

# Theory of thermomagnetic effects in the transition regime

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A simple model is presented that describes the complex behavior of the magnetic field dependence of the thermal conductivity of a polyatomic gas as a function of the Knudsen number. The model treats the solid surface as one component of a gas mixture, and a first-order Chapman–Enskog solution is adequate to account for the thermomagnetic effects in single gases. The results provide an interpolation scheme between the continuum and Knudsen regimes, in the form of scaling rules in which the Knudsen number appears in the coefficients and arguments of the functions that describe the limiting cases. Good agreement is obtained with the available experimental data, and leads to the conclusion that different surface accommodation coefficients are needed for the translational and internal energies of the gas molecules. This conclusion is consistent with analysis of independent field-free conductivity data, and with independent vibrating-surface measurements.

## I. INTRODUCTION

The purpose of this paper is to show how the complex behavior of the magnetic field dependence of the thermal conductivity of a polyatomic gas in the transition region can be described by a simple model. This model describes the behavior over the range from the completely hydrodynamic regime to the completely collisionless free-molecule regime, and in principle allows the effects of molecule–molecule and molecule–surface collisions to be disentangled.

In a gas, the transport of mass, momentum, or energy along a gradient tends to produce a partial alignment of the angular momenta of the molecules responsible for the transport. This alignment can be destroyed by the imposition of an external magnetic (or electric) field, with the result that the transport coefficients show field dependences. These dependences, as well as the various field-induced cross effects that accompany them, are usually called Senftleben–Beenakker effects. Although small in magnitude (less than a percent or so), these effects can be measured with considerable precision, and have the important property of depending entirely on just the nonspherical part of the molecular force field. Many results are available.<sup>1–8</sup>

Partial alignment of momentum in a gradient can be produced both by collisions with other molecules and by collisions with solid surfaces. The former dominates in the continuum or hydrodynamic regime in which the Knudsen number is small, and the latter dominates in the free molecule or Knudsen regime in which the Knudsen number is large. In principle it is possible to study molecule–molecule collisions and molecule–surface collisions separately by working in either the completely hydrodynamic or the completely free-molecule regime, but in practice most measurements fall at least partly in the transition region where neither molecule–molecule nor molecule–surface collisions

are completely dominant. Because the dependence of the effects on field strength and on gas pressure are quite different in the two extreme regimes, the dependence in the transition region is typically quite complex.

The model covers the transition region by treating the solid surface as one component of a gas mixture. The dependence of a transport coefficient on the Knudsen number then comes from the dependence of the coefficient on the “mole fraction” of the solid component. The results take the form of scaling rules in which the Knudsen number appears in the arguments and coefficients of the functions that describe the field dependence of the effects in the hydrodynamic regime.<sup>9</sup> No expansion as power series in  $\text{Kn}$  or  $\text{Kn}^{-1}$  is involved, where  $\text{Kn}$  is the Knudsen number, although such expansions are easily developed if wanted. This is in contrast with more conventional approaches, which involve either corrections to the hydrodynamic results in powers of  $\text{Kn}$ ,<sup>10–12</sup> or corrections to the free-molecule results<sup>13</sup> in terms of powers of  $\text{Kn}^{-1}$ .<sup>14</sup>

In the cases so far treated in detail by this model—namely the viscomagnetic effects for single gases in a previous paper<sup>9</sup> and the effects on the thermal conductivity of single gases in the present paper—it has not been necessary to proceed beyond the Navier–Stokes level of hydrodynamic description and the first-order Chapman–Enskog type of solution of the Wang Chang–Uhlenbeck and Waldmann–Snider kinetic equations. In these cases the model gives in effect a first-order scheme for interpolation through the transition region. The influence of geometry, such as the shape of the container and the orientation of the field with respect to it, are put into the problem in standard ways before the model itself is invoked. Details of molecule–surface collisions need not be known, being absorbed into a small number of adjustable parameters, just as details of molecule–molecule collisions are absorbed into cross sections in the theory of the hydrodynamic regime.

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## II. KINETIC-THEORY MODEL

The aim of the model is to describe how the heat conduction in a stationary gas depends on the Knudsen number, both in the absence and presence of an external magnetic field. We begin with the field-free case to establish the description of the surface as one component of a gas mixture, and then proceed to a corresponding description of the field effects.

### A. Field-free conduction

The transport equation in the absence of a field is very simple (Fourier's law),

$$\mathbf{q} = -\lambda \nabla T, \tag{1}$$

where  $\mathbf{q}$  is the heat flux,  $\nabla T$  is the temperature gradient, and the thermal conductivity  $\lambda$  is a scalar. The kinetic-theory treatment of  $\lambda$  for a molecular gas is rather complicated, however, because the molecules transport energy both as translational energy and as internal (rotational) energy, and there is coupling between the two kinds of energy owing to inelastic molecular collisions. We must consider mixtures in the hydrodynamic regime, by which the effects of surface collisions are introduced.

#### 1. Hydrodynamic regime

For the treatment of the transition regime we need the expression for  $\lambda$  of a mixture in the hydrodynamic regime. The essential feature needed in this expression is the dependence of  $\lambda$  on the mixture composition, which is later translated into the dependence on Knudsen number. The fact that only the composition dependence is needed allows a useful simplification of the general mixture formulas. The general expression for  $\lambda$  of a mixture is complicated because it contains many new cross sections that describe inelastic collisions between unlike species. Fortunately, it has been found that these cross sections do not have much effect on the form of the dependence of  $\lambda$  on composition, but mainly change the overall magnitude of  $\lambda$  without changing the shape of the  $\lambda$  vs composition curve appreciably.<sup>15</sup> Thus a good approximation can be obtained by using the simple mixture formulas without inelastic collisions as interpolation formulas for the composition dependence, as long as the end points for the pure components are given correctly, either by an accurate theoretical formula<sup>15-17</sup> or by experiment. The same argument also justifies our using only the first approximation formulas for  $\lambda$ , and ignoring small correction terms involving the polarization of molecular angular momentum.<sup>18,19</sup>

For a mixture we can describe the total heat flux as a sum of contributions from each of the species  $i$  in the mixture,

$$\mathbf{q}_i = -\lambda_i \nabla T, \tag{2}$$

where the partial thermal conductivity due to species  $i$  nevertheless depends on all the species in the mixture because of collisions. The translational contribution to  $\lambda_i$  for a mixture of  $\nu + 1$  species (considering the surface as one species) is<sup>15</sup>

$$\lambda_{i, \text{tr}} = x_i \sum_{j=1}^{\nu+1} x_j \frac{|\Lambda|_{ji}}{|\Lambda|}, \tag{3}$$

in which the  $x$ 's are mole fractions,  $|\Lambda|$  is a determinant with elements  $\Lambda_{ik}$ , and  $|\Lambda|_{ki}$  is the cofactor of the element  $\Lambda_{ki}$  of the determinant. The elements are

$$\Lambda_{ii} = \frac{x_i^2}{(\lambda_{ii})_{\text{tr}}} + \frac{4}{25k} \sum_{j \neq i}^{\nu+1} \frac{x_i x_j}{(m_i + m_j)^2 n D_{ij}} \times \left[ \frac{1}{2} m_i^2 + \frac{1}{2} (\frac{5}{2} - \frac{1}{3} B_{ij}^*) m_j^2 + 4 m_i m_j A_{ij}^* \right], \tag{4a}$$

$$\Lambda_{ij} (i \neq j) = -\frac{4}{25k} \frac{m_i m_j}{(m_i + m_j)^2} \frac{x_i x_j}{n D_{ij}} \left[ \frac{5}{4} - 3 B_{ij}^* - 4 A_{ij}^* \right], \tag{4b}$$

where  $(\lambda_{ii})_{\text{tr}}$  is the translational thermal conductivity of pure species  $i$ ,  $n$  is the total number density,  $D_{ij}$  is the diffusion coefficient of species  $i$  and  $j$  in the mixture, and  $A_{ij}^*$  and  $B_{ij}^*$  are dimensionless ratios of effective cross sections whose numerical values are usually near unity.<sup>20</sup> The internal contribution to  $\lambda_i$  is<sup>15</sup>

$$\lambda_{i, \text{int}} = (\lambda_{ii})_{\text{int}} \left[ 1 + \sum_{j \neq i}^{\nu+1} \frac{x_j}{x_i} \frac{D_{ii}^{\text{int}}}{D_{ij}^{\text{int}}} \right]^{-1}, \tag{5}$$

where  $(\lambda_{ii})_{\text{int}}$  is the internal thermal conductivity of pure species  $i$ , and  $D_{ij}^{\text{int}}$  is the coefficient of diffusion for the internal energy associated with species  $i$  through molecules of species  $j$ . Notice that  $D_{ij}^{\text{int}}$  is not necessarily equal to  $D_{ji}^{\text{int}}$ . It is usually the case that  $D_{ij}^{\text{int}}$  is not much different from the diffusion coefficient  $D_{ij}$ , unless there is some mechanism whereby internal energy is easily transferred in glancing collisions.<sup>15,16</sup>

The foregoing results enable us to describe heat conduction in the transition regime by considering the surface as one species in the mixture.

