λ and η reduce to scalars. In nonvanishing fields, however, \mathcal{J}_ζ will only have cylindrical symmetry about the field direction, taken here to be the z axis. Again considering the transformations under infinitesimal rotations, it can be shown that the tensors λ and η have the form required by the phenomenological theory.⁽¹⁸⁾ These relationships have been displayed so often^(1,17) that there is no need to do so here.

It is now convenient to write \mathcal{J}_M as

$$\mathcal{J}_M = \zeta \mathcal{F} \quad (13)$$

where ζ is a scalar proportional to the field strength and \mathcal{F} is a superoperator. In the inner product space \mathcal{H} the adjoint of a superoperator will be designated by the superscript \dagger . The cyclic character of the trace operation and the Hermitian character of H_F may now be used to show that \mathcal{F} is anti- (or skew-) symmetric:

$$\mathcal{F}^\dagger = -\mathcal{F} \quad (14)$$

As a consequence, all diagonal matrix elements of \mathcal{F} are pure imaginary and so \mathcal{J}_ζ is dissipative if \mathcal{L} is. This means, too, that μ ($\text{Re } \mu > 0$) is still in the resolvent set of \mathcal{J}_ζ . For diatomic and spherical molecules \mathcal{F} takes the particularly simple form

$$\mathcal{F} = i[J_z,]_- \quad (15)$$

$$\zeta = |B| g_{\text{rot}} \mu_N / \hbar \quad (16)$$

where J is the angular momentum operator, \mathbf{B} is the magnetic field, g_{rot} is the rotational g factor, and μ_N is the nuclear magneton. The form for symmetric

and asymmetric tops is more complicated but can be calculated from the gyromagnetic tensor.^(19,20) But for our purposes it is sufficient to note that the maximum effect of \mathcal{F} is to multiply ϕ by a polynomial in \mathbf{J} . This means that \mathcal{F} is bounded in the sense that the norm of \mathcal{F} in \mathcal{H} , $\|\mathcal{F}\|$, is bounded:

$$\begin{aligned}\|\mathcal{F}\| &= \max[(\mathcal{F}u, \mathcal{F}u)^{1/2}/(u, u)] \\ &\leq \text{const} \times [(|J|^n u, |J|^n u)^{1/2}/(u, u)^{1/2}] \\ &= O(\langle |J|^{2n} \rangle_0), \quad \forall u \text{ in } \mathcal{H}\end{aligned}\tag{17}$$

where the brackets with subscript zero denote an equilibrium average. Moreover, since H_F commutes with all operator functions of \mathbf{J}^2 and \mathbf{W} , \mathcal{F} has a sizable null space. This null space, then, is not affected by a magnetic field and may be expected to be the only part of ϕ remaining at large field strengths. For diatomic and spherical molecules this null space may be identified as the operator functions of \mathbf{W} , J^2 , and J_z , i.e., operators diagonal in all quantum numbers, magnetic as well as principal. Since $i\mathcal{F}$ is bounded and symmetric, operators in the null space are orthogonal to those that are not. Denoting the null space and its orthogonal complement by \mathcal{H}_0 and \mathcal{H}_1 and the associated projection superoperators by \mathcal{P}_0 and \mathcal{P}_1 , we have

$$\mathcal{H} = \mathcal{H}_0 \oplus \mathcal{H}_1, \quad \mathcal{I} = \mathcal{P}_0 + \mathcal{P}_1\tag{18}$$

Another useful way of partitioning \mathcal{H} is suggested by the work of Levi and McCourt.⁽⁵⁾ Define \mathcal{A} as a superoperator that reverses the sign of all angular momenta, magnetic moments, and magnetic fields. This may be regarded as the successive operation of space inversion and time reversal.^(5,14) Again \mathcal{H} may be partitioned into two mutually orthogonal sets of operators, namely the operators even and odd, respectively, in \mathbf{J} . These will be denoted by \mathcal{H}_+ and \mathcal{H}_- , and the associated projection superoperators by \mathcal{P}_+ and \mathcal{P}_- . We then have that

$$\mathcal{H} = \mathcal{H}_+ \oplus \mathcal{H}_-, \quad \mathcal{I} = \mathcal{P}_+ + \mathcal{P}_-, \quad \mathcal{A}\mathcal{P}_\pm\phi = \pm\mathcal{P}_\pm\phi\tag{19}$$

