

THEORY OF FIELD EFFECTS ON TRANSPORT PROPERTIES OF POLYATOMIC GASES IN THE TRANSITION REGIME

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Received 24 September 1984

A simple method is presented for describing the effects of external magnetic or electric fields on the transport properties of polyatomic gases over the entire range from the continuum to the Knudsen regime. Instead of treating bulk and boundary-layer effects separately, both molecular and surface scattering are included from the beginning in the collisional part of the Boltzmann equation, and the surface is treated as one component of a multicomponent mixture. A simple first-order solution of this problem is sufficient to account for the dependence of the transport coefficients on the Knudsen number in the presence of a field. Detailed results for the longitudinal and transverse viscomagnetic effects in a single gas are presented, and shown to be in good agreement with experimental data for CO and N₂.

1. Introduction

The effects of magnetic and electric fields on the transport properties of polyatomic gases have been extensively studied, both theoretically and experimentally, for over 20 years¹⁻⁷). The basic physical mechanism is well understood. Collisions between nonspherical molecules in the presence of gradients produce net anisotropies in the internal angular momentum distribution ("polarization"), and an external field tends to destroy this polarization. If the transport cross sections depend at all on the molecular internal angular momenta—e.g. if the intermolecular forces depend on molecular orientation—then the transport coefficients will show a dependence on the external field. The magnitude of this dependence is determined by the dependence of the cross sections on the polarization, and ultimately by the orientation dependence of the intermolecular forces. The effects on measured transport coefficients are typically a few percent or less. The field strengths needed to make the effects observable depend on the entirely independent magnetic and electric properties of the individual molecules.

At lower gas densities, the collisions of the molecules with the walls become important, and these collisions may also produce net polarization of the molecular angular momentum and hence field effects. Such effects have been observed experimentally, both with temperature gradients and with velocity gradients⁸⁻¹³). Several important differences between the effects due to molecule-wall collisions and molecule-molecule collisions are expected. In the regime where only molecule-molecule collisions are important (hereafter called the continuum regime), the dependence of the field effects on the magnitude of the field strength and on the gas density or pressure are coupled. When only binary collisions are important, dimensional considerations on the Hamiltonian show that the transport coefficients of linear diamagnetic molecules, for example, depend only on the ratio B/p and not on B and p separately, where B is the magnetic field strength and p is the gas pressure. However, in the regime where only molecule-wall collisions are important (the Knudsen regime), the effects will depend on B and p separately. Moreover, different kinds of angular momentum polarization are possible, having different tensorial characters, and there is no reason to expect wall collisions to produce the same predominant polarizations as do molecular collisions. Recent measurements of the dependence of gas flow in the Knudsen regime on the orientation of the magnetic field show that the polarizations are in fact quite different¹³).

We may therefore expect the dependence of the field effects on field strength and gas pressure to be rather complicated in the transition region between continuum and Knudsen behavior. The purpose of this paper is to present a method for characterizing the field effects in the transition region, where neither molecule-molecule nor molecule-wall collisions are completely dominant. The method is applicable to situations involving gradients of velocity, composition, and temperature, and to mixtures of any number of components, but for simplicity we give detailed results here only for the longitudinal and transverse viscomagnetic effects in a single polyatomic gas.

A standard approach to the transition region is to start with a theory of the continuum regime and introduce molecule-wall collisions as a perturbation, treating the Knudsen number Kn as a small parameter, where Kn is the ratio of the mean free path to a characteristic apparatus dimension¹⁴⁻¹⁶). Such an approach in effect produces a power series in Kn . Similarly, one can start with a theory of the Knudsen regime, introduce molecule-molecule collisions as a perturbation, and produce a power series in Kn^{-1} ¹⁷). Such series inevitably diverge or become useless because Kn varies between 0 and ∞ , and so the expansion parameter is unbounded, whether it is Kn or Kn^{-1} . It may be possible to avoid these troubles by means of Padé approximants, for instance by using $(1 + Kn)^{-1}$ as an expansion parameter, but such tricks have only an empirical status.

The present method covers the entire range from the Knudsen to the continuum regime by the conceptually simple device of considering the solid surface as one component of a gas mixture, and no expansion in Kn or Kn^{-1} is involved. In principle, this method is perfectly rigorous, but of course the problem is made no easier by just adding a surface-scattering operator to the Boltzmann or the Waldmann–Snider equation, which must still be solved. A simplifying approximation is needed to obtain a solution, and it is this approximation that is the key to the whole procedure. In order to clarify the basic ideas and to justify the use of the approximation for such subtle “higher-order” phenomena as the field effects, it is helpful to consider first how the problem is approached from the continuum regime^{14,16}).

In zero order, the transport is described by the hydrodynamic Navier–Stokes equations with coefficients characteristic of the gas alone, such as viscosity, thermal conductivity, and diffusion. The effects of the walls appear only as simple boundary conditions for various moments of the molecular velocity distribution function—that is the gas velocity and temperature match those of the wall. A first-order correction to this description keeps the Navier–Stokes equations intact, but recognizes the existence of a boundary layer next to the wall whose thickness is of the order of a mean free path, by modifying the boundary conditions. A viscous slip velocity and a temperature jump are introduced as boundary conditions, which are equivalent to linear extrapolations of the gradients in the bulk region of the gas a distance beyond the wall of the order of a mean free path. The slip or jump distances can be calculated (not an easy calculation in general) if a model of molecule–wall scattering is assumed, but they are more often left as adjustable parameters. In a second order of correction, more attention is paid to the boundary layer by performing other than a linear extrapolation, that is by allowing nonlinear variations of moments of the distribution function within the boundary layer. More detailed boundary conditions at the wall can be found, in principle, from a surface scattering model. However, these refinements require changes in the hydrodynamic equations in order to match the conditions in the boundary layer with those in the bulk region. New terms involving higher derivatives and products of derivatives are introduced, and the Navier–Stokes equations are replaced by, for example, the Burnett equations. There is still some difference of opinion on how to treat polarization at this level. Can it be introduced via the higher-order hydrodynamic equations^{14,15}), or must it appear via the boundary layer by wall collisions¹⁶)? The procedure can in principle be continued to higher and higher orders, introducing more details in the boundary layer and more terms in the hydrodynamic equations (to produce, for example, the super-Burnett equations), but obviously becomes extremely complicated even if it converges.

However, instead of dividing the problem into bulk and boundary-layer

parts which have to be matched, we can imagine treating the problem as a whole from the beginning by putting surface-scattering terms in the collisional part of the Boltzmann or Waldmann-Snider equation, and then constructing solutions by an expansion or moment method with a cleverly chosen set of basis functions. This is formally analogous to the Chapman-Enskog procedure of classical kinetic theory, which uses Burnett functions (Sonine or Laguerre polynomials multiplied by spherical harmonics) as a basis set¹⁸⁻²⁰). This is still not an easy procedure to carry through in detail, but in a first order of approximation it is equivalent to taking the result for a multicomponent gas mixture in the continuum regime and letting the solid surface be one component of the mixture. This component has some special conditions on it, such as large mass, no contribution to fluxes, and an external body force to keep it motionless, but is otherwise considered in the same way as the other components. The dependence of any transport property on the Knudsen number then arises through its dependence on the "mole fraction" of the solid component. The first approximation is thus easily obtained, and in a sense gives a model for interpolation through the transition region.

The advantage of the model is that it gives the behavior of transport coefficients throughout the entire range from the continuum regime to the Knudsen regime, in the form of a set of scaling rules involving the Knudsen number. In the case of gas mixtures, the dependence on composition is also given throughout the entire range. These are precisely the properties that are likely to be given accurately by just a first-order theory, because only the counting of collisions is involved and not their detailed nature. The details of the molecule-surface collisions are absorbed into effective cross sections, which then appear as parts of adjustable constants in the final formulas. The geometrical parts of the problem – the orientation of the external field, whether flow occurs through a circular or a rectangular duct, etc. – are handled initially, before the conditions of the model are invoked. For example, to obtain the result for a single gas at all Knudsen numbers, we first write down the equations for a binary gas in the continuum regime, subject to the geometric features for the particular problem, and then pass to the model limit by taking one component of the binary mixture as the solid surface. The model has had substantial success for a number of problems where no external field is involved²¹), and the foregoing discussion suggests that it should be equally applicable to field effects.