#### 2. Transition regime

We now let species  $\nu + 1$  represent the surface (denoted by a subscript  $s$ ), and impose the following conditions:

(1) The surface makes no direct contribution to the thermal conductivity:  $\lambda_s = 0$ .

(2) The surface "molecules" are much heavier than the real molecules:  $m_s \gg m_i$ .

(3) The quantities  $n$  and  $x_i$  appearing in the formulas are not the actual gas number density and mole fractions, but include the surface species in the counting. Using primes when the surface species are included and dropping the primes when only actual gas molecules are included, we write

$$n' = n + n_s, \quad x'_i = x_i (n/n'). \tag{6}$$

(4) Whatever counting is used, the binary collision assumption requires that<sup>21,22</sup>

$$n' D'_{ij} = n D_{ij} \tag{7}$$

and similarly for  $D_{ij}^{\text{int}}$ .

Inserting these conditions into Eqs. (3)–(5) for  $\lambda_i$ , we find that  $\Lambda_{is} = 0$  because  $m_i/m_s = 0$ . This allows  $\Lambda_{ss}$  to be factored out of the determinants in Eq. (3), whereby it cancels between numerator and denominator. Similarly, the factors of  $n/n'$  that appear when  $x'_i$  is converted to  $x_i$  cancel between numerators and denominators in Eqs. (3) and (5).

The net result of the above conditions on the surface species is that Eq. (3) for  $\lambda_{i\text{tr}}$  has the same formal appearance as the continuum formula in which the surface species is neglected; the only effect of the surface species is to contribute one extra term to the summation in each of the  $\Lambda_{ii}$ . Similarly, the only effect of the surface species on  $\lambda_{i\text{int}}$  is to contribute one extra term to the summation in Eq. (5).

The case of particular interest here is a single gas plus the surface species. For the translational contribution we obtain

$$\lambda_{\text{tr}} = \lambda_{i\text{tr}} = x_i^2 / \Lambda_{ii}, \quad (8a)$$

with

$$\Lambda_{ii} = \frac{x_i^2}{(\lambda_{ii})_{\text{tr}}} + \frac{2}{5k} \left( \frac{5}{2} - \frac{6}{5} B_{is}^* \right) \frac{x_i x_s}{nD_{is}} \quad (8b)$$

and for the internal contribution we obtain

$$\lambda_{\text{int}} = \lambda_{i\text{int}} = (\lambda_{ii})_{\text{int}} \left[ 1 + \frac{x_s}{x_i} \frac{D_{ii}^{\text{int}}}{D_{is}^{\text{int}}} \right]^{-1}. \quad (9)$$

These expressions all contain the number density of surface species  $n_s$  and, through  $D_{is}$ , cross sections for gas-surface collisions,  $\sigma_{is}$ . The precise physical interpretation given to these quantities is unimportant, because they always occur in the combination  $n_s \sigma_{is}$  and are absorbed into phenomenological coefficients that are determined separately. For concreteness, however, one can think of the surface as covered by these surface molecules.

In particular, the above expressions can be written in terms of a Knudsen diffusion coefficient  $D_{iK}$  for species  $i$ , defined as<sup>21</sup>

$$D_{iK} \equiv (n/n_s) D_{is}. \quad (10)$$

The Knudsen diffusion coefficients must ultimately be found experimentally, but free-molecule calculations for various geometric arrangements show that  $D_{iK}$  is always of the form<sup>23</sup>

$$D_{iK} \propto \bar{v} d, \quad (11)$$

where  $\bar{v}$  is the mean molecular speed and  $d$  is a geometric quantity such as a tube diameter or plate spacing. We can further extract a mean free path  $l$  from  $(\lambda_{ii})_{\text{tr}}$ , for which elementary kinetic theory gives the form,<sup>24</sup>

$$(\lambda_{ii})_{\text{tr}} \propto kn\bar{v}l. \quad (12)$$

The Knudsen number  $l/d$  will therefore appear in this model through the dimensionless group

$$(\lambda_{ii})_{\text{tr}} / knD_{iK} \propto \text{Kn}. \quad (13)$$

The behavior of the translational thermal conductivity in the transition regime can thus be written as

$$\lambda_{\text{tr}} = (\lambda_{ii})_{\text{tr}} \left[ 1 + \frac{2}{5} \left( \frac{5}{2} - \frac{6}{5} B_{is}^* \right) \frac{(\lambda_{ii})_{\text{tr}}}{knD_{iK}} \right]^{-1} \quad (14)$$

or

$$\lambda_{\text{tr}} = \frac{\lambda_{\text{tr}}^0}{1 + a_{\text{tr}} \text{Kn}}, \quad (15a)$$

where  $\lambda_{\text{tr}}^0 = (\lambda_{ii})_{\text{tr}}$  is the translational thermal conductivity

of the gas in the continuum regime ( $\text{Kn} = 0$ ), and

$$a_{\text{tr}} \text{Kn} \equiv \frac{2}{5} \left( \frac{5}{2} - \frac{6}{5} B_{is}^* \right) \frac{\lambda_{\text{tr}}^0}{knD_{iK}}. \quad (15b)$$

Similarly, the behavior of the internal conductivity in the transition regime can be written as

$$\lambda_{\text{int}} = (\lambda_{ii})_{\text{int}} \left[ 1 + \frac{D_{ii}^{\text{int}}}{D_{iK}^{\text{int}}} \right]^{-1}, \quad (16)$$

or

$$\lambda_{\text{int}} = \frac{\lambda_{\text{int}}^0}{1 + a_{\text{int}} \text{Kn}}, \quad (17a)$$

where  $\lambda_{\text{int}}^0 = (\lambda_{ii})_{\text{int}}$  is the internal thermal conductivity of the gas in the continuum regime ( $\text{Kn} = 0$ ), and

$$a_{\text{int}} \text{Kn} \equiv D_{ii}^{\text{int}} / D_{iK}^{\text{int}}. \quad (17b)$$

The total thermal conductivity in the transition regime is therefore

$$\lambda = \frac{\lambda_{\text{tr}}^0}{1 + a_{\text{tr}} \text{Kn}} + \frac{\lambda_{\text{int}}^0}{1 + a_{\text{int}} \text{Kn}}, \quad (18)$$

or if  $a_{\text{tr}}$  and  $a_{\text{int}}$  are not too different,

$$\lambda \approx \frac{\lambda^0}{1 + a \text{Kn}}, \quad (19)$$

where  $\lambda^0 = \lambda_{\text{tr}}^0 + \lambda_{\text{int}}^0$ , and  $a$  is some average of  $a_{\text{tr}}$  and  $a_{\text{int}}$ .

The above expressions for the behavior of  $\lambda$  in the transition region are not new, although this is the first time they have been derived from this particular model. A simple temperature-jump calculation gives Eq. (19) with<sup>25</sup>

$$a = \frac{2 - \alpha}{\alpha} \frac{4}{\gamma + 1} \frac{m\lambda^0}{\eta c_v}, \quad (20)$$

where  $\alpha$  is the accommodation coefficient for energy,  $\gamma = c_p / c_v$ ,  $c_v = c_{\text{tr}} + c_{\text{int}}$ ,  $c_{\text{tr}}$  is the translational heat capacity (per molecule),  $c_{\text{int}}$  is the internal heat capacity, and  $\eta$  is the viscosity,

$$\eta = \frac{1}{2} nm(\bar{v}/2^{1/2})l, \quad (21)$$

in which the factor of  $2^{1/2}$  gives the conversion from mean relative speed to mean speed. The dimensionless ratio  $m\lambda^0 / \eta c_v$ , called the Eucken factor, ranges from 2.50 for atoms to about 1.5 for polyatomic molecules.<sup>25</sup> More elaborate kinetic-theory calculations by a variety of methods give Eqs. (18) and (19) as first approximations, and in higher approximations usually give expressions involving ratios of polynomials in  $\text{Kn}$ .<sup>26-31</sup> All calculations of course reduce to  $\lambda \propto \text{Kn}^{-1}$  in the free-molecule limit. A surprising result of these calculations is that the very simple Eq. (19), with the single parameter  $a$  treated as adjustable, gives a remarkably accurate representation of the results, as will be demonstrated below. This gives us some assurance that the simplifications we have made in obtaining Eq. (18) will not have serious consequences.