Levi and McCourt⁽⁵⁾ then show that

$$\mathcal{A}\mathcal{F}\mathcal{A}^{-1} = \mathcal{F}\tag{20}$$

$$\mathcal{A}\mathcal{L}\mathcal{A}^{-1} = \mathcal{L}^*\tag{21}$$

The adjoint of \mathcal{L} has been given elsewhere.⁽¹⁶⁾ Equations (20) and (21) imply that \mathcal{H}_+ and \mathcal{H}_- are reducing spaces⁽²¹⁾ for \mathcal{F} and the symmetric part of \mathcal{L} , $\mathcal{L}_s = \frac{1}{2}(\mathcal{L} + \mathcal{L}^*)$. That is, $\mathcal{P}_+\mathcal{L}_s\mathcal{P}_- = \mathcal{P}_-\mathcal{L}_s\mathcal{P}_+ = \mathcal{P}_+\mathcal{F}\mathcal{P}_- = \mathcal{P}_-\mathcal{F}\mathcal{P}_+ = 0$. Similarly, the antisymmetric part of \mathcal{L} , $\mathcal{L}_a = \frac{1}{2}(\mathcal{L} - \mathcal{L}^*) =$

$-\mathcal{L}_a^\dagger$, has no nonvanishing matrix elements within \mathcal{H}_+ or \mathcal{H}_- : $\mathcal{P}_+\mathcal{L}_a\mathcal{P}_+ = \mathcal{P}_-\mathcal{L}_a\mathcal{P}_- = 0$.

The kinetic theory presented here is a partial rephrasing of the usual formulas.^(1,4-6) Its chief advantage, useful in the next section, is that the coefficients are functionals of vectors in a Hilbert space. Another, the simplicity of the indexing notation, is partly due to the fact that a matrix representation of \mathcal{L} or a vector expansion of ϕ is not attempted.

3. ASYMPTOTIC PROPERTIES

The quantity ϕ is restricted to the orthogonal complement of the null space of \mathcal{J}_ζ because $f^{(0)}$ is already normalized to yield the local density of the collisional invariants, mass, momentum, and energy. At zero field angular momentum may also be added with suitable modifications of \mathcal{L} .^(6,22) Furthermore, we shall assume that $\mu = 0$ is in the resolvent set of \mathcal{J}_ζ and \mathcal{L}_s , or at least that $(\mu - \mathcal{J}_\zeta)^{-1}$ and $(\mu - \mathcal{L}_s)^{-1}$ exist in the limit $\text{Re } \mu \rightarrow 0+$. Since the operators g , g_u^T , and g_{uv}^S ($u, v = x, y, z$) all lie in the intersection of \mathcal{H}_+ and \mathcal{H}_0 , one need only consider the projection of ϕ on either of these two subspaces or on the region where they intersect. For simplicity we may drop the indices u, v, T , and S and consider matrix elements of the form

$$\xi_\zeta(g, h) = -(\mathcal{J}_\zeta^{-1}g, h) = (\phi_g(\zeta), h) \tag{22}$$

where g and h are Hermitian operators in $\mathcal{H}_+ \cap \mathcal{H}_0$. By forming the adjoint of $f^{(0)}\mathcal{J}_\zeta\phi$ in wave function space, it is evident that Eq. (3) holds because g is Hermitian. The cyclic property of traces and the Hermitian character of h then imply that ξ_ζ is real.