The model has two main disadvantages. The first is that it is not improvable in any simple way. Although it is possible to imagine how higher approximations might proceed in principle, they would be very difficult to carry out in practice. One symptom of this feature is that in some field-free flow problems no terms involving $\ln Kn$ appear in the model results, although they

should be there in principle²²⁻²⁴). Such terms arise from special kinds of correlated collisions and have never turned out to be of any numerical importance, but their absence is a reminder that the model is only a first approximation. For field effects the analogue is the production of additional polarizations in the boundary layer due to sequences of alternating molecule-molecule and molecule-wall collisions^{16,25}). The second disadvantage is that the model absorbs the details of molecule-wall collisions into adjustable constants, and does not furnish an exact procedure for their calculation. That is, even if the exact molecule-surface scattering behavior were known, it would not be possible to calculate these adjustable constants in other than a fairly crude approximation. This is more a flaw of principle than a practical disadvantage, however, because the molecule-surface scattering is almost never known with any precision, so that even in an exact theory it would have to be handled in terms of adjustable parameters.

The overall results take the form of a set of scaling rules. These are particularly simple in the cases worked out in detail here, which are the viscomagnetic effects in a single polyatomic gas, and can be summarized briefly as follows. In the continuum regime the relative change in the quantity measured, $\delta R/R$, is equal to a sum of functions F_i of B/p , one for each tensorial type of polarization produced by molecule-molecule collisions,

$$\begin{aligned}\delta R/R &= h_1^0 F_1(\beta_1^0 B/p) + h_2^0 F_2(\beta_2^0 B/p) + \dots \\ &= \sum h_i^0 F_i(\beta_i^0 B/p),\end{aligned}\quad (1)$$

where the h_i^0 and β_i^0 are parameters giving the magnitude and position of the effect in terms of cross sections and other molecular properties in the limit of $Kn = 0$. Wall collisions change this expression to the form

$$(\delta R/R)(1 + aKn) = \sum h_i F_i(\beta_i B/p) + (Kn)^2 \sum \phi_j G_j(\gamma_j B/p), \quad (2)$$

where

$$h_i = h_i^0(1 + b_i Kn)^{-1}, \quad (3a)$$

$$\beta_i = \beta_i^0(1 + b_i Kn)^{-1}, \quad (3b)$$

$$\phi_j = \phi_j^0(1 + c_j Kn)^{-1}, \quad (3c)$$

$$\gamma_j = \gamma_j^0(1 + c_j Kn)^{-1}. \quad (3d)$$

Wall collisions thus affect $\delta R/R$ in three ways. The first is a field-free slip effect that reduces everything by a factor of $(1 + aKn)^{-1}$, in which a is a dimensionless

slip parameter that can be found independently from flow measurements in the absence of a field. The second effect scales the parameters of the continuum effect by factors of $(1 + b_i \text{Kn})^{-1}$, which represent the destruction by surface collisions of the polarization produced by molecule-molecule collisions. It is interesting that the same factors affect both the magnitudes (h_i) and the positions (β_i) of the field functions F_i . The dimensionless parameters b_i measure the ratio of the effectiveness of surface collisions to gas collisions in destroying polarization of the i th type. These first two effects produce initial deviations from continuum behavior that are linear in Kn . The third effect adds new terms due to the production of polarization by surface collisions, and its subsequent destruction by both molecule and surface collisions. Each tensorial type of polarization produced by surface collisions gives rise to a new field-dependent function G_j , and the surface production as a whole is quadratic in Kn . In addition, there are factors of the form $(1 + c_j \text{Kn})^{-1}$ in which the dimensionless parameters c_j measure the ratio of the effectiveness of surface collisions to gas collisions in destroying polarization of the j th type that was produced by surface collisions. The same factors affect both the magnitudes and positions of the field functions G_j . The parameters σ_j^0 and γ_j^0 , which are analogous to h_i^0 and β_i^0 , give the magnitudes and positions of the surface-produced polarization in terms of properties of the molecules and the surface, and of their interaction.

Thus surface collisions introduce four kinds of new parameters to describe the deviations from continuum behavior. There is first an overall slip parameter a . Then for each kind of molecular-produced polarization there is a parameter b_i describing its destruction by surface collisions. For each kind of surface-produced polarization there are two parameters: ϕ_j describing its production by surface collisions and its subsequent destruction by molecular collisions, and c_j describing its destruction by surface collisions. In terms of an expansion for $\delta R/R$ in powers of Kn , a and b_i appear first with the linear terms, ϕ_j appears first with the quadratic terms, and c_j appears first with the cubic terms. Thus the destruction of polarization by surface collisions first makes its appearance as a first-order slip effect, whereas the production of polarization by surface collisions appears in the deviations from first-order slip. But expansions in powers of Kn or Kn^{-1} are neither necessary nor desirable, because the form given by eq. (2) covers the entire range.

2. Kinetic-theory model

Here we outline the general steps and assumptions made in treating the solid surface as one component of a gas mixture, before taking up applications to

specific cases. It is convenient to consider first how the procedure goes in the absence of an external field. To treat a gas mixture containing ν species we first write down the transport equations for a mixture of $\nu + 1$ species. These equations, obtained from standard kinetic theory, are of three types¹⁸⁻²⁰). First there is a set of diffusion equations, usually written in the Stefan–Maxwell form, which are the equations that describe relative mass transport. Next there is an equation of momentum transport, essentially Newton’s second law for an element of the mixture, including terms for viscous stress (Navier–Stokes equation). Finally there is an equation of energy transport, including terms for thermal conduction. We can ignore the last equation here because we are going to consider only isothermal systems. The two other equations are independent in first approximation, in the sense that there are no diffusion terms in the equation of motion, and no terms corresponding to the viscous transport of momentum in the diffusion equations. This independence is the justification for assuming simple additivity of diffusive and viscous components of the flux of any species of the mixture. It is this additivity that makes the results simple in the first approximation, and it is deviations from this additivity that make the improvement of the results so difficult.

The procedure is thus as follows. The total flux \mathbf{J}_i of a species i is taken as the sum of a diffusive component, \mathbf{J}_{iD} , and a viscous component, $\mathbf{J}_{i\text{ visc}}$,

$$\mathbf{J}_i = \mathbf{J}_{iD} + \mathbf{J}_{i\text{ visc}}. \quad (4)$$

It is further assumed that the viscous component of the flow is non-separative, so that

$$\mathbf{J}_{i\text{ visc}} = x_i \mathbf{J}_{\text{ visc}}, \quad (5)$$

where x_i is the mole fraction of species i and $\mathbf{J}_{\text{ visc}}$ is the viscous flow of the mixture as a whole. We find $\mathbf{J}_{\text{ visc}}$ by solving the Navier–Stokes equation for the particular geometry of interest. For steady-state flow in the x -direction through a long straight tube, for example, only the x -component of $\mathbf{J}_{\text{ visc}}$ is nonzero, the rotational and dilatational terms in the Navier–Stokes equation are zero, and the result is²⁶)

$$\frac{\partial p}{\partial x} = \eta \left(\frac{\partial^2 u_{\text{ visc}}}{\partial y^2} + \frac{\partial^2 u_{\text{ visc}}}{\partial z^2} \right) = \text{constant}, \quad (6)$$

where η is the viscosity, $u_{\text{ visc}} \equiv \mathbf{J}_{\text{ visc}}/n$ is the x -component of the viscous component of the velocity, and n is the number density. For no-slip boundary conditions this equation can be integrated to yield

$$u_{\text{visc}} = - \frac{B_0}{\eta} \frac{dp}{dx}, \quad (7)$$

where B_0 is a geometrical constant whose value depends on the cross-sectional shape of the tube. The value of B_0 is $r^2/8$ for a circular tube of radius r , and is $r^2/3$ for a rectangular tube of width w and thickness $2r \ll w$ ²⁶). Any slip arises from the diffusive component of the flux, \mathbf{J}_{iD} , which we find from the Stefan–Maxwell diffusion equations. For an isothermal mixture of $\nu + 1$ species (counting the surface as one species), these equations are^{18–20})

$$\sum_{j=1}^{\nu+1} \frac{x_i x_j}{D_{ij}} (\mathbf{u}_{iD} - \mathbf{u}_{jD}) = -\nabla x_i - x_i \left(1 - \frac{\rho_i}{\rho}\right) \nabla \ln p + \frac{x_i}{p} \left[n \mathbf{F}_i - \frac{\rho_i}{\rho} \sum_{j=1}^{\nu+1} n_j \mathbf{F}_j \right], \quad (8)$$

where $\mathbf{u}_{iD} \equiv \mathbf{J}_{iD}/n_i$ is the diffusive component of the velocity of species i , D_{ij} is the diffusion coefficient of species i and j in the mixture, ρ_i is the mass density of species i , ρ is the total mass density of the mixture, and \mathbf{F}_i is the external force per particle on species i . The three terms on the right-hand side of eq. (8) represent concentration diffusion, pressure diffusion, and forced diffusion, respectively. Eq. (8) is the i th member of a set of $\nu + 1$ equations, of which only ν are independent (any one of the set is equal to the sum of the other ν equations).