It must be emphasized that the present model does not give a method to calculate  $a_{\text{tr}}$  and  $a_{\text{int}}$  from first principles. Such calculations must be based on a more detailed theory that describes the molecule-surface interactions. In particular, the model does not treat any details of surface accommo-

dation. The *ad hoc* introduction of accommodation coefficients modifies the results to<sup>25</sup>

$$a_{tr} = \frac{2 - \alpha_{tr}}{\alpha_{tr}} a_{tr}^0, \quad (22a)$$

$$a_{int} = \frac{2 - \alpha_{int}}{\alpha_{int}} a_{int}^0, \quad (22b)$$

where  $\alpha_{tr}$  and  $\alpha_{int}$  are the accommodation coefficients for translational and internal energy, respectively, and the superscripts 0 on the  $a$ 's denote their values for  $\alpha = 1$ . Nevertheless, it is reasonable to expect that the model can yield a fairly reliable value for the ratio of  $a_{int}^0$  to  $a_{tr}^0$ . To put this ratio in simple form, we use the relations,

$$\lambda_{tr}^0 = \frac{5}{2} \eta c_{tr} / m, \quad (23a)$$

$$nmD_{ii} / \eta = \frac{5}{2} A_{ii}^*, \quad (23b)$$

where  $D_{ii}$  is the self-diffusion coefficient of species  $i$ , and  $A_{ii}^*$  is a dimensionless ratio of two effective cross sections for molecule-molecule collisions.<sup>20</sup> We then find that

$$\frac{a_{int}^0}{a_{tr}^0} = \frac{4}{5} A_{ii}^* \left( \frac{5}{2} - \frac{6}{5} B_{is}^* \right)^{-1} \left( \frac{D_{ii}^{int}}{D_{ii}} \right) \left( \frac{D_{iK}}{D_{iK}^{int}} \right), \quad (24a)$$

in which all of the dimensionless ratios are about unity. Since the ratios  $A^*$  and  $B^*$  are usually somewhat greater than unity,<sup>20</sup> we take the plausible values of  $A_{ii}^* \approx 9/8$  and  $B_{is}^* \approx 5/4$  to make the formula simple; we also take the ratios of the  $D$ 's as unity, and find

$$a_{int}^0 / a_{tr}^0 \approx 0.90. \quad (24b)$$

This is a reasonable value to use when fitting experimental data; the fit will not be sensitive to this value, since deviations can automatically be compensated by a change in  $\alpha_{int}$ .

We can further obtain useful estimates of  $a_{tr}^0$  and  $a_{int}^0$  separately, by adopting the temperature-jump formula of Eq. (20) for just the translational contribution to the parameter  $a$ . That is, we carry out a temperature-jump calculation for just the translational contribution to  $\lambda$ . Then we have  $\gamma = 5/3$ ,  $m\lambda_{tr}^0 / \eta c_{tr} = 5/2$ , and

$$a_{tr}^0 \approx 15/4. \quad (25a)$$

Combining this result with Eq. (24b), we find

$$a_{int}^0 \approx 3.4 \quad (25b)$$

These are reasonable values to use in fitting experimental data, since any deviations will be absorbed in  $\alpha_{tr}$  and  $\alpha_{int}$ .

Another relation useful in fitting data is

$$\frac{\lambda_{int}^0}{\lambda_{tr}^0} \approx \frac{nmD_{ii}^{int}c_{int}}{\frac{5}{2}\eta c_{tr}} = \frac{12}{25} A_{ii}^* \left( \frac{c_{int}}{c_{tr}} \right) \left( \frac{D_{ii}^{int}}{D_{ii}} \right). \quad (26)$$

Using the same plausible numerical values for  $A_{ii}^*$  and the ratio of the  $D$ 's as above, we find

$$\frac{\lambda_{int}^0}{\lambda_{tr}^0} \approx \frac{27}{50} \frac{c_{int}}{c_{tr}}, \quad (27)$$

which is equal to 0.36 for a diatomic gas.

We can compare the foregoing formulas with the experimental measurements of Teagan and Springer<sup>26</sup> on the heat conduction of nitrogen between parallel plates in the transition regime. The measurements are reported as the ratio

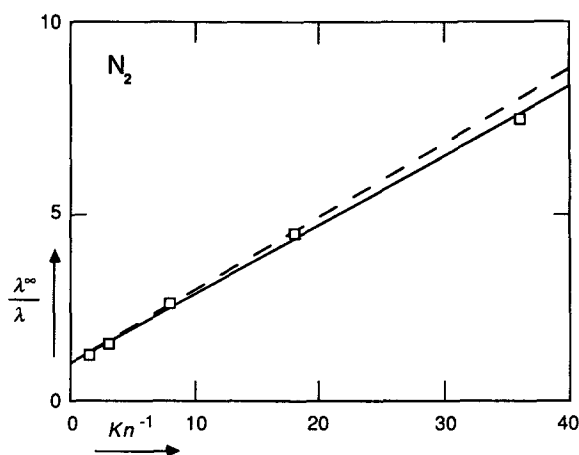


FIG. 1. Field-free thermal conductivity of  $N_2$  in the transition region (measurements of Teagan and Springer). The dashed line is the fit according to Eq. (19) with  $a = 5.17$ , and the solid curve is the fit according to Eq. (18) with  $a_{tr} = 5.0$  and  $a_{int}/a_{tr} = 20$ .

$\lambda / \lambda^\infty$ , where  $\lambda^\infty$  is the free-molecule effective conductivity ( $Kn = \infty$ ). We can rearrange Eq. (19) into the form

$$\frac{\lambda^\infty}{\lambda} = 1 + \frac{1}{aKn}, \quad (28)$$

from which we are led to expect that a plot of  $\lambda^\infty / \lambda$  vs  $Kn^{-1}$  should be nearly a straight line. Such a plot is shown in Fig. 1. Teagan and Springer fitted their measurements with this equation (among others), taking  $m\lambda^0 / \eta c_v = 1.90$  and  $\alpha = 0.76$  or  $a = 5.17$ . Although the measurements are rather well represented by this straight line, which is shown dashed in Fig. 1, they show small systematic deviations from it. The measurements can be fitted somewhat more accurately by Eq. (18) with  $a_{tr} = 5.0$  and  $a_{int}/a_{tr} = 20$ , assuming  $\lambda_{int}^0 / \lambda_{tr}^0 = 0.36$  as above; this equation is shown as the solid curve in Fig. 1. It is of course not surprising that Eq. (18) with two parameters gives a better fit than Eq. (19) with only one parameter. Nevertheless, the values obtained for the two parameters of Eq. (18) are physically reasonable. The corresponding accommodation coefficients are  $\alpha_{tr} = 0.86$ , and  $\alpha_{int} = 0.065$  if  $a_{int}^0 / a_{tr}^0$  is taken as 0.90. The value of  $\alpha_{tr}$  near unity is not surprising.<sup>25</sup> The striking result is the small value of the ratio  $\alpha_{int} / \alpha_{tr} = 0.076$ , indicating that internal energy is much less easily transferred to the surface by collisions than is translational energy; this was not suggested by older measurements of thermal conductivity.<sup>25</sup> However, recent measurements by a vibrating-surface technique with  $N_2$  on several metal surfaces put this ratio at about 0.1, and the value of  $\alpha_{int}$  in the range 0.03–0.11,<sup>32</sup> which is remarkably good agreement. However, our actual numerical values should not be taken too literally, because  $a_{tr}$  can be varied by about 20% and  $a_{int}$  by about 50% without significantly spoiling the fit of the measurements. Even so,  $a_{tr}$  cannot be reduced as low as 15/4, implying that  $\alpha_{tr}$  must be less than unity.

The foregoing details on curve fitting are relatively unimportant—the essential point is that the present model gives a satisfactory account of field-free heat conduction in the transition regime with at most two adjustable parameters of reasonable magnitude.