We now wish to argue that \mathcal{L} is bounded in the metric, (\dots, \dots) . This is equivalent to the statement that no infinitely fast relaxation processes exist. A definition of the norm of \mathcal{L} , equivalent to Eq. (17), is

$$\|\mathcal{L}\| = \max \frac{|(\phi_i, \mathcal{L}\phi_j)|}{(\phi_i, \phi_i)^{1/2}(\phi_j, \phi_j)^{1/2}}, \quad \phi_i, \phi_j \in \mathcal{H} \tag{23}$$

By interchange of particles and energy and momentum conservation and remembering that $f^{(0)}$ commutes with t , we have

$$\begin{aligned} (\phi_i, \mathcal{L}\phi_j) \propto & \sum_{j_1 k_1 m_1} \sum_{j_2 k_2 m_2} \int d^3\mathbf{p}_1 \int d^3\mathbf{p}_2 \langle \psi_{j_1 k_1 m_1} \psi_{j_2 k_2 m_2} | \phi_i^\dagger \\ & \times \left\{ \int d\delta_r' t_{v_r}' \phi_{j_1}' t_{v_r}' + (1/2\pi i)(t_{v_r}^{v_r} \phi_{j_1} - \phi_{j_1} t_{v_r}^{\dagger v_r}) \right\} \\ & \times | \psi_{j_1 k_1 m_1} \psi_{j_2 k_2 m_2} \rangle \end{aligned} \tag{24}$$

$$\phi_{kl} \equiv (f_1^{(0)})^{1/2} (f_2^{(0)})^{1/2} [\phi_k(1)I(2) + \phi_l(2)I(1)] \tag{25}$$

$I(1)$ and $I(2)$ are unit operators in the wave function space of molecules 1 and 2. It is evident that if $(f^{(0)})^{1/2} \phi$ is in the Schmidt class $\sigma(c)$, the operator in the product space, $(f_1^{(0)})^{1/2} (f_2^{(0)})^{1/2} \phi_k \phi_l$, is too. Let us call the product space $\sigma_{12}(c)$. We note that $\phi_{k;l}$ is diagonal in energy and that the only elements appearing of $t_{v_r}^{v_r'}$ are on the energy shell. They are thus projections of $(2\pi i)^{-1}[I(1)I(2) - S]$, where S is the S -matrix. As is well known, S is unitary and thus bounded (for real momenta) in wave function space. Since products of a Schmidt class operator and a bounded operator are still in $\sigma_{12}(c)$ (Ref. 16, Lemma II 3iv), the quantity in curly brackets in Eq. (24) is also in $\sigma_{12}(c)$. This implies that $\mathcal{L}\phi$ is in $\sigma(c)$ and thus that \mathcal{L} is bounded. This property is very convenient because the resolvent

$$\mathcal{R}(\mathcal{L} + \zeta\mathcal{F}, 0+) \equiv \lim_{\mu \rightarrow 0+} (\mu - \mathcal{L} - \zeta\mathcal{F})^{-1}$$

is now expandable as a power series in $\zeta\mathcal{F}$ (Ref. 12, Section VI 3.3), implying that the asymptote of $\phi_g(\zeta)$ as $\zeta \rightarrow 0$ is well defined.

Let $\phi_g^0(\zeta)$ and $\phi_g^+(\zeta)$ be the projections of $\phi_g(\zeta)$ on \mathcal{H}_0 and \mathcal{H}_+ . With the partitioning method introduced by Zwanzig⁽²³⁾ and found useful elsewhere in transport calculations,^(24,25) $\phi_g^0(\zeta)$ is determined formally by

$$[\mathcal{L}_{00} - \mathcal{L}_{01}(\mathcal{L}_{11} + \zeta\mathcal{F})^{-1}\mathcal{L}_{10}]\phi_g^0(\zeta) = -g; \quad \mathcal{L}_{ij} \equiv \mathcal{P}_i \mathcal{L} \mathcal{P}_j, \quad i, j = 0, 1 \quad (26)$$