We now let species $\nu + 1$ in eq. (8) represent the solid surface, and impose the following conditions:

- 1) The surface species are motionless and uniformly distributed, so that $\mathbf{u}_s = 0$ and $\nabla n_s = 0$, where the subscript s denotes the surface.
- 2) The quantities n, p, ρ , and x_i appearing in eq. (8) are not the actual gas density, pressure, etc., but include the surface species in the counting. To avoid confusion, we use primes on quantities when the surface species are counted as molecules and drop the primes when only the actual gas molecules are counted; thus we write

$$n' = n + n_s, \quad p' = p + n_s kT, \quad x'_i = x_i (n/n'), \quad \text{etc.}, \quad (9)$$

where k is Boltzmann's constant. However the counting is done, it is a result of kinetic theory that^{27,28})

$$n' D'_{ij} = n D_{ij}. \quad (10)$$

- 3) The surface species are held motionless by an external force that balances any pressure gradients in the gas. A simple force-balance argument leads to the expression^{21,27})

$$n_s F_s = \nabla p, \quad (11)$$

where p is the actual gas pressure, and we assume no external forces act on the other species.

Applying these conditions to eq. (8), we obtain after some algebra the result^{21,27)}

$$\sum_{j=1}^{\nu} \frac{x_i x_j}{D_{ij}} (\mathbf{u}_{iD} - \mathbf{u}_{jD}) + \frac{x_i}{D_{iK}} \mathbf{u}_{iD} = -\nabla x_i - x_i \nabla \ln p, \quad (12)$$

where we have defined the Knudsen diffusion coefficient D_{iK} as

$$D_{iK} \equiv (n/n_s) D_{is}. \quad (13)$$

From the kinetic-theory formula for the binary diffusion coefficient between a molecular species i and a very large and heavy species s ¹⁸⁻²⁰⁾, we find to a good approximation that D_{iK} can be written as

$$D_{iK} \approx \text{constant}(T/m_i)^{1/2}. \quad (14)$$

In eq. (12) most of the complicated parts of the pressure-diffusion and forced-diffusion terms have cancelled out because of eq. (11). From eqs. (4) and (5) we find

$$\mathbf{u}_{iD} = \mathbf{u}_i - \mathbf{u}_{\text{visc}}, \quad (15)$$

which on substitution into eq. (12) yields the final result

$$\sum_{j=1}^{\nu} \frac{x_i x_j}{D_{ij}} (\mathbf{u}_i - \mathbf{u}_j) + \frac{x_i}{D_{iK}} (\mathbf{u}_i - \mathbf{u}_{\text{visc}}) = -\nabla x_i - x_i \nabla \ln p. \quad (16)$$

All ν equations of this set are independent, because the equation for the surface species has been explicitly eliminated. From the kinetic-theory formulas for diffusion coefficients we find that D_{ij} in a multicomponent mixture is, to a good approximation, equal to D_{ij} in a binary mixture of just species i and j ^{19,20,28)}.

For the special case of a single gas in steady-state flow through a long straight tube, we can combine eq. (16) with eq. (7) for u_{visc} and find the flux to be

$$J = nu = -\frac{1}{kT} \left(D_K + \frac{B_0 p}{\eta} \right) \frac{dp}{dx}, \quad (17a)$$

$$= -\frac{1}{kT} \frac{B_0 p}{\eta} (1 + aKn) \frac{dp}{dx}, \quad \text{with } aKn \equiv \eta D_K / B_0 p. \quad (17b)$$

Here we see explicitly that the viscous (Kundt and Warburg) slip is accounted for by the Knudsen diffusion coefficient D_K . The viscosity η refers to the gas only. The surface species does not contribute directly to η because it is stationary, and its influence on η through molecule-surface collisions has already been taken into account through the no-slip boundary condition used in deriving eq. (7) for u_{visc} .

The imposition of an external magnetic or electric field greatly complicates the formal appearance of the transport equations. The transport coefficients become tensors instead of scalars: the viscosity coefficient becomes a tensor of rank four with five independent components, and each diffusion coefficient becomes a tensor of rank two with three independent components. For example, if the field is in the z -direction, considerations of spatial symmetry require that a diffusion tensor have the form²⁹⁾

$$\mathbf{D} = \begin{pmatrix} D^\perp & -D^{\text{tr}} & 0 \\ D^{\text{tr}} & D^\perp & 0 \\ 0 & 0 & D^\parallel \end{pmatrix}. \quad (18)$$

Fortunately, the field effects are small in magnitude, so that a perturbation treatment is permissible, which greatly reduces the complexity of the results. It is easiest to do this on a case-by-case basis, and we will present the formal results only for the viscomagnetic effects in a single polyatomic gas and in a binary mixture of a polyatomic gas and a noble gas. In all cases the gas is in steady-state flow in the x -direction down a tube whose cross section has the shape of a slit of thickness $2r$, and a magnetic field is applied in the yz plane.

We consider first the longitudinal effect in a single polyatomic gas. The magnetic field is applied in a direction along the width of the slit. The change in the transport coefficients causes a change in the flow, which is detected by the unbalance of a flow-resistance bridge in which the tube is one leg^{9,30)}. In practice the flow through the tube is kept constant and the change in the pressure drop, $\delta(\Delta p)$, is measured. This change is caused by a change $\delta\eta$ in the viscosity and a change δD_K in the Knudsen diffusion coefficient that describes the slip. The geometry of the flow and the field determines which component of η is represented by $\delta\eta$ and which component of D_K is represented by δD_K , where the operator δ represents turning on the field. If we operate on eq. (17) with δ , holding J constant, we obtain

$$0 = \left(\delta D_K - \frac{B_0 p}{\eta} \frac{\delta \eta}{\eta} \right) \Delta p + \left(D_K + \frac{B_0 p}{\eta} \right) \delta(\Delta p), \quad (19)$$

which can be solved for the measured relative change in the pressure drop,

$$\frac{\delta(\Delta p)}{\Delta p} \left(1 + \frac{\eta D_K}{B_0 p} \right) = \frac{\delta \eta}{\eta} - \left(\frac{\eta D_K}{B_0 p} \right) \frac{\delta D_K}{D_K}. \quad (20)$$

The transport coefficients for this geometrical arrangement are^{29,31)}

$$\frac{\delta D_K}{D_K} = \frac{D_K^\perp - D_K(0)}{D_K(0)}, \quad (21a)$$

$$\frac{\delta \eta}{\eta} = \frac{\eta_2^+ - \eta(0)}{\eta(0)}, \quad (21b)$$

where $D_K(0)$ and $\eta(0)$ are the zero-field values, and the notation of Coope and Snider³²⁾ is used for the viscosity components. Notice that in the continuum (high-pressure) limit, eq. (20) reduces to $\delta(\Delta p)/\Delta p = (\eta_2^+ - \eta)/\eta$, as it should. This is as far as we can go without explicit kinetic-theory expressions for the transport coefficients.