## B. Field effects

Application of an external magnetic field converts the thermal conductivity and diffusion coefficients from scalars to tensors of rank two with three independent components,

$$\lambda^0 = \begin{pmatrix} \lambda^\perp & -\lambda^{\text{tr}} & 0 \\ \lambda^{\text{tr}} & \lambda^\perp & 0 \\ 0 & 0 & \lambda^\parallel \end{pmatrix}, \quad D = \begin{pmatrix} D^\perp & -D^{\text{tr}} & 0 \\ D^{\text{tr}} & D^\perp & 0 \\ 0 & 0 & D^\parallel \end{pmatrix}, \quad (29)$$

where, for example,  $\lambda^\perp$  is the thermal conductivity when the field is perpendicular to  $\nabla T$ . The coefficients  $\lambda^{\text{tr}}$  and  $D^{\text{tr}}$  only enter into the description of the flux induced *transverse* to the temperature gradient by the magnetic field, and are not considered further in this paper; except for Eq. (29), the notation "tr" indicates molecular translational motion. The heat flux thus changes slightly by  $\delta q$  when the field is switched on. To first order,  $\delta q$  can be found by taking the variation of the transport Eq. (1) with  $\lambda$  given by Eqs. (18) or (19), holding  $\nabla T$  constant. Using Eq. (19) for  $\lambda$  we obtain the result

$$\frac{\delta q}{q} = -\frac{\delta \lambda}{\lambda} = -\frac{1}{1 + a\text{Kn}} \left( \frac{\delta \lambda^0}{\lambda^0} + a\text{Kn} \frac{\delta D_K}{D_K} \right). \quad (30)$$

The last term arises because  $a$  is proportional to  $\lambda^0/D_K$ . The same result is obtained if  $q$  is held constant and the change in  $\nabla T$  is measured. If we treat the translational and internal contributions separately and use Eq. (18) for  $\lambda$ , we obtain a similar but more complicated result,

$$\frac{\delta q}{q} = -\frac{\delta \lambda}{\lambda} = -\frac{(\lambda_{\text{tr}}/\lambda)}{1 + a_{\text{tr}}\text{Kn}} \left( \frac{\delta \lambda_{\text{tr}}^0}{\lambda_{\text{tr}}^0} + a_{\text{tr}}\text{Kn} \frac{\delta D_K}{D_K} \right) - \frac{(\lambda_{\text{int}}/\lambda)}{1 + a_{\text{int}}\text{Kn}} \left( \frac{\delta \lambda_{\text{int}}^0}{\lambda_{\text{int}}^0} + a_{\text{int}}\text{Kn} \frac{\delta D_K^{\text{int}}}{D_K^{\text{int}}} \right), \quad (31)$$

which reduces to Eq. (30) if  $a_{\text{tr}} = a_{\text{int}}$ . These results have the same form whether the field is applied perpendicular or parallel to the temperature gradient. In particular,  $\delta \lambda^0$  refers to either  $\lambda^\perp$  or  $\lambda^\parallel$ , and  $\delta D_K$  to either  $D_K^\perp$  or  $D_K^\parallel$ .

Equations (30) and (31) show only how the presence of the surface manifests itself through its influence on the field-free thermal conductivity. In other words, these are the Knudsen effects that will appear regardless of the details of the magnetic-field phenomena. This can be made obvious by setting the  $a$ 's equal to zero, which makes all the explicit Knudsen effects vanish. Since the  $a$ 's have nothing to do with the magnetic field, it is evident that the Knudsen effects in Eqs. (30) and (31) also do not. To include the Knudsen effects on the magnetic-field phenomena, we must again invoke the model to obtain expressions for the dependence of  $\delta \lambda^0/\lambda^0$  and  $\delta D_K/D_K$  on Kn.

### 1. General formulas

The general expressions for  $\delta \lambda^0/\lambda^0$ , whether translational or internal, are of the form<sup>7</sup>

$$\left( \frac{\delta \lambda^0}{\lambda^0} \right)^\perp = \frac{\lambda^\perp - \lambda^0}{\lambda^0} = -\psi_{12} [f(\xi_{12}) + 2f(2\xi_{12})] + \psi_{11} f(\xi_{11}), \quad (32)$$

$$\left( \frac{\delta \lambda^0}{\lambda^0} \right)^\parallel = \frac{\lambda^\parallel - \lambda^0}{\lambda^0} = -2\psi_{12} f(\xi_{12}) + 2\psi_{11} f(\xi_{11}), \quad (33)$$

where the field-dependent function is

$$f(\xi) = \xi^2 / (1 + \xi^2). \quad (34)$$

These expressions contain two types of polarization, denoted as 12 and 11, which seem to be the minimum required to account for the continuum results on  $N_2$  and CO (although  $\psi_{11} \ll \psi_{12}$ ).<sup>7</sup> The field parameters  $\psi$  and  $\xi$  for a binary mixture (in this case, gas  $i$  and surface  $s$ ) are<sup>9,33,34</sup>

$$\psi_{12} = \frac{x_i \bar{v}_{ii} \sigma_{ii} (12 \text{ prod})^2}{2\sigma_{ii}(\lambda) S_{12}(\text{decay})}, \quad (35)$$

$$\xi_{12} = \frac{(\text{const})(B/p)x_i}{S_{12}(\text{decay})}, \quad (36)$$

with similar expressions for  $\psi_{11}$  and  $\xi_{11}$ . Here  $B$  is the magnetic field strength,  $p$  is the gas pressure,  $S_{12}(\text{decay})$  is a decay factor given by

$$S_{12}(\text{decay}) = x_i \bar{v}_{ii} \sigma_{ii} (12 \text{ decay}) + x_s \bar{v}_{is} \sigma_{is} (12 \text{ decay}), \quad (37)$$

in which  $\bar{v}_{ii}$  and  $\bar{v}_{is}$  are average relative speeds given by

$$\bar{v}_{ij} = (8kT/\pi\mu_{ij})^{1/2}, \quad (38)$$

$\mu_{ij}$  being the reduced mass. In  $\psi_{12}$  the cross section  $\sigma_{ii}$  (12 prod) represents the production of the 12 polarization by  $ii$  (molecule-molecule) collisions, and  $\sigma_{ii}(\lambda)$  is the cross section related to the field-free thermal conductivity. In  $S_{12}(\text{decay})$  the cross sections  $\sigma_{ii}$  (12 decay) and  $\sigma_{is}$  (12 decay) represent the decay of the 12 polarization by molecule-molecule and molecule-surface collisions, respectively.

It is convenient to again eliminate the product  $n_s \sigma_{is}$  and parameterize  $\psi$  and  $\xi$  in terms of the Knudsen number by defining a dimensionless parameter  $b_{12}$  as

$$b_{12}\text{Kn} \equiv \frac{n_s kT \sigma_{is} (12 \text{ decay})}{2^{1/2} p \sigma_{ii} (12 \text{ decay})}. \quad (39)$$

The Knudsen number is to be calculated as  $\text{Kn} \equiv l/d$ , with  $l$  obtained from the viscosity according to Eq. (21). The dependence of  $\psi$  and  $\xi$  on Kn can then be written explicitly as

$$\psi_{12} = \frac{\psi_{12}^0}{1 + b_{12}\text{Kn}}, \quad (40)$$

$$\xi_{12} = \frac{\xi_{12}^0}{1 + b_{12}\text{Kn}}, \quad (41)$$

where, as usual, the superscript 0 denotes the limiting continuum result at  $\text{Kn} = 0$ . Explicit expressions for  $\psi_{12}^0$  and  $\xi_{12}^0$  can be obtained by setting  $x_i = 1$ ,  $x_s = 0$  in Eqs. (35)–(37). Similar expressions hold for  $\psi_{11}$  and  $\xi_{11}$ .

The foregoing expressions are those in which the translational and internal contributions to the thermal conductivity have been combined.<sup>33</sup> If the more complicated formulas are used, in which the translational and internal contributions are kept separate, it is obvious by inspection of the

formulas that the production cross sections are different for the translational and internal contributions, but that the decay cross sections are unchanged. The result is that  $\xi$  is unchanged, but  $\psi_{12}^0$  in Eq. (40) is replaced by  $\psi_{12}^{tr}$  or  $\psi_{12}^{int}$ , so that Eqs. (32) and (33) take the forms

$$\frac{\delta\lambda_{tr}^0}{\lambda_{tr}^0} \sim \frac{\psi_{12}^{tr}}{1 + b_{12} \text{Kn}}, \quad (42a)$$

$$\frac{\delta\lambda_{int}^0}{\lambda_{int}^0} \sim \frac{\psi_{12}^{int}}{1 + b_{12} \text{Kn}}, \quad (42b)$$

with similar expressions involving  $\psi_{11}^{tr}$  and  $\psi_{11}^{int}$ .