The inverse in (26) is really to be regarded as $(\mathcal{L}_{11} + \zeta\mathcal{F} - 0-)^{-1}$. With this and the boundedness of \mathcal{L}_{ij} the second term of the reduced superoperator in Eq. (26) exists and is well defined. The resolvent of $(\mathcal{F} + \zeta^{-1}\mathcal{L}_{11})$ may now be expanded in powers of $\zeta^{-1}\mathcal{L}_{11}$ and the asymptotic equation for $\phi_g^0(\zeta)$ becomes

$$\phi_g^0(\zeta) \sim -\mathcal{L}_{00}^{-1}g - \zeta^{-1}\mathcal{L}_{00}^{-1}\mathcal{L}_{01}\mathcal{F}^{-1}\mathcal{L}_{10}g + O(\zeta^{-2}) \quad (27)$$

At large field strengths ϕ_g^1 vanishes:

$$\begin{aligned} \phi_g^1(\zeta) &= \mathcal{P}_1 \phi_g(\zeta) = -(\mathcal{L}_{11} + \zeta\mathcal{F})^{-1}\mathcal{L}_{10}\phi_g^0(\zeta) \\ &= O(\zeta^{-1}), \quad \zeta \rightarrow \infty \end{aligned} \quad (28)$$

This is equivalent in the elementary theory⁽²⁶⁾ to a partial averaging of the \hat{x}, \hat{y} polarization of the angular momenta, and in terms of the expansion of ϕ in spherical harmonics $\mathcal{Y}_l^m(J)$,^(10,27) to the vanishing of all terms with $m \neq 0$.

It has already been established that the elements of the viscosity and thermal conductivity tensors may be written as $-(\mathcal{J}_\zeta^{-1}g, h)$. It is well known^(1,18) that these fall into one of three groups: those that vanish identically and those that are even or odd with respect to interchanges of g and h .

This can be verified quickly by studying the behavior under infinitesimal rotational transformations. In the following it will prove convenient to study the latter two groups separately and to carry out the manipulations formally since they can be justified in a manner similar to that above. The separation into even and odd groups was also found useful by Beenakker *et al.*⁽²⁸⁾

3.1. Odd Tensor Elements

Here we partition ϕ_g into its components ϕ_g^+ and ϕ_g^- . With an easy extension of the notation of Eq. (26)

$$[(\mathcal{L}_s + \zeta\mathcal{F})_{++} - \mathcal{L}_{+-}(\mathcal{L}_{s--} + \zeta\mathcal{F}_{--})^{-1}\mathcal{L}_{-+}]\phi_g^+(\zeta) = -g \quad (29)$$

$$\phi_g^-(\zeta) = -(\mathcal{L}_{s--} + \zeta\mathcal{F}_{--})^{-1}\mathcal{L}_{a+-}\phi_g^+(\zeta) \quad (30)$$

It is evident from (29) and (30) that the odd-in-J components contribute only in second order to λ and η . With these relationships and the fact that the odd tensor elements change sign when g and h are interchanged we have that

$$\begin{aligned} \xi_{gh}(\zeta) &\equiv -(\mathcal{J}_\zeta^{-1}g, h) = (\mathcal{J}_\zeta^{-1}h, g) = (g, \mathcal{J}_\zeta^{-1}h) \\ &= (h, \mathcal{J}_\zeta^{-1}(\mathcal{L}_a + \zeta\mathcal{F})\mathcal{J}_\zeta^{-1}g) = (\phi_h(\zeta), (\mathcal{L}_a + \zeta\mathcal{F})\phi_g(\zeta)) \\ &= \zeta(\phi_h^+(\zeta), [\mathcal{F}_{++} - \mathcal{L}_{a+-}(\mathcal{L}_{s--} + \zeta\mathcal{F}_{--})^{-1}\mathcal{F}_{--}(\mathcal{L}_{s--} + \zeta\mathcal{F}_{--})^{-1} \\ &\quad \times \mathcal{L}_{a+-}]\phi_g^+(\zeta)) \end{aligned} \quad (31)$$

where the third equality is due to the real character of ζ_{gh} established earlier. As $\zeta \rightarrow 0$ the odd tensor elements approach zero with finite slope.