In the transverse viscomagnetic effect, the magnetic field is applied perpendicular to the width of the slit, and a measurement is made of the small pressure difference that develops across the width of the slit, Δp^{tr} . That is the field induces a flow perpendicular to the main flow, which is eventually stopped by the pressure difference it generates because the sides are closed¹¹⁾. The initial transverse flow is proportional to the main longitudinal flow, and involves off-diagonal parts of the transport coefficient tensors. The reverse flow opposing it is proportional to Δp^{tr} and involves the diagonal parts of the transport coefficients. The result at steady state is

$$\frac{\Delta p^{\text{tr}}}{\Delta p} \left(1 + \frac{\eta D_K}{B_0 p} \right) = \frac{\delta \eta}{\eta} - \left(\frac{\eta D_K}{B_0 p} \right) \frac{\delta D_K}{D_K}. \quad (22)$$

This has the same appearance as the corresponding formula for the longitudinal effect, eq. (20), but the coefficients are different^{11,29)}:

$$\frac{\delta D_K}{D_K} = \frac{D_K^{\text{tr}}}{D_K(0)}, \quad (23a)$$

$$\frac{\delta\eta}{\eta} = \frac{\eta_1^-}{\eta(0)}. \quad (23b)$$

The geometric coefficients B_0 are the same in both eqs. (20) and (22) because $B_0 = r^2/3$ for flow between two closely spaced surfaces regardless of the direction. Notice that in the continuum limit eq. (22) reduces to $\Delta p^{\text{tr}}/\Delta p = \eta_1^-/\eta$, as it should.

The trick of generating the field-effect equations from the field-free equations by applying the operator δ corresponding to turning on the field is generally applicable, provided that the effects of geometry are known. It is especially convenient for discussing mixtures. We could have obtained the above result for Δp^{tr} in this way from eq. (19) by recognizing that in this case $\delta(\Delta p)$ would be Δp^{tr} and that δD_K and $\delta\eta$ would be D_K^{tr} and η_1^- , respectively, from the geometry of the experiment. We will obtain the general formulas here for the transverse effects in a binary mixture of a polyatomic gas and a noble gas in this way, but will defer comparison with experimental results for future work. In place of eq. (17) for a single gas we have two equations:

$$\frac{x_1 x_2}{D_{12}}(u_1 - u_2) + \frac{x_1 u_1}{D_{1K}} = -\frac{dx_1}{dx} - \frac{x_1}{p} \left(1 + \frac{B_0 p}{\eta D_{1K}} \right) \frac{dp}{dx}, \quad (24a)$$

$$\frac{x_2 x_1}{D_{12}}(u_2 - u_1) + \frac{x_2 u_2}{D_{2K}} = -\frac{dx_2}{dx} - \frac{x_2}{p} \left(1 - \frac{B_0 p}{\eta D_{2K}} \right) \frac{dp}{dx}. \quad (24b)$$

Application of the magnetic field produces both a transverse pressure difference, Δp^{tr} , and a transverse composition difference, Δx_1^{tr} , even if the flowing gas mixture is initially uniform in composition¹¹). We now apply the operator δ to these equations and make the following identifications: $\delta u_1 = \delta u_2 = 0$ because of steady state operation; $\delta(\Delta p) = \Delta p^{\text{tr}}$ as for a single gas; $\delta(\Delta x_1) = \Delta x_1^{\text{tr}}$, but $\Delta x_1 = 0$ because no longitudinal concentration gradient is imposed; $\delta D_{12} = D_{12}^{\text{tr}}$, $\delta D_{1K} = D_{1K}^{\text{tr}}$, and $\delta D_{2K} = 0$, if we take species 1 as the polyatomic gas and species 2 as the noble gas; $\delta\eta = \eta_1^-$ as for a single gas, but now the viscosity refers to the gas mixture; and x_1 , x_2 , and p can all be taken as constant within the first order of small quantities.

After considerable algebra, we obtain the following results:

$$\begin{aligned} \frac{\Delta p^{\text{tr}}}{\Delta p} \left(1 + \frac{\eta \bar{D}_K}{B_0 p} \right) &= \frac{\eta_1^-}{\eta} - x_1 \left(\frac{\eta \bar{D}_K}{B_0 p} \right) \left(1 + \frac{D_{12}}{D_{2K}} \right) \left(\frac{D_{1K}}{\bar{D}_K} + \frac{D_{12}}{D_{2K}} \right)^{-1} \frac{D_{1K}^{\text{tr}}}{D_{1K}}, \\ \frac{p \Delta x_1^{\text{tr}}}{\Delta p} &= x_1 x_2 \bar{D}_K \left(\frac{1}{D_{1K}} - \frac{1}{D_{2K}} \right) \left[\frac{\Delta p^{\text{tr}}}{\Delta p} + \frac{D_{1K}}{\bar{D}_K} \left(\frac{D_{1K}}{\bar{D}_K} + \frac{D_{12}}{D_{2K}} \right)^{-1} \frac{D_{12}^{\text{tr}}}{D_{12}} \right] \end{aligned} \quad (25)$$

$$-x_1x_2\left(1+\frac{D_{12}}{D_{2K}}\right)\frac{\bar{D}_K}{D_{2K}}\left(\frac{D_{1K}}{\bar{D}_K}+\frac{D_{12}}{D_{2K}}\right)^{-1}\frac{D_{1K}^{\text{tr}}}{D_{1K}}, \quad (26)$$

where

$$\frac{1}{\bar{D}_K} \equiv \frac{x_1}{D_{1K}} + \frac{x_2}{D_{2K}}. \quad (27)$$

Some simplification can result from the use of eq. (14) for the D_{iK} , but the explicit expression for η_1^- of a mixture is inherently complicated^{33,34}). It will be sufficient here to point out a relation between Δx_1^{tr} and Δp^{tr} in the continuum limit. At high pressures, D_{12}/D_{2K} and $D_{1K}^{\text{tr}}/D_{1K}$ approach zero, but $D_{12}^{\text{tr}}/D_{12}$ approaches a constant, as can readily be seen from the explicit expressions²⁹) by setting the mole fraction of surface species to zero. From eq. (26) we therefore obtain

$$\frac{p\Delta x_1^{\text{tr}}}{\Delta p} = x_1x_2\left(\frac{m_1^{1/2}-m_2^{1/2}}{x_1m_1^{1/2}+x_2m_2^{1/2}}\right)\left(\frac{\Delta p^{\text{tr}}}{\Delta p} + \frac{D_{12}^{\text{tr}}}{D_{12}}\right), \quad (28)$$

in which we have used eq. (14) for the D_{iK} . This is a relation that is capable of direct experimental test. It is the kind of relation that is easily obtained by the present model, but that is difficult to obtain by more conventional kinetic-theory approaches. This is indicated by the fact that slip terms appear in eq. (28), as signaled by the presence of the $m_i^{1/2}$ in the first parentheses, even though it is a continuum result. In this model slip always appears through the D_{iK} , which are the source of the $m_i^{1/2}$ terms. This rather unusual continuum slip is related to the phenomenon of diffusive slip, first investigated by Kramers and Kistemaker in the absence of an external field^{21,35}).

Further progress requires explicit expressions for the field-dependent transport coefficients D_K^\perp , D_K^{tr} , η_2^+ , η_1^- , and D_{12}^{tr} . Because of the complexity of η_2^+ and η_1^- for mixtures consisting of two gas species and one surface species, we limit the discussion from here on to single gases. We implicitly make the customary assumption that the field affects only the molecular motion between collisions, and not the collisions themselves.

3. Viscomagnetic effects in single cases

We next need expressions for D^\perp , D^{tr} , η_2^+ , and η_1^- in terms of cross sections for the production and decay of polarization by molecular and surface col-

lisions. The nature of the polarization produced by molecule-molecule collisions has been determined from viscosity experiments in the continuum regime^{3,30,31,33,36,37}), and it is only necessary to add a term for the decay of the polarization by surface collisions to the theoretical formulas. The possible polarizations produced by surface collisions have been discussed and classified^{6,8,38-41}), and experimental information is now becoming available as to which types of polarization are important for real systems^{6,12,13}). However, in the following analysis of experimental data, we first seek conclusions that can be drawn without explicit assumptions about the nature of the surface-produced polarization.

3.1. Longitudinal viscomagnetic effect in CO

Here the dominant polarization produced by molecule-molecule collisions is of the $[\mathbf{J}]^2$ or 02π type⁴²), and the effect of a magnetic field on the viscosity has the same form as for a mixture of a polyatomic gas (species 1) and a noble gas (species 2), but there is no contribution of species 2 to the viscosity because species 2 is really the surface. For simplicity we assume that the only effect of species 2 is to cause decay of the polarization produced by 11 collisions. The result can be written as⁴²)

$$\frac{\eta_2^+ - \eta(0)}{\eta(0)} = -hf(2\beta B/p), \quad (29)$$

where the field-dependent function is

$$f(x) = \frac{x^2}{1 + x^2}, \quad (30)$$

and

$$h = \frac{x_1 \overline{P^2} \bar{v}_{11} \mathfrak{S}^2(02\pi)_{11}}{\mathfrak{S}(20)_{11} [x_1 \bar{v}_{11} \mathfrak{S}(02\pi)_{11} + x_2 \bar{v}_{12} \mathfrak{S}(02\pi)_{12}]}, \quad (31)$$

$$\beta = \frac{x_1 g \mu_N k T / \hbar}{x_1 \bar{v}_{11} \mathfrak{S}(02\pi)_{11} + x_2 \bar{v}_{12} \mathfrak{S}(02\pi)_{12}}. \quad (32)$$

The average relative speeds are

$$\bar{v}_{ij} = (8kT/\pi\mu_{ij})^{1/2}, \quad (33)$$

in which the reduced masses μ_{ij} are $\mu_{11} = m_1/2$ and $\mu_{12} = m_1$, because $m_2 \gg m_1$.