It remains to consider the effect of the magnetic field on the parameters  $\psi^{tr}$ ,  $\psi^{int}$ , and  $b$ . The cross section most likely to be affected by a magnetic field is  $\sigma_{is}$  (12 decay), which is the only one involving molecule-surface collisions. The molecular precession induced by the magnetic field seems likely to affect the nature of the surface collisions,<sup>13</sup> but not the gas collisions (on the average). Hence  $\psi^{tr}$  and  $\psi^{int}$  would not depend on the field orientation, but  $b$  could take on different values, such as  $b^\perp$  and  $b^\parallel$ . Experimental results in the near-continuum regime support this view.<sup>8</sup>

We turn next to the terms  $\delta D_K/D_K$  and  $\delta D_K^{int}/D_K^{int}$  in Eq. (31). Since their expressions are of the same form, we consider them together. For simplicity, we assume that only one type of polarization contributes to  $\delta D_K/D_K$ ; this assumption is easily removed. It is the polarization produced by the surface collisions that appears in  $\delta D_K/D_K$ , which has the form,

$$\delta D_K/D_K = -\psi_{pq} L_{pq}(\xi_{pq}, \alpha), \quad (43)$$

where possible forms of the field-dependent function  $L_{pq}(\xi_{pq}, \alpha)$  have been discussed and classified.<sup>13,35</sup> This function depends parametrically on the accommodation coefficients  $\alpha$ . Whatever this function may be, the field parameters  $\psi_{pq}$  and  $\xi_{pq}$  for a binary mixture will have the forms<sup>9</sup>

$$\psi_{pq} = \frac{(\text{const})x_s \bar{v}_{is} \sigma_{is}(pq \text{ prod})^2}{\sigma_{is}(D) S_{pq}(\text{decay})}, \quad (44)$$

$$\xi_{pq} = \frac{(\text{const})(B/p)x_i}{S_{pq}(\text{decay})}, \quad (45)$$

$$S_{pq}(\text{decay}) = x_i \bar{v}_{ii} \sigma_{ii}(pq \text{ decay}) + x_s \bar{v}_{is} \sigma_{is}(pq \text{ decay}), \quad (46)$$

in which  $\sigma_{is}(pq \text{ prod})$  is the cross section that describes the production of  $pq$  polarization due to molecule-surface collisions,  $\sigma_{is}(D)$  is the cross section related to the field-free Knudsen diffusion coefficient  $D_K$ , and  $\sigma_{ii}(pq \text{ decay})$  and  $\sigma_{is}(pq \text{ decay})$  are the cross sections that describe the decay of the surface-produced  $pq$  polarization by molecule-molecule and molecule-surface collisions, respectively. We again eliminate  $n_s \sigma_{is}$  and parametrize these results in terms of Kn by defining a dimensionless parameter  $b_{pq}$  as

$$b_{pq} \text{Kn} \equiv \frac{n_s kT}{2^{1/2} p} \frac{\sigma_{is}(pq \text{ decay})}{\sigma_{ii}(pq \text{ decay})}, \quad (47)$$

which yields

$$\psi_{pq} = \frac{b_{pq} \psi_{pq}^\infty \text{Kn}}{1 + b_{pq} \text{Kn}}, \quad (48)$$

$$\xi_{pq} = \frac{\xi_{pq}^0}{1 + b_{pq} \text{Kn}}, \quad (49)$$

where  $\psi_{pq}^\infty$  is the constant limiting value of  $\psi_{pq}$  in the Knudsen regime ( $\text{Kn} \rightarrow \infty$ ), obtained by setting  $x_i = 0$ ,  $x_s = 1$  in Eqs. (44) and (46), and  $\xi_{pq}^0$  is the limiting form of  $\xi_{pq}$  in the continuum regime ( $\text{Kn} = 0$ ), obtained by setting  $x_i = 1$ ,  $x_s = 0$  in Eqs. (45) and (46).

The orientation of the magnetic field is presumed, as before, to possibly affect only the molecule-surface cross section  $\sigma_{is}$ .

The result for  $\delta D_K/D_K$  thus has the form

$$\frac{\delta D_K}{D_K} = -\frac{b_{pq} \psi_{pq}^\infty \text{Kn}}{1 + b_{pq} \text{Kn}} L_{pq}(\xi_{pq}, \alpha). \quad (50)$$

Other forms are obtained by simply adding subscripts "tr" and "int" to  $\psi_{pq}^\infty$  and  $\alpha$ , or superscripts  $\perp$  and  $\parallel$  where needed. Additional types of surface-produced polarization merely produce further terms of the same general form.

Combining the foregoing results and substituting them into Eq. (31), we obtain the final formulas,

$$\begin{aligned} \frac{\delta q^\perp}{q} = & \frac{(\lambda_{tr}/\lambda)}{1 + a_{tr} \text{Kn}} \left[ \frac{\psi_{12}^{tr}}{1 + b_{12}^\perp \text{Kn}} \{f(\xi_{12}^\perp) + 2f(2\xi_{12}^\perp)\} - \frac{\psi_{11}^{tr}}{1 + b_{11}^\perp \text{Kn}} f(\xi_{11}^\perp) \right. \\ & \left. + \frac{a_{tr} b_{pq}^\perp (\psi_{pq}^\infty)_{tr}^\perp (\text{Kn})^2}{1 + b_{pq}^\perp \text{Kn}} L_{pq}^\perp(\xi_{pq}^\perp, \alpha_{tr}) \right] \\ & + \frac{(\lambda_{int}/\lambda)}{1 + a_{int} \text{Kn}} \left[ \frac{\psi_{12}^{int}}{1 + b_{12}^\perp \text{Kn}} \{f(\xi_{12}^\perp) + 2f(2\xi_{12}^\perp)\} - \frac{\psi_{11}^{int}}{1 + b_{11}^\perp \text{Kn}} f(\xi_{11}^\perp) \right. \\ & \left. + \frac{a_{int} b_{pq}^\perp (\psi_{pq}^\infty)_{int}^\perp (\text{Kn})^2}{1 + b_{pq}^\perp \text{Kn}} L_{pq}^\perp(\xi_{pq}^\perp, \alpha_{int}) \right], \quad (51) \end{aligned}$$

$$\begin{aligned} \frac{\delta q^\parallel}{q} = & \frac{(\lambda_{tr}/\lambda)}{1 + a_{tr} \text{Kn}} \left[ \frac{2\psi_{12}^{tr}}{1 + b_{12}^\parallel \text{Kn}} f(\xi_{12}^\parallel) - \frac{2\psi_{11}^{tr}}{1 + b_{11}^\parallel \text{Kn}} f(\xi_{11}^\parallel) + \frac{a_{tr} b_{pq}^\parallel (\psi_{pq}^\infty)_{tr}^\parallel (\text{Kn})^2}{1 + b_{pq}^\parallel \text{Kn}} L_{pq}^\parallel(\xi_{pq}^\parallel, \alpha_{tr}) \right] \\ & + \frac{(\lambda_{int}/\lambda)}{1 + a_{int} \text{Kn}} \left[ \frac{2\psi_{12}^{int}}{1 + b_{12}^\parallel \text{Kn}} f(\xi_{12}^\parallel) - \frac{2\psi_{11}^{int}}{1 + b_{11}^\parallel \text{Kn}} f(\xi_{11}^\parallel) + \frac{a_{int} b_{pq}^\parallel (\psi_{pq}^\infty)_{int}^\parallel (\text{Kn})^2}{1 + b_{pq}^\parallel \text{Kn}} L_{pq}^\parallel(\xi_{pq}^\parallel, \alpha_{int}) \right], \quad (52) \end{aligned}$$

where

$$\xi_{ij}^{\perp,\parallel} = \frac{\xi_{ij}^0}{1 + b_{ij}^{\perp,\parallel} \text{Kn}} \tag{53}$$

If the translational and internal energies do not need to be treated separately, these formulas reduce to

$$\begin{aligned} \frac{\delta q^{\perp}}{q} (1 + a \text{Kn}) &= \frac{\psi_{12}^0}{1 + b_{12}^{\perp} \text{Kn}} [f(\xi_{12}^{\perp}) + 2f(2\xi_{12}^{\perp})] \\ &\quad - \frac{\psi_{11}^0}{1 + b_{11}^{\perp} \text{Kn}} f(\xi_{11}^{\perp}) \\ &\quad + \frac{ab_{pq}^{\perp} (\psi_{pq}^{\infty})^{\perp} (\text{Kn})^2}{1 + b_{pq}^{\perp} \text{Kn}} L_{pq}^{\perp}(\xi_{pq}^{\perp}, \alpha), \end{aligned} \tag{54}$$

with an analogous expression for  $\delta q^{\parallel}/q$ .