To evaluate the asymptotic behavior as $\zeta \rightarrow \infty$, it is necessary to evaluate $\mathcal{P}_i(\mathcal{L}_{s--} + \zeta\mathcal{F}_{--})^{-1}\mathcal{P}_j$ where i or j or both equal one. The subscripts $-$ may be dropped in the following as long as they are understood. It is not difficult to show the asymptotic properties of $\mathcal{R}(\mathcal{A} + \zeta\mathcal{B}, 0+)$ (\mathcal{A} and \mathcal{B} bounded) that the following hold:

$$\begin{aligned} \mathcal{P}_0(\mathcal{L} + \zeta\mathcal{F})^{-1}\mathcal{P}_0 &= (\mathcal{L}_{00} - \zeta^{-1}\mathcal{L}_{01}(\mathcal{L}_{11}\zeta^{-1} + \mathcal{F})^{-1}\mathcal{L}_{10})^{-1} \\ &= \mathcal{L}_{00}^{-1} + O(\zeta^{-1}) \end{aligned} \quad (32a)$$

$$\begin{aligned} \mathcal{P}_0(\mathcal{L} + \zeta\mathcal{F})^{-1}\mathcal{P}_1 &= -\zeta^{-1}(\mathcal{L}_{00} - \zeta^{-1}\mathcal{L}_{01}(\mathcal{L}_{11} + \zeta\mathcal{F})^{-1}\mathcal{L}_{10})^{-1} \\ &\quad \times \mathcal{L}_{01}(\zeta^{-1}\mathcal{L}_{11} + \mathcal{F})^{-1} \\ &= O(\zeta^{-1}) \end{aligned} \quad (32b)$$

$$\begin{aligned} \mathcal{P}_1(\mathcal{L} + \zeta\mathcal{F})^{-1}\mathcal{P}_0 &= -\zeta^{-1}(\mathcal{F} + \zeta^{-1}(\mathcal{L}_{11} - \mathcal{L}_{10}\mathcal{L}_{00}^{-1}\mathcal{L}_{01}))^{-1}\mathcal{L}_{01}\mathcal{L}_{00}^{-1} \\ &= O(\zeta^{-1}) \end{aligned} \quad (32c)$$

$$\begin{aligned} \mathcal{P}_1(\mathcal{L} + \zeta\mathcal{F})^{-1}\mathcal{P}_1 &= \zeta^{-1}(\mathcal{F} + \zeta^{-1}(\mathcal{L}_{11} - \mathcal{L}_{10}\mathcal{L}_{00}^{-1}\mathcal{L}_{01}))^{-1} \\ &= O(\zeta^{-1}). \end{aligned} \quad (32d)$$

With (32b)–(32d) we see that

$$\xi_{gh}(\zeta) = \zeta(\phi_h^+(\zeta), \mathcal{F}\phi_g^+(\zeta)) + O(\zeta^{-1}) \quad (33)$$

By the same argument that yielded Eq. (28), we may infer that $\mathcal{P}_1\phi_h^+(\zeta)$ and $\mathcal{P}_1\phi_g^+(\zeta)$ are both of order ζ^{-1} , which in turn implies that all odd tensor elements vanish at least as quickly as ζ^{-1} as $\zeta \rightarrow \infty$.

3.2. Even Tensor Elements

Tensor elements that do not change sign when g and h are interchanged may always be expressed as linear combinations of diagonal matrix elements of the form

$$\xi_g(\zeta) \equiv (\phi_g(\zeta), g) = -(\mathcal{J}_\zeta^{-1}g, g) \quad (34)$$