Here $\mathfrak{S}_{(02\pi)_{11}}^{(20)}$ is an effective cross section for the production of the 02π -polarization by 11 collisions, $\mathfrak{S}(20)_{11}$ is a cross section related to the field-free viscosity $\eta(0)$, and $\mathfrak{S}(02\pi)_{11}$ and $\mathfrak{S}(02\pi)_{12}$ are effective cross sections for the decay of the 02π -polarization by 11-collisions and 12-collisions, respectively. The dimensionless scalar factor \overline{P}^2 depends on the angular momentum, but its value does not concern us here because it will eventually be absorbed into an adjustable parameter. The quantity $\beta(B/p)$ is the ratio of a Larmor precession frequency to a collision frequency for polarization decay; most of the factors in β will be absorbed into an adjustable parameter and so their details do not matter.

We define the Knudsen number as $l/2r$, where l is the mean free path and $2r$ is the slit thickness, and take l from the field-free viscosity as¹⁸⁻²⁰)

$$l = \frac{8}{5} \left(\frac{2kT}{\pi m_1} \right)^{1/2} \frac{\eta(0)}{p}. \quad (34)$$

We can then parameterize the surface decay of polarization by a dimensionless parameter b_{02} , defined as

$$b_{02}\text{Kn} \equiv \frac{n_2 kT}{2^{1/2} p} \frac{\mathfrak{S}(02\pi)_{12}}{\mathfrak{S}(02\pi)_{11}}, \quad (35)$$

which is a measure of the relative effectiveness of surface collisions compared to gas collisions in causing the decay of polarization. The quantities h and β can then be written as explicit functions of the Knudsen number,

$$h = \frac{h^0}{1 + b_{02}\text{Kn}}, \quad (36)$$

$$\beta = \frac{\beta^0}{1 + b_{02}\text{Kn}}, \quad (37)$$

where $h^0 = \overline{P}^2 \mathfrak{S}_{(02\pi)_{11}}^{(20)} / \mathfrak{S}(20)_{11} \mathfrak{S}(02\pi)_{11}$ and $\beta^0 = g\mu_N kT / \hbar \bar{v}_{11} \mathfrak{S}(02\pi)_{11}$ are the constant limiting values of h and β determined in the continuum regime ($\text{Kn} = 0$).

We have already similarly parameterized the field-free slip contribution to the longitudinal viscomagnetic effect, which is given by the factor $\eta D_K / B_0 p$ in eq. (20), by the dimensionless parameter a defined in eq. (17b), which can be determined independently by field-free flow measurements as a function of pressure, according to eq. (17).

The polarization produced by surface collisions appears through the Knudsen diffusion coefficient D_K . We assume for simplicity that only a single type of

polarization is important, as is usually the case for gas collisions, but do not specify its type. Then we can write

$$\frac{D_K^\perp - D_K(0)}{D_K(0)} = -\psi_{pq} L(\gamma_{pq} B/p), \quad (38)$$

where the possible forms of the field function $L(x)$ have been discussed and classified³⁹⁻⁴¹). These functions also depend parametrically on a surface accommodation coefficient and show damped oscillations³⁹⁻⁴¹). Whatever the detailed nature of $L(x)$ may be, the quantities ψ_{pq} and γ_{pq} will have the following forms:

$$\psi_{pq} = \frac{(\text{constant})x_2\bar{v}_{12}\mathfrak{S}^2(\text{prod})_{12}}{\mathfrak{S}(10)_{12}[x_1\bar{v}_{11}\mathfrak{S}(\text{dec})_{11} + x_2\bar{v}_{12}\mathfrak{S}(\text{dec})_{12}]}, \quad (39)$$

$$\gamma_{pq} = \frac{(\text{constant})x_1}{x_1\bar{v}_{11}\mathfrak{S}(\text{dec})_{11} + x_2\bar{v}_{12}\mathfrak{S}(\text{dec})_{12}}, \quad (40)$$

where $\mathfrak{S}(\text{prod})_{12}$ is the cross section that describes the production of polarization due to collisions between species 1 and 2, $\mathfrak{S}(10)_{12}$ describes $D_K(0)$, the field-free Knudsen diffusion (slip), and $\mathfrak{S}(\text{dec})_{11}$ and $\mathfrak{S}(\text{dec})_{12}$ describe the decay of the surface-produced polarization by 11-collisions and 12-collisions, respectively. These forms follow because we are essentially only counting collisions. We again parameterize the surface decay of polarization by a dimensionless parameter b_{pq} , defined as

$$b_{pq}\text{Kn} \equiv \frac{n_2 kT}{2^{1/2}p} \frac{\mathfrak{S}(\text{dec})_{12}}{\mathfrak{S}(\text{dec})_{11}}, \quad (41)$$

which is a measure of the relative effectiveness of surface collisions compared to gas collisions in causing the decay of the surface-produced polarization. The quantities ψ_{pq} and γ_{pq} can then be written as explicit functions of the Knudsen number,

$$\psi_{pq} = \frac{b_{pq}\psi_{pq}^\infty \text{Kn}}{1 + b_{pq}\text{Kn}}, \quad (42)$$

$$\gamma_{pq} = \frac{\gamma_{pq}^0}{1 + b_{pq}\text{Kn}}, \quad (43)$$

where $\gamma_{pq}^0 = (\text{constant})/\bar{v}_{11}\mathfrak{S}(\text{dec})_{11}$ is the constant limiting value of γ_{pq} in the

continuum regime ($\text{Kn} = 0$), and

$$\psi_{pq}^\infty \equiv \frac{(\text{constant})\mathfrak{S}^2(\text{prod})_{12}}{\mathfrak{S}(10)_{12}\mathfrak{S}(\text{dec})_{12}} \quad (44)$$

is the constant limiting value of ψ_{pq} in the Knudsen regime ($\text{Kn} \rightarrow \infty$).

Inserting the foregoing results back into eq. (20) for the longitudinal viscomagnetic effect, we obtain

$$\frac{\delta(\Delta p)}{\Delta p} (1 + a\text{Kn}) = - \frac{h^0}{1 + b_{02}\text{Kn}} f\left(\frac{2\beta^0 B/p}{1 + b_{02}\text{Kn}}\right) + \frac{ab_{pq}\psi_{pq}^\infty (\text{Kn})^2}{1 + b_{pq}\text{Kn}} L\left(\frac{\gamma_{pq}^0 B/p}{1 + b_{pq}\text{Kn}}\right). \quad (45)$$

This is the final result when only one kind of polarization produced by gas collisions is important, and only one kind of polarization produced by surface collisions is important. Production of other additional kinds of polarization just introduces additional terms of the same general form. It is easy to see that eq. (45) has the correct limiting behavior in the continuum and Knudsen regimes. When $\text{Kn} = 0$ (continuum regime) eq. (45) correctly reduces to

$$\frac{\delta(\Delta p)}{\Delta p} = -h^0 f(2\beta^0 B/p), \quad (46)$$

so that measurements at different values of B and p scale together on a single curve when plotted against the single variable B/p . This behavior is predicted by more elaborate kinetic theory, and has been amply confirmed by experiment¹⁻⁵). When $\text{Kn} \rightarrow \infty$ (Knudsen regime) eq. (45) reduces to

$$\frac{\delta(\Delta p)}{\Delta p} = \psi_{pq}^\infty L(\varepsilon_{pq} B), \quad (47)$$

where

$$\varepsilon_{pq} \equiv \frac{\gamma_{pq}^0}{b_{pq}\text{Kn} p} = \frac{\text{constant}}{n_2 k T \bar{v}_{12} \mathfrak{S}(\text{dec})_{12}} \quad (48)$$

is a constant. Thus $\delta(\Delta p)/\Delta p$ in the Knudsen region is independent of pressure and depends only on B , a behavior that is also predicted by other kinetic-theory calculations³⁹⁻⁴¹). Eq. (45) may be regarded as a simple interpolation formula between these two limiting regimes.