Although the above formulas seem to contain a very large number of parameters, many of them can be found from independent measurements made in the near-continuum and continuum regimes. Very few remain to be adjusted to fit the transition regime itself. To exhibit this behavior, we consider several limiting cases before proceeding to a comparison with experimental data.

### 2. Limiting cases

We first check that Eqs. (51)–(53) reduce to the known continuum and Knudsen limits. When  $\text{Kn} = 0$ , we obtain

$$\delta q^{\perp}/q \rightarrow \psi_{12}^0 [f(\xi_{12}^0) + 2f(2\xi_{12}^0)] - \psi_{11}^0 f(\xi_{11}^0), \tag{55}$$

$$\delta q^{\parallel}/q \rightarrow 2\psi_{12}^0 f(\xi_{12}^0) - 2\psi_{11}^0 f(\xi_{11}^0), \tag{56}$$

where

$$\psi_{12}^0 = \frac{\lambda_{\text{tr}}^0}{\lambda^0} \psi_{12}^{\text{tr}} + \frac{\lambda_{\text{int}}^0}{\lambda^0} \psi_{12}^{\text{int}} = \frac{\sigma_{ii} (12 \text{ prod})^2}{2\sigma_{ii}(\lambda) \sigma_{ii} (12 \text{ decay})}, \tag{57}$$

$$\xi_{12}^0 = \frac{(\text{const}) m_i^{1/2} (B/p)}{\sigma_{ii} (12 \text{ decay})}, \tag{58}$$

with analogous expressions for  $\psi_{11}^0$  and  $\xi_{11}^0$ . Measurements at different values of  $B$  and  $p$  scale together as a function of the single variable  $B/p$ . These expressions agree with the known continuum results,<sup>7</sup> as given by Eqs. (32)–(36).

In the Knudsen limit, there seems to be no prospect with present data for distinguishing between  $\alpha_{\text{tr}}$  and  $\alpha_{\text{int}}$  in the functions  $L_{pq}(\xi_{pq}, \alpha)$ , so we will ignore this distinction. Then we obtain for  $\text{Kn} \rightarrow \infty$ ,

$$\delta q^{\perp,\parallel}/q \rightarrow (\psi_{pq}^{\infty})^{\perp,\parallel} L_{pq}^{\perp,\parallel}(\xi_{pq}^{\infty}, \alpha), \tag{59}$$

where

$$\begin{aligned} (\psi_{pq}^{\infty})^{\perp,\parallel} &= \frac{\lambda_{\text{tr}}^{\infty}}{\lambda^{\infty}} (\psi_{pq}^{\infty})_{\text{tr}}^{\perp,\parallel} + \frac{\lambda_{\text{int}}^{\infty}}{\lambda^{\infty}} (\psi_{pq}^{\infty})_{\text{int}}^{\perp,\parallel} \\ &= \frac{(\text{const}) \sigma_{is}^{\perp,\parallel} (\text{prod})^2}{\sigma_{is} (D) \sigma_{is}^{\perp,\parallel} (pq \text{ decay})}, \end{aligned} \tag{60}$$

$$\xi_{pq}^{\infty} = \frac{(\text{const}) m_i^{1/2} B}{\sigma_{is}^{\perp,\parallel} (pq \text{ decay})}. \tag{61}$$

Notice that the results are now independent of pressure and

depend only on  $B$ , in agreement with the known Knudsen results.<sup>13,35</sup>

These results show that measurements in the continuum limit can be used to determine the parameters  $\psi_{12}^0$  and  $\psi_{11}^0$ , and also the parameters contained in  $\xi_{12}^0$  and  $\xi_{11}^0$ . Similarly, measurements in the Knudsen limit can be used to determine  $\psi_{pq}^{\infty}$  and the parameters contained in  $\xi_{pq}^{\infty}$ . The individual translational and internal components of the  $\psi$ 's cannot be found from measurements in these limiting regions, but only their linear combinations, as in Eq. (57). Information on these components and on the  $b$ 's can be obtained from analysis of measurements in the near-continuum and near-Knudsen regions, to which we now turn.

For algebraic simplicity, we deal explicitly only with the saturation limit of high field strength. Most of the measurements in the transition region that are available for testing the present model are saturation results. At saturation,  $f(\xi) = 1$  and  $L_{pq}(\xi_{pq}, \alpha) = L_{pq}(\infty) = \text{const}$ . Expanding Eq. (51) in powers of  $\text{Kn}$  and keeping only the linear terms, we obtain

$$\begin{aligned} \left(\frac{\delta q^{\perp}}{q}\right)_{\text{sat}} &= (3\psi_{12}^0 - \psi_{11}^0) - [(3\psi_{12}^0 - \psi_{11}^0)(b_{12}^{\perp} + a_{\text{tr}}) \\ &\quad + \psi_{11}^0(b_{12}^{\perp} - b_{11}^{\perp})] \text{Kn} \\ &\quad + (a_{\text{int}} - a_{\text{tr}}) \frac{\lambda_{\text{int}}^0}{\lambda^0} [(3\psi_{12}^0 - \psi_{11}^0) \\ &\quad - 2(3\psi_{12}^{\text{int}} - \psi_{11}^{\text{int}})] \text{Kn} + \dots, \end{aligned} \tag{62}$$

where  $\psi^0$  is as defined by Eq. (57). From Eq. (52) we obtain similarly

$$\begin{aligned} \left(\frac{\delta q^{\parallel}}{q}\right)_{\text{sat}} &= 2(\psi_{12}^0 - \psi_{11}^0) - 2[(\psi_{12}^0 - \psi_{11}^0)(b_{12}^{\parallel} + a_{\text{tr}}) \\ &\quad + \psi_{11}^0(b_{12}^{\parallel} - b_{11}^{\parallel})] \text{Kn} \\ &\quad + 2(a_{\text{int}} - a_{\text{tr}}) \frac{\lambda_{\text{int}}^0}{\lambda^0} [(\psi_{12}^0 - \psi_{11}^0) \\ &\quad - 2(\psi_{12}^{\text{int}} - \psi_{11}^{\text{int}})] \text{Kn} + \dots. \end{aligned} \tag{63}$$

The first-order Knudsen deviations are often measured directly in order to correct the raw data to the continuum limit, and give information primarily on  $b_{12}$  and  $b_{11}$ .

To find the near-Knudsen behavior, we expand Eqs. (51) and (52) in powers of  $\text{Kn}^{-1}$  and keep only the linear terms, thereby obtaining

$$\begin{aligned} \left(\frac{\delta q^{\perp,\parallel}}{q}\right)_{\text{sat}} &= \Lambda_{\text{sat}}^{\perp,\parallel} \left[ 1 - \left( \frac{1}{b_{pq}^{\perp,\parallel}} + \frac{\lambda_{\text{tr}}^{\infty}}{a_{\text{tr}} \lambda^{\infty}} + \frac{\lambda_{\text{int}}^{\infty}}{a_{\text{int}} \lambda^{\infty}} \right) \text{Kn}^{-1} + \dots \right], \end{aligned} \tag{64}$$

where

$$\Lambda_{\text{sat}}^{\perp,\parallel} \equiv (\psi_{pq}^{\infty})^{\perp,\parallel} L^{\perp,\parallel}(\infty). \tag{65}$$

More specifically, the directly-measured ratio is

$$\left(\frac{\delta q^{\perp}}{\delta q^{\parallel}}\right)_{\text{sat}} = \frac{\Lambda_{\text{sat}}^{\perp}}{\Lambda_{\text{sat}}^{\parallel}} \left[ 1 - \left( \frac{1}{b_{pq}^{\perp}} - \frac{1}{b_{pq}^{\parallel}} \right) \text{Kn}^{-1} + \dots \right], \tag{66}$$

which gives a direct measure of the difference between  $b_{pq}^\perp$  and  $b_{pq}^\parallel$ .

We turn now to the use of these results in the analysis of experimental data in order to test the present model.