Since ξ_g is real (see above), ϕ_g may be replaced by an associated density matrix $\phi_g^{(16)}$

$$(\phi_g(\zeta), g) = \text{Re}(\phi_g(\zeta), g) = (\tilde{\phi}_g(\zeta), g) \quad (35)$$

$$\tilde{\mathcal{J}}_\zeta \tilde{\phi}_g(\zeta) = -g \quad (36)$$

$$\tilde{\mathcal{J}}_\zeta \equiv \mathcal{J}_\zeta^\dagger \mathcal{L}_s^{-1} \mathcal{J}_\zeta = \mathcal{J}_\zeta \mathcal{L}_s^{-1} \mathcal{J}_\zeta^\dagger \quad (37)$$

where $\tilde{\mathcal{J}}_\zeta$ is not only still dissipative, but now symmetric. By the assumption on $\mathcal{H}(\mathcal{L}_s, 0+)$ it is also bounded. The limiting form as $\zeta \rightarrow 0$ is

$$\tilde{\mathcal{L}}\tilde{\phi}_g(0) = -g \quad (38)$$

Since $\mathcal{A}g = g$ and $\mathcal{A}\tilde{\mathcal{L}}\mathcal{A}^{-1} = \tilde{\mathcal{L}} = \mathcal{L}_s - \mathcal{L}_\alpha\mathcal{L}_s^{-1}\mathcal{L}_\alpha$, \mathcal{H}_+ and \mathcal{H}_- are reducing spaces for $\tilde{\mathcal{L}}$ and $\tilde{\phi}_g(0)$ lies in \mathcal{H}_+ . It is thus identical with $\phi_g^+(0)$. The same construction can be carried out at infinite field strength, with the result

$$\mathcal{L}_{00}^*(\mathcal{L}_{s00})^{-1}\mathcal{L}_{00}\tilde{\phi}_g(\infty) = (\mathcal{L}_{s00} - \mathcal{L}_{\alpha00}(\mathcal{L}_{s00})^{-1}\mathcal{L}_{\alpha00})\phi_g(\infty) = -g \quad (39)$$

$$\mathcal{P}_+\tilde{\phi}_g(\infty) = \tilde{\phi}_g(\infty) \quad (40)$$

From the Rayleigh–Ritz lower bound formula

$$\xi_g(0) = -(g, \tilde{\mathcal{L}}^{-1}g) \geq (g, (\tilde{\mathcal{L}}_{00})^{-1}g) \quad (41)$$

and the upper bound formula^(16,29)

$$\mathcal{L}_{00}^*\mathcal{L}_{s00}^{-1}\mathcal{L}_{00} \geq \mathcal{P}_0\mathcal{L}_s^*\mathcal{L}_s^{-1}\mathcal{L}\mathcal{P}_0 = \tilde{\mathcal{L}}_{00} \quad (42)$$

$$\xi_g(\infty) = -(g, (\mathcal{L}_{00}^*(\mathcal{L}_{s00})^{-1}\mathcal{L}_{00})^{-1}g) \geq -(g, (\tilde{\mathcal{L}}_{00})^{-1}g)$$

it is impossible, without further input, to determine the direction of the Senftleben–Beenakker shift unless $\mathcal{L}_a = 0$. In this particular case we find that $\xi_g(\infty) \leq \xi_g(0)$, as well as the more general result that the decrease is monotonic. This will be more obvious in the following.

It is convenient to separate $\tilde{\mathcal{J}}_\zeta$ into the sum of three self-adjoint operators:

$$\tilde{\mathcal{J}}_\zeta = \tilde{\mathcal{L}} + \zeta \mathcal{Q} + \zeta^2 \mathcal{S} \tag{43a}$$

$$\mathcal{Q} = \mathcal{F} \mathcal{L}_s^{-1} \mathcal{L}^\dagger + \mathcal{L} \mathcal{L}_s^{-1} \mathcal{F}^\dagger = \mathcal{Q}^\dagger = -\mathcal{A} \mathcal{Q} \mathcal{A}^{-1} \tag{43b}$$

$$\mathcal{S} = \mathcal{F} \mathcal{L}_s^{-1} \mathcal{F}^\dagger = \mathcal{S}^\dagger = \mathcal{A} \mathcal{S} \mathcal{A}^{-1} \tag{43c}$$

Since \mathcal{L}_s is dissipative, \mathcal{S} is, too. It is also apparent that \mathcal{H}_+ and \mathcal{H}_- are reducing spaces for \mathcal{S} as well as for \mathcal{L} and \mathcal{L}_s . Although \mathcal{Q} itself cannot be said to be entirely dissipative or accretive, the following discussion indicates that its net effect on ξ_g is accretive.