Some meaningful comparison with experiment is possible even if the function $L(x)$ is not known explicitly. For large B/p both $f(x)$ and $L(x)$ should approach limiting (saturation) values. From eq. (30) we see that $f(\infty) = 1$, and we can take $L(\infty)$ as some unknown number. Then the saturation value of the longitudinal viscomagnetic effect is predicted to have the following dependence on the Knudsen number:

$$\frac{\delta(\Delta p)_{\text{sat}}}{\Delta p} (1 + a \text{Kn}) = -\frac{h^0}{1 + b_{02} \text{Kn}} + \frac{[ab_{pq}\psi_{pq}^\infty L(\infty)](\text{Kn})^2}{1 + b_{pq} \text{Kn}}. \quad (49)$$

Notice that if surface collisions were without any effect whatsoever, the right-hand side of eq. (49) would be simply the constant $-h_0$, and the entire pressure dependence of the saturation value would be due to the field-free slip. If surface collisions were ineffective in the production of polarization but caused decay of polarization, then a plot of $[\delta(\Delta p)_{\text{sat}}/\Delta p]^{-1}(1 + a \text{Kn})^{-1}$ vs. Kn would give a straight line of slope b_{02} . Deviations from linearity of such a plot would indicate the production of polarization by surface collisions, and a change in sign of $\delta(\Delta p)_{\text{sat}}$ with changing Kn would be a certain indication of surface production.

All these predictions of the model are borne out by the measurements of Breunese et al. on CO⁹⁾. We have fitted eq. (49) to these measurements, plus the earlier measurements of Hulsman et al.³⁰⁾ at smaller values of Kn , with the results shown in fig. 1. This is essentially a three-parameter fit of the Breunese

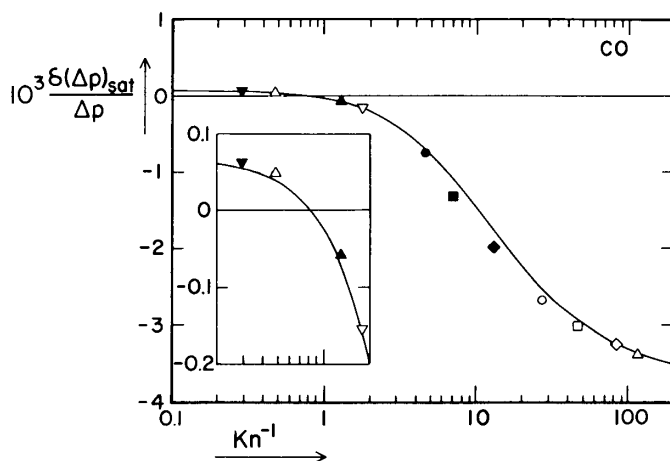


Fig. 1. Saturation value of the longitudinal viscomagnetic effect for CO at 295 K versus the inverse Knudsen number. The symbols are the measurements of Breunese et al. ($\text{Kn}^{-1} < 20$) and of Hulsman et al. ($\text{Kn}^{-1} > 20$). The curve is calculated from eq. (49) with the parameters listed in table I.

data, because h^0 is largely determined by the higher-pressure measurements of Hulsman, and a is taken from independent field-free flow measurements. Of the three freely adjustable parameters b_{02} , b_{pq} , and $\psi_{pq}^\infty L(\infty)$, the parameter b_{02} is essentially determined by the higher-pressure measurements; this can be seen from eq. (49), where b_{pq} and $\psi_{pq}^\infty L(\infty)$ occur in a term that is of order $(Kn)^2$ different from the term in which b_{02} occurs. In the least-squares fitting, the measurements of $\delta(\Delta p)_{\text{sat}}/\Delta p$ were given weights inversely proportional to their magnitudes, to avoid virtually discarding the low-pressure points of small magnitude. The parameters obtained are given in table I, including the continuum values from Hulsman's work. A small adjustment ($<10\%$) has been made in $\psi_{pq}^\infty L(\infty)$ to improve the agreement with the field dependence of $\delta(\Delta p)/\Delta p$, which is discussed below.

The agreement in fig. 1 is quite good. It could even be improved somewhat by introducing another surface-polarization term. Although experiments on the similar molecule N_2 have shown that at least two kinds of surface-produced polarization are important¹³), an improved agreement here would prove nothing because two new adjustable parameters would have to be introduced with the new term.

We conclude that the present model predicts the dependence of the saturation value of the longitudinal viscomagnetic pressure difference on Knudsen number in reasonable agreement with experiment, subject to the simplifying assumption of only one dominant form of surface-produced polarization. In addition, the model gives the correct limiting behavior in the Knudsen regime and in the continuum regime. This success clearly supports the validity of the model.

Some comparison with experiments on the field dependence of the viscomagnetic effect can also be made without even knowing the type of surface polarization that is produced. It is only necessary to assume that a single type of surface-produced polarization is dominant, in order to obtain a scaling rule from the model. If we define a surface production quantity Δ_s as

TABLE I
Parameters from fitting the longitudinal viscomagnetic effect in CO.

$10^3 h^0$	$(\beta^0)^{-1}$ (mT/Pa)	a	b_{02}	b_{pq}	$10^4 \psi_{pq}^\infty L(\infty)$	$L(\infty)$	$(\gamma_{pq}^0)^{-1}$ (mT/Pa)
3.70 ^(a)	7.88 ^(b)	5.9 ^(c)	5.8	7.9	0.69	1	0.35

^(a) Hulsman's value is 3.63³⁰).

^(b) Hulsman's higher-pressure measurements³⁰).

^(c) Hulsman's field-free flow measurements³⁶).

$$\Delta_s \equiv \frac{\delta(\Delta p)}{\Delta p} (1 + a \text{Kn}) + \frac{h^0}{1 + b_{02} \text{Kn}} f\left(\frac{2\beta^0 B/p}{1 + b_{02} \text{Kn}}\right), \quad (50)$$

then eq. (45) predicts that the quantity $\Delta_s(1 + b_{pq} \text{Kn})/(\text{Kn})^2$ will be a function of the single variable $(B/p)/(1 + b_{pq} \text{Kn})$. This can be tested with the field-dependent measurements of Breunese et al.⁹) at their three largest values of Kn, as shown in fig. 2. The upper plot shows the original data, and the lower plot shows the data scaled as suggested by eq. (45). The reduced data do fall approximately on a single curve, within experimental scatter. Note that no new parameters have been introduced in this test. From fig. 2 we can conclude that the scaling predicted by the present model is consistent with the measured field dependence, but the sensitivity of this test and the accuracy of the measurements are not sufficient to tell us anything very definite about the nature of the surface-produced polarization.

We can proceed still further without knowing the specific type of surface polarization produced, if we make the additional plausible assumption that the surface accommodation coefficient occurring in $L(x)$ is unity. Then the mathematical form of $L(x)$ is determined³⁹⁻⁴¹); its computation is discussed in the appendix. The final adjustable parameter γ_{pq}^0 is found by requiring that the maximum in $L(x)$ occurs at the correct field strength in fig. 2b, and its value is

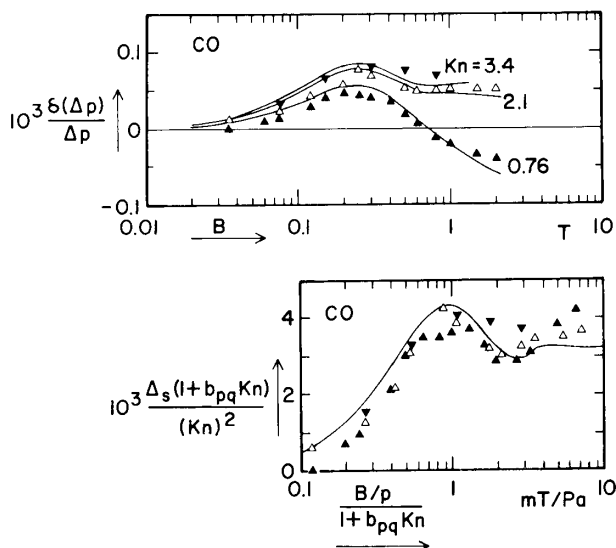


Fig. 2. Test of the predicted scaling rule for surface-produced polarization for the field dependence of the longitudinal viscomagnetic effect for CO at 295 K. The upper plot shows the data of Breunese et al. at the three lowest pressures, and the lower plot shows how these scale together as predicted by eqs. (45) and (50). The symbols correspond to the first three points in fig. 1. The curves are drawn on the assumption that the surface accommodation coefficient is unity.

given in table I. The calculated curves are shown in fig. 2, and the agreement with the measurements seems very reasonable in view of the simplifying assumptions made. In particular, a predicted maximum and minimum are clearly noticeable in the reduced data plotted in fig. 2b. However, the physical interpretation of γ_{pq}^0 requires knowing the specific type of surface polarization, which cannot be determined from these data alone. Measurements of the dependence of $\delta(\Delta p)/\Delta p$ on the orientation of the field are needed for this purpose¹³).