### III. COMPARISON WITH EXPERIMENT

The parameters to be determined are  $a_{tr}$ ,  $a_{int}$ ,  $\psi_{12}^{tr}$ ,  $\psi_{12}^{int}$ ,  $\psi_{11}^{tr}$ ,  $\psi_{11}^{int}$ ,  $b_{12}^\perp$ ,  $b_{12}^\parallel$ ,  $b_{11}^\perp$ ,  $b_{11}^\parallel$ ,  $\Lambda_{sat}^\perp$ ,  $\Lambda_{sat}^\parallel$ ,  $b_{pq}^\perp$ , and  $b_{pq}^\parallel$ , an overwhelming total of 14 parameters needed to test the present model in the transition regime. As remarked earlier, however, many are readily found from independent measurements. In particular,  $a_{tr}$  and  $a_{int}$  can be found in principle from field-free thermal conductivity measurements,  $\psi_{12}^0$  and  $\psi_{11}^0$  from the continuum limits,  $\Lambda_{sat}^\perp$  and  $\Lambda_{sat}^\parallel$  from the Knudsen limits, and the difference between  $b_{pq}^\perp$  and  $b_{pq}^\parallel$  from the near-Knudsen region. Further information is available from near-continuum measurements, but comes in somewhat more complicated form, as follows.

In the near-continuum region it is customary to represent the first-order Knudsen corrections by scaling the measurements according to the formulas<sup>4-6,8</sup>

$$\lambda = \lambda^0 (1 + K_\lambda/p)^{-1}, \quad (67)$$

$$\delta q/q = (\delta q^0/q^0) (1 + K_{\delta q}/p)^{-1}, \quad (68)$$

$$B/p = (B/p)^0 (1 + K_p/p), \quad (69)$$

where the superscript 0 denotes the continuum limit ( $\text{Kn} = 0$  or  $p \rightarrow \infty$ ). No distinction is made between  $a_{tr}$  and  $a_{int}$  in Eq. (67), since a single average value of  $a$  usually suffices to fit the field-free measurements, as was shown in Sec. II A 2. We can see that, except for a numerical factor that relates  $p$  and  $\text{Kn}$ , the coefficient  $K_\lambda$  is proportional to the coefficient  $a$ ,  $K_p$  is proportional to a combination of  $b_{12}$  and  $b_{11}$ , and  $K_{\delta q}$  is proportional to a rather complicated combination of coefficients according to Eqs. (62) and (63).

At this point we can make some simplifications by recognizing that the only measurements suitable for testing the present model are those for  $\text{N}_2$  and  $\text{CO}$  on a gold surface at

300 K by the Moscow group,<sup>8</sup> which cover essentially the entire transition region. Extensive measurements by the Leiden group<sup>4-7</sup> cover only the continuum and near-continuum region; although they furnish some parameter values, they do not test the model. Measurements involving  $\text{O}_2$  in the transition region<sup>36</sup> are very difficult to analyze because of the extra angular momentum carried by the electron spin in the triplet ground state.<sup>37</sup> For  $\text{N}_2$  and  $\text{CO}$  we can safely take  $b_{11}^\perp = b_{11}^\parallel$ , on the grounds that the 11 polarization is much less important than the 12 polarization and so the results are insensitive to the value of  $b_{11}^\perp$ . This is shown by the fact that

$$\left(\frac{\delta q^\perp}{\delta q^\parallel}\right)_{\text{sat}}^0 = \frac{3\psi_{12}^0 - \psi_{11}^0}{2(\psi_{12}^0 - \psi_{11}^0)} \quad (70)$$

differs only slightly from 3/2 (1.57 for  $\text{N}_2$  and 1.52 for  $\text{CO}$ ).<sup>4,8</sup> With this simplification we can identify the  $K$  coefficients of Eqs. (67)–(69) as

$$K_\lambda = (p\text{Kn})a, \quad (71)$$

$$K_p^\perp = (p\text{Kn})b_{12}^\perp, \quad (72)$$

$$K_{\delta q}^\perp = (p\text{Kn}) [b_{12}^\perp + a_{tr} - (a_{int} - a_{tr}) \times (\lambda_{int}^0/\lambda^0) (1 - 2\phi^\perp)], \quad (73)$$

where

$$p\text{Kn} = (\pi kT/2m)^{1/2} (\eta/d), \quad (74)$$

$$\phi^\perp \equiv (3\psi_{12}^{int} - \psi_{11}^{int}) / (3\psi_{12}^0 - \psi_{11}^0), \quad (75a)$$

$$\phi^\parallel \equiv (\psi_{12}^{int} - \psi_{11}^{int}) / (\psi_{12}^0 - \psi_{11}^0). \quad (75b)$$

The factor  $p\text{Kn}$  for  $\text{N}_2$  and  $\text{CO}$  at 300 K is equal to 0.69 Pa for the Leiden experiments<sup>4,5</sup> and 3.2 Pa for the Moscow experiments.<sup>8</sup>

Comparison of Eqs. (72) and (73) immediately gives an interesting result concerning  $a_{tr}$  and  $a_{int}$ . If  $a_{tr} = a_{int}$ , then  $K_{\delta q}$  must be larger than  $K_p$  by an amount corresponding to  $a_{tr}$ . But the Moscow measurements give  $K_p$  more than twice as large as  $K_{\delta q}$  for both  $\text{N}_2$  and  $\text{CO}$  on Au, so that these near-continuum measurements require that  $a_{tr}$  and  $a_{int}$  be different. This is in at least qualitative agreement with the

TABLE I. Fixed and constrained parameters.

Parameter	$\text{N}_2$ on Au	$\text{CO}$ on Au
$\lambda_{int}^0/\lambda_{tr}^0$ <sup>a</sup>	0.36	0.36
$a$ <sup>b</sup>	4.12	4.33
$\alpha$	0.87	0.84
$b_{12}^\perp = b_{11}^\perp$ <sup>c</sup>	2.08	2.49
$b_{12}^\parallel = b_{11}^\parallel$ <sup>c</sup>	1.71	1.83
$10^3\psi_{12}^0$ <sup>d</sup>	3.82	3.50
$\psi_{11}^0/\psi_{12}^0$ <sup>e</sup>	0.06 <sub>5</sub>	0.02 <sub>0</sub>
(Bor) <sup>tr</sup>	5.20	6.24
(Bor) <sup>int</sup>	4.99	5.82
$\Lambda_{sat}^\perp/\Lambda_{sat}^\parallel$ <sup>g</sup>	2.33	2.18

<sup>a</sup> Equation (27); fixed value.

<sup>b</sup>  $K_\lambda$  of Ref. 8; fixed values.

<sup>c</sup>  $K_p$  of Ref. 8; constrained values.

<sup>d</sup> Equation (57) and cross sections listed in Refs. 6 and 33; fixed values.

<sup>e</sup> Continuum limit of measured  $(\delta q^\perp/\delta q^\parallel)_{\text{sat}}$  in Refs. 4 and 8; constrained values.

<sup>f</sup> Equation (76) and  $K$  coefficients of Ref. 8; fixed values.

<sup>g</sup> Knudsen limit of measured  $(\delta q^\perp/\delta q^\parallel)_{\text{sat}}$  in Ref. 8; constrained values.

TABLE II. Final parameter values.

Parameter	$\text{N}_2$ on Au	$\text{CO}$ on Au
$a_{tr}$	4.0	4.0
$\alpha_{tr}$	0.97	0.97
$a_{int}/a_{tr}$	20	50
$\alpha_{int}$	0.08 <sub>1</sub>	0.03 <sub>3</sub>
$b_{12}^\perp = b_{11}^\perp$	1.89	1.04
$b_{12}^\parallel = b_{11}^\parallel$	1.70	0.91
$10^3\psi_{12}^{tr}$	4.68	4.20
$10^3\psi_{12}^{int}$	1.42	1.54
$10^3\psi_{11}^{tr}$	0.3 <sub>1</sub>	0.03 <sub>3</sub> <sup>a</sup>
$10^3\psi_{11}^{int}$	0.0 <sub>6</sub>	0.0 <sub>0</sub> <sup>a</sup>
$b_{pq}^\perp = b_{pq}^\parallel$	4	10
$10^4\Lambda_{sat}^\perp$	3	2 <sup>b</sup>

<sup>a</sup>The value of  $\psi_{11}^0$  has been adjusted for a better fit so that  $(\delta q^\perp/\delta q^\parallel)_{\text{sat}}^0 = 1.50$ , instead of 1.52.

<sup>b</sup>The value of  $\Lambda_{sat}^\perp/\Lambda_{sat}^\parallel$  has been adjusted to 2.20 instead of 2.18 for a better fit.