Now, partitioning $\tilde{\phi}_g$ into $\tilde{\phi}_g^+$ and $\tilde{\phi}_g^-$, we have

$$(\tilde{\mathcal{L}} + \zeta^2 \mathcal{S}) \tilde{\phi}_g^+(\zeta) = -g \tag{44}$$

$$\mathcal{G} \equiv \mathcal{S} - \mathcal{Q}(\tilde{\mathcal{L}} + \zeta^2 \mathcal{S})^{-1} \mathcal{Q} \tag{45}$$

\mathcal{G} is thus the sum of two operators, one dissipative and one accretive. Then since $(\tilde{\phi}_g^+, g) = (\tilde{\phi}_g, g)$, it is seen that ξ_g is a function of ζ^2 . It may be verified that \mathcal{Q} vanishes if \mathcal{L}_a does. In this particular case we may set up the inequality

$$(u, (\tilde{\mathcal{L}} + \zeta^2 \mathcal{S})u) \leq (u, \tilde{\mathcal{L}}u) \leq 0, \quad \forall u \text{ in } \mathcal{H} \tag{46}$$

which would then imply that $\xi_g(\zeta)$ decreases monotonically with ζ , i.e., that $\xi_g(\zeta') \leq \xi_g(\zeta)$, $\zeta' \geq \zeta$.⁽²⁹⁾ Remembering that in the general case

$$\xi_g(\zeta) = (\phi_g^0, g)$$

and that by the arguments of the first part of this section ϕ_g^0 is expandable as a series in ζ^{-1} , it is evident that ξ_g may also be expanded as a power series in ζ^{-1} . However, the foregoing discussion indicates that $\xi_g(\zeta)$ is an even function of ζ . We may conclude, then, that the even-parity tensor elements approach their asymptotes $\xi_g(\infty)$ at least as quickly as ζ^{-2} .

The preceding discussion was predicated on the assumption that \mathcal{F} was independent of magnetic field strength, i.e., ζ . In certain cases⁽²⁸⁾ this is not so. However, \mathcal{F} in general is never likely to have more than a polynomial dependence on ζ . Let the minimum and maximum powers of ζ in \mathcal{F} be N and M . Then retracing the argument *mutatis mutandis*, the asymptotic dependence of the odd and even elements will be ζ^{N+1} and ζ^{2N} as $\zeta \rightarrow 0$ and ζ^{-M-1} and $\zeta^{-2(M+1)}$ as $\zeta \rightarrow \infty$.

4. DISCUSSION

In summary, the last section has demonstrated that in the original Waldman–Snider equation in the linearized approximation the collision superoperator is bounded in the metric adopted. Consequently, the thermal conductivity and shear viscosity tensors retain well-defined limiting forms as the magnetic field strength increases indefinitely. The asymptote is zero for those tensor elements that have odd symmetry when a rotation is carried out about the field line. Even tensor elements are even functions of ζ , the measure of field strength, and for simple molecules approach their asymptotes as ζ^2 and ζ^{-2} , odd elements as ζ and ζ^{-1} . The extension to more complicated molecules is outlined at the end of the last section.

The only information used was the boundedness of \mathcal{L} and \mathcal{F} and their behavior under symmetry transformations. Without further input no more can be inferred. For instance, the well-known double frequency dependence found in most experiments⁽¹⁾ can be derived if, besides the usual expansion functions scalar in \mathbf{J} , one tensor function, $[\mathbf{J}\mathbf{J}]^{(2)}$ or $\mathbf{W}[\mathbf{J}\mathbf{J}]^{(2)}$, is included in the trial function approximating ϕ .⁽¹⁰⁾ Furthermore, without any definite knowledge as to the matrix elements of \mathcal{L}_s and \mathcal{L}_a it is difficult to predict the direction of the Senftleben–Beenakker effect or the direction of approach to the asymptotes.