3.2. *Transverse viscomagnetic effect in N₂*

Here the dominant polarization produced by molecule-molecule collisions is again the $[J]^2$ or 02π type, and the results are similar to those for CO. The viscous contribution can be written as⁴²)

$$\frac{\eta_1^-}{\eta(0)} = -hg(\beta B/p), \quad (51)$$

where the field-dependent function is

$$g(x) = \frac{x}{1+x^2}, \quad (52)$$

and

$$h = \frac{h^0}{1+b_{02}Kn}, \quad (53)$$

$$\beta = \frac{\beta^0}{1+b_{02}Kn}, \quad (54)$$

in which the definitions of h^0 , β^0 , and b_{02} are the same as in the case of CO. (The numerical values for N₂ will of course be different from those for CO.) The diffusive, or surface-produced, contribution can be written as (assuming that only one type of polarization is important)

$$\frac{D_K^{\text{tr}}}{D_K(0)} = -\psi_{pq}T(\gamma_{pq}B/p), \quad (55)$$

where the form of the field-dependent function $T(x)$ need not be known. Whether the polarization that is most important in the transverse viscomagnetic effect is the same type as that in the longitudinal effect is not known, but

the form of the scaling in which Kn appears will be the same as given in eqs. (42) and (43).

We can thus write the final result in the form

$$\frac{\Delta p^{\text{tr}}}{\Delta p} (1 + a\text{Kn}) = -\frac{h^0}{1 + b_{02}\text{Kn}} g\left(\frac{\beta^0 B/p}{1 + b_{02}\text{Kn}}\right) + \frac{ab_{pq}\psi_{pq}^\infty (\text{Kn})^2}{1 + b_{pq}\text{Kn}} T\left(\frac{\gamma_{pq}^0 B/p}{1 + b_{pq}\text{Kn}}\right). \quad (56)$$

Again production of additional kinds of polarization just adds further terms of the same general form to this expression. This expression reduces to the correct limiting forms in the continuum and Knudsen regimes. When $\text{Kn} = 0$, $\Delta p^{\text{tr}}/\Delta p$ is a function of the single variable B/p , and when $\text{Kn} \rightarrow \infty$, $\Delta p^{\text{tr}}/\Delta p$ is independent of pressure and depends only on B .

Comparison with experiment is more difficult because we cannot escape the shape of $T(x)$ by passing to a saturation limit at large B/p . Measurements of $\Delta p^{\text{tr}}/\Delta p$ as a function of B/p show a maximum, whose location and height both depend on the details of $T(x)$. It is first necessary to extrapolate $(\Delta p^{\text{tr}}/\Delta p)_{\text{max}}$ and $(B/p)_{\text{max}}$ to $\text{Kn} = 0$ to determine h^0 and β^0 . The value of a is known from independent field-free flow measurements. If surface collisions were without any effect whatever, then $(B/p)_{\text{max}}$ would be independent of Kn and $(\Delta p^{\text{tr}}/\Delta p)_{\text{max}}$ would vary as $(1 + a\text{Kn})^{-1}$. If surface collisions produced no polarization but caused decay of polarization, then a plot of $(\Delta p^{\text{tr}}/\Delta p)_{\text{max}}^{-1}(1 + a\text{Kn})^{-1}$ vs. Kn would give a straight line of slope b_{02} and intercept $-h^0/2$ (because $g_{\text{max}} = 1/2$). Deviations from linearity of such a plot would indicate the production of polarization by surface collisions. Similarly, a plot of $(B/p)_{\text{max}}$ vs. Kn would give a straight line of slope b_{02} and intercept $1/\beta^0$, and deviations from linearity would indicate the production of polarization by surface collisions. The measurements of Breunese on N_2 show all these features¹¹), and the parameters obtained are given in table II.

To find the remaining parameters, we define a surface-production quantity Δ_s^{tr} as

TABLE II
Parameters from fitting the transverse viscomagnetic effect in N_2 .

$10^3 h^0$	$(\beta^0)^{-1}$ (mT/Pa)	a	b_{02}	b_{pq}	$10^4 \psi_{pq}^\infty T_{\text{max}}$	T_{max}	$(\gamma_{pq}^0)^{-1}$ (mT/Pa)
2.68 ^(a)	2.83 ^(a)	5.9 ^(b)	4.2	5	6	0.680	2.6

^(a) Breunese's values¹¹).

^(b) Hulsman's field-free flow measurements³⁶).

$$-\Delta_s^{\text{tr}} \equiv \frac{\Delta p^{\text{tr}}}{\Delta p} (1 + a \text{Kn}) + \frac{h^0}{1 + b_{02} \text{Kn}} g \left(\frac{\beta^0 B/p}{1 + b_{02} \text{Kn}} \right). \quad (57)$$

According to eq. (56), a plot of $(\text{Kn})^2/(\Delta_s^{\text{tr}})_{\text{max}}$ vs. Kn should be a straight line whose slope gives b_{pq} and whose intercept at $\text{Kn} = 0$ gives $\psi_{pq}^\infty T_{\text{max}}$. The parameter values obtained in this way, which are given in table II, are not very accurate because of the error amplification involved in forming Δ_s^{tr} .

Once b_{pq} is known, the model predicts a scaling rule. The quantity $\Delta_s^{\text{tr}}(1 + b_{pq} \text{Kn})/(\text{Kn})^2$ should be a function of the single variable $(B/p)/(1 + b_{pq} \text{Kn})$, provided that only a single type of surface-produced polarization is dominant, according to eq. (56). This can be tested with the measurements of Breunese¹¹⁾ at the four largest values of Kn , as shown in fig. 3. The results for three values of Kn fall roughly together within the rather large experimental uncertainty, but the results for the lowest pressure ($\text{Kn} = 0.453$) are distinctly out of line with the others. We cannot say definitely whether this is caused by the greater experimental error in the lowest-pressure measurements, whether it indicates that more than one kind of surface-produced polarization is important, or whether it means a failure of the present kinetic-theory model.

As before, we can proceed beyond the scaling rule alone if we assume that the surface accommodation coefficient occurring in $T(x)$ is unity. Then the mathematical form of $T(x)$ is determined³⁹⁻⁴¹⁾ (see appendix), and the final adjustable parameter γ_{pq}^0 can be found by requiring that the maximum in $T(x)$ occurs at the correct field strength in fig. 3. The values of T_{max} and γ_{pq}^0 are given in table II, and the calculated reduced curve is shown in fig. 3. The agreement with the measurements is about as good as could be expected in view of the fact that the measurements at the lowest pressure do not seem to follow the

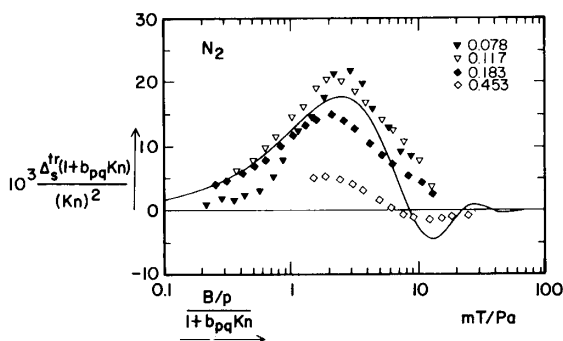


Fig. 3. Test of the predicted scaling rule for surface-produced polarization for the field dependence of the transverse viscomagnetic effect for N_2 at 295 K, at $\text{Kn} = 0.453, 0.183, 0.117$ and 0.078 , using the measurements of Breunese. The results for $\text{Kn} = 0.453$ do not follow the scaling rule predicted by eqs. (56) and (57). The curve is drawn on the assumption that the surface accommodation coefficient is unity.

scaling rule. It is interesting that the curve of $T(x)$ nevertheless predicts the sign reversal shown by the lowest-pressure measurements. Further progress probably requires measurements of the dependence of $\Delta p''/\Delta p$ on the orientation of the field, in order to determine the specific type or types of surface polarization involved.