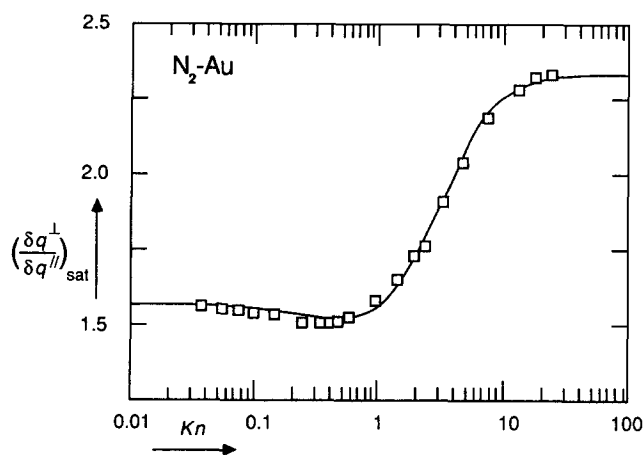


FIG. 2.  $(\delta q^\perp/\delta q^\parallel)_{\text{sat}}$  in the transition region for  $\text{N}_2$  on Au (measurements of Borman *et al.*). The curve is calculated from Eqs. (51) and (52) with the parameters listed in Table II.

analysis of the field-free measurements of Teagan and Springer discussed in Sec. II A 2.

To fit the data in the transition region, we have found that it is necessary to allow some variation in  $b_{12}$ . This is permissible because  $K_p$  and  $K_{\delta q}$  are not individually well determined, but can be varied together and still fit the near-continuum measurements. We have therefore used a combination of the  $K$  coefficients as a fixed quantity rather than the individual coefficients as follows

$$\begin{aligned} (\text{Bor})^{\perp\parallel} &\equiv (\rho \text{Kn})^{-1} (K_\lambda + K_p^{\perp\parallel} - K_{\delta q}^{\perp\parallel}) \\ &= (a - a_{\text{tr}}) + (a_{\text{int}} - a_{\text{tr}}) (\lambda_{\text{int}}^0 / \lambda^0) (1 - 2\phi^{\perp\parallel}). \end{aligned} \quad (76)$$

This combination does not involve the  $b_{12}$ . The various parameters that we have taken to be fixed or constrained are listed in Table I, together with their sources. In addition, a plot of the near-Knudsen data according to Eq. (66) shows the absence of a term linear in  $\text{Kn}^{-1}$ , so that we can take  $b_{pq}^\perp = b_{pq}^\parallel$ . We are left with only four parameters to be determined:  $a_{\text{tr}}$ ,  $a_{\text{int}}$ ,  $\Lambda_{\text{sat}}^\perp$ , or  $\Lambda_{\text{sat}}^\parallel$ , and  $b_{pq}$ . Of these,  $a_{\text{tr}}$  is highly constrained by the field-free measurements: it must be

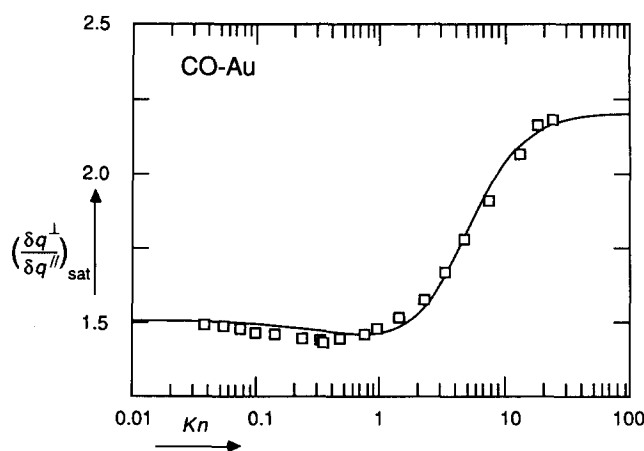


FIG. 3. Same as Fig. 2 for CO on Au.

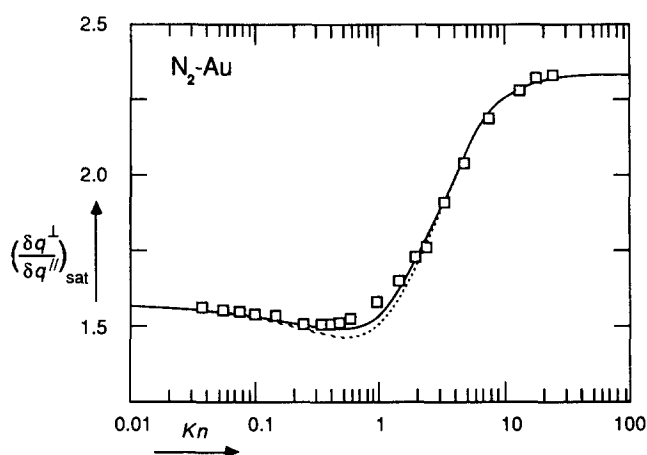


FIG. 4.  $(\delta q^\perp/\delta q^\parallel)_{\text{sat}}$  in the transition region for  $\text{N}_2$  on Au with  $a_{\text{tr}} = a_{\text{int}}$ . The curves are calculated from Eq. (54) with the parameters listed in Table I: dashed curve,  $b_{pq} = 2.5$  and  $\Lambda_{\text{sat}}^\perp = 3.3 \times 10^{-4}$ ; solid curve,  $b_{pq} = \infty$  and  $\Lambda_{\text{sat}}^\perp = 2.9 \times 10^{-4}$ .

greater than  $15/4$  according to Eqs. (22a) and (25a), and according to the analysis in Sec. II A 2 it is probably somewhat less than the value of  $a$ . The value of  $a_{\text{tr}}$  should therefore be close to 4. Furthermore, the discussion in Sec. II A 2 indicates that the magnitude of  $a_{\text{int}}/a_{\text{tr}}$  is about 20.

The actual fitting of the experimental values of  $(\delta q^\perp/\delta q^\parallel)_{\text{sat}}$  from Ref. 8 proceeded by first least-squaring for the four main parameters plus the  $b_{12}$ , and then allowing minor adjustments in some of the constrained parameters in Table I to improve the final fit. The final parameter values are listed in Table II. The overall fit of the data is rather insensitive to the values of  $a_{\text{int}}/a_{\text{tr}}$  and  $b_{pq}$ , which can be varied by roughly a factor of two without substantially changing the quality of the fit.

The results are shown in Figs. 2 and 3 as  $(\delta q^\perp/\delta q^\parallel)_{\text{sat}}$  vs  $\text{Kn}$ . Although not perfect, the fit is within stated experimental uncertainties.<sup>8</sup> While this is not the most sensitive test of the model, because it involves only ratios of saturation values rather than  $\delta q^{\perp\parallel}/q$  vs  $B/p$  at different values of  $\text{Kn}$ , it is the best test available at present. It is therefore of interest to demonstrate directly that these data do in fact require different values of  $a_{\text{tr}}$  and  $a_{\text{int}}$ . We took  $a_{\text{tr}} = a_{\text{int}}$  and used Eq. (54) with the parameter values of Table I, chose a series of values for  $b_{pq}$  and least squared for the remaining parameter,  $\Lambda_{\text{sat}}^\perp$ . The results for  $\text{N}_2$  on Au are shown in Fig. 4. Clearly, the fit in the transition region is unsatisfactory no matter what value of  $b_{pq}$  is chosen. The results for CO on Au are even worse. It is of course possible to improve the fit by varying  $b_{12}$ , but the values needed are very different from those in Table I and II.

#### IV. DISCUSSION

The present model appears to be successful in describing the thermomagnetic effect through the transition region, insofar as experimental data are available for testing it. It gives the correct results in the continuum and Knudsen limits: in the continuum regime the effects depend on the single variable  $B/p$ , and in the Knudsen regime they are independent of

$p$  and depend on  $B$  alone. In the transition regime the Knudsen number invades the coefficients and arguments of the functions that describe the two limits, thereby providing scaling rules involving the single variable  $Kn$ . No expansions in powers of  $Kn$  or  $Kn^{-1}$  are needed. A small number of new parameters are introduced that must be found experimentally or calculated from a more detailed microscopic theory. The model does not furnish a recipe for the calculation of parameters, it only furnishes an interpolation scheme between the continuum and Knudsen limits.

An interesting physical result is that different accommodation coefficients are required for the translational and internal energies of the gas molecules in order to fit the field-effect data. This result is consistent with analysis of independent field-free thermal conductivity data, and with independent measurement using a vibrating-surface technique.

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