The difficulty in predicting the sign of $\Delta\xi_g(\zeta) = \xi_g(\zeta) - \xi_g(0)$, or, in the equivalent problem, of ascertaining whether the operator \mathcal{G} [Eq. (45)] is dissipative or not, is connected with the tendency of \mathcal{H}_+ components of $\tilde{\phi}$ to maximize ξ_g and of \mathcal{H}_- components to minimize it.^(5,24,30) Freezing out terms of opposite symmetry then has opposite effects on $\Delta\xi_g$. This also introduces an error of uncertain sign in calculations made with trial function approximations to ϕ . Although the second tendency is contrary to the usual behavior of kinetic theory approximations,⁽³¹⁾ it can be understood when it is recalled that ξ_g may be regarded as a measure of the steady-state deviation from equilibrium⁽³²⁾ and that cross matrix elements of \mathcal{H}_+ and \mathcal{H}_- components increase the number of relaxation modes of $\tilde{\phi}^+$. This should increase the rate of equilibration and minimize ξ_g . On the other hand, truncating the number of \mathcal{H}_+ terms in $\tilde{\phi}^+(0)$ is equivalent to requiring certain \mathcal{H}_+ modes to relax infinitely quickly, again leading to a decreased ξ_g .

One possible procedure to estimate the error would be to calculate successively better upper and lower bounds to $\xi_g(\zeta)$ until the “noise” of the calculation is substantially less than $\Delta\xi_g(\zeta)$. Another would be to estimate upper and lower bounds directly on the difference

$$\Delta\xi_g(\zeta) = \zeta^2(\tilde{\phi}^+(0), [\mathcal{G} - \mathcal{G}(\mathcal{L} + \zeta^2\mathcal{G})^{-1}\mathcal{G}]\tilde{\phi}^+(0)) \quad (47)$$

Either of these procedures, however, requires lower bounds to the spectrum of \mathcal{L}_s and the computation of many more matrix elements than are carried

in the present theories.⁽¹⁾ This is probably not necessary, because the internal consistency of truncated trial function theories with experiment indicates that they probably have attained an accuracy sufficient for most purposes. This implies a high degree of diagonality in \mathcal{L} and suggests an approximation leading to a well-known relation. Starting with the inequality

$$\tilde{\mathcal{L}} + \zeta^2 \mathcal{G} \geq \tilde{\mathcal{L}} + \zeta^2 \mathcal{S} \quad (48)$$

we find the following chain of inequalities:

$$\begin{aligned} \Delta \xi_g(\zeta) &\geq \zeta^2 (\tilde{\phi}^+(0), [\mathcal{S} - \zeta^2 \mathcal{S}(\tilde{\mathcal{L}} + \zeta^2 \mathcal{S})^{-1} \mathcal{S}] \tilde{\phi}^+(0)) \\ &\xrightarrow{\zeta \rightarrow \infty} (\tilde{\phi}_1^+(0), [\tilde{\mathcal{L}}_{11} - \tilde{\mathcal{L}}_{10}(\tilde{\mathcal{L}}_{00})^{-1} \tilde{\mathcal{L}}_{01}] \tilde{\phi}_1^+(0)) \\ &\geq (\tilde{\phi}_1(0), \tilde{\mathcal{L}}_{11} \tilde{\phi}_1(0)) \sim (\tilde{\phi}_1(0), \mathcal{L}_s \tilde{\phi}_1(0)) \end{aligned} \quad (49)$$

That is, the Senftleben–Beenakker effect is approximately proportional to the entropy production or the relaxation rate of the component of $\phi(0)$ with J_x, J_y polarization.

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