The mixed success and failure of the results in fig. 3 can be shown more dramatically by using the curve of $T(x)$ in fig. 3 to back-calculate $\Delta p''/\Delta p$ vs. B/p for direct comparison with experiment. The results are shown in fig. 4. The agreement is quite good except for the single case of $\text{Kn} = 0.453$. The cause is unclear, as mentioned above.

4. Discussion

The status of the present kinetic-theory model can be briefly summarized as follows. By treating the solid surface formally as one component of a gas mixture, and assuming additivity for the diffusive and viscous components of the flux of any gas species, we obtain relatively simple explicit formulas for the dependence of the field effects on Knudsen number over the entire range from the continuum regime to the pure Knudsen regime. For gas mixtures the composition dependence is also given over the whole range. Although the full machinery of kinetic theory is apparently used, in fact only the part concerned with classifying and counting collisions contributes to the final result. In other words, kinetic theory is used only as an interpolation scheme for pressure and composition dependence.

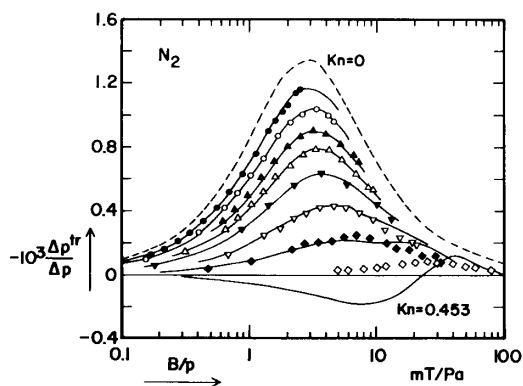


Fig. 4. Transverse viscomagnetic effect for N_2 at 295 K as a function of B/p at various pressures. The symbols are the measurements of Breunese, and correspond to those in fig. 3. The curves are calculated from eq. (56) using the curve of fig. 3 to represent surface-produced polarization, with parameters listed in table II. The symbols correspond to the following Knudsen numbers: ● 0.0134, ○ 0.0260, ▲ 0.041, △ 0.056, ▼ 0.078, ▽ 0.117, ◆ 0.183, ◇ 0.453.

The results give the correct limits in the continuum and Knudsen regimes. In particular, the relative field effects depend on field strength and pressure as the single variable B/p in the continuum regime, and in the Knudsen regime are independent of p and depend on B alone. The results also agree with more elaborate kinetic theories where these exist; e.g. in the "signatures" for the decay and production of molecular polarization due to surface collisions¹⁴⁻¹⁷).

Comparison with experiment has so far been limited to viscomagnetic effects in CO and in N₂. We have made only the simplest possible assumptions concerning the surface-produced polarization. In particular, we have assumed that only one type of surface-produced polarization is important, and that it appears only through the Knudsen diffusion coefficient and not through the viscosity as well. The model is consistent with most of the experimental measurements, but further work involving the tensorial nature of the surface-produced polarization is needed for fuller testing of the model. Additional tests are also possible through available measurements of field effects on gas mixtures, but we believe that the present work is sufficient to establish that the model is worth taking seriously.

Acknowledgements

We wish to thank Professor J.J.M. Beenakker for his interest and his many useful comments, Dr. J.N. Breunese and Dr. L.J.F. Hermans for supplying experimental information and helpful discussions, and Dr. R.G. Cole for clarifying comments.

This work was supported in part by NSF grant CHE 81-17056.

Appendix

The functions $L(x)$ and $T(x)$ are related to a complex function $G(x, \eta)$ introduced by Knaap and Kuščer⁴¹),

$$G(x, \eta) \equiv \int_0^{\infty} \frac{2te^{-t^2}}{e^{ix/t} + \eta} dt. \quad (\text{A.1})$$

When the surface accommodation coefficient is unity, $\eta = 0$ and

$$L(x) = 1 - \text{Re } G(x, 0), \quad (\text{A.2})$$

$$T(x) = -\text{Im } G(x, 0). \quad (\text{A.3})$$

The function $G(x, \eta)$ is related to the functions $f_m(x)$ discussed in the handbook of Abramowitz and Stegun⁴³), and in particular

$$G(x, 0) = 2f_1(ix). \quad (\text{A.4})$$

Owing to the lack of numerical tables, it is necessary for the present purposes to compute $L(x)$ and $T(x)$ from convergent and asymptotic series that can be obtained from the formulas given in Abramowitz and Stegun⁴³).

The convergent series can be written as follows:

$$L(x) = -A(x) \ln x + B_{\text{even}}(x), \quad (\text{A.5})$$

$$T(x) = -(\pi/2)A(x) + B_{\text{odd}}(x), \quad (\text{A.6})$$

where

$$A(x) = |a_2|x^2 + |a_4|x^4 + |a_6|x^6 + \dots, \quad (\text{A.7})$$

$$B_{\text{even}}(x) = |b_2|x^2 + |b_4|x^4 + |b_6|x^6 + \dots, \quad (\text{A.8})$$

$$B_{\text{odd}}(x) = |b_1|x + |b_3|x^3 + |b_5|x^5 + \dots, \quad (\text{A.9})$$

and

$$a_k = \frac{-2a_{k-2}}{k(k-1)(k-2)}, \quad a_2 = -1, \quad (\text{A.10})$$

$$b_k = \frac{-2b_{k-2} - (3k^2 - 6k + 2)a_k}{k(k-1)(k-2)}, \quad (\text{A.11})$$

$$b_1 = -\pi^{1/2}, \quad b_2 = (3/2)(1 - \gamma), \quad \gamma = 0.5772 \dots (\text{Euler's constant}). \quad (\text{A.12})$$

Terms through at least x^{14} must be retained in order to achieve an accuracy of better than 1% up to $x = 5$.

The convergence of these series rapidly becomes poor for $x > 5$, requiring many terms to be carried for accuracy, but the following asymptotic series, obtained from the formulas given in Abramowitz and Stegun, can then be used:

$$L(x) \sim 1 - 2 \left(\frac{\pi}{3} \right)^{1/2} \left(\frac{x}{2} \right)^{1/3} \exp \left[-\frac{3}{2} \left(\frac{x}{2} \right)^{2/3} \right] \left[C \cos \left(\theta - \frac{\pi}{6} \right) - D \sin \left(\theta - \frac{\pi}{6} \right) \right], \quad (\text{A.13})$$

$$T(x) \sim 2 \left(\frac{\pi}{3} \right)^{1/2} \left(\frac{x}{2} \right)^{1/3} \exp \left[-\frac{3}{2} \left(\frac{x}{2} \right)^{2/3} \right] \left[C \sin \left(\theta - \frac{\pi}{6} \right) + D \cos \left(\theta - \frac{\pi}{6} \right) \right], \quad (\text{A.14})$$

where

$$\theta = 3^{1/2} \frac{3}{2} \left(\frac{x}{2} \right)^{2/3}, \quad (\text{A.15})$$

$$C = 1 + \frac{5}{72} \left(\frac{2}{x} \right)^{2/3} + \frac{35}{432} \left(\frac{2}{x} \right)^{4/3} + \dots, \quad (\text{A.16})$$

$$D = 3^{1/2} \left[\frac{5}{72} \left(\frac{2}{x} \right)^{2/3} - \frac{35}{432} \left(\frac{2}{x} \right)^{4/3} + \dots \right]. \quad (\text{A.17})$$

These series give results to an accuracy of about 1% at $x = 5$, and better accuracy for $x > 5$. Because of their asymptotic nature, it does no good to take more terms than those shown; higher terms improve the accuracy only at large x , where it is not needed.

The foregoing expressions permit the easy calculation of $L(x)$ and $T(x)$ to about 1% accuracy or better. Greater accuracy can be obtained straightforwardly, but at the expense of substantially greater computational effort.

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