Quantum Mechanical Calculation of the Magnitude of the Senftleben-Beenakker Effect of the Heat Conductivity for p-H_2 at Room Temperature

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(Z. Naturforsch. **28 a**, 815—823 [1973] ; received 14th September 1972)

Dedicated to Prof. Dr. L. Waldmann on the occasion of his 60th birthday

The magnetic Senftleben-Beenakker effect of the heat conductivity is considered for a gas of p-H_2 molecules. The magnitude of the saturation value is expressed in terms of collision integrals of the linearized Waldmann-Snider collision term. The collision integrals are, in turn, connected with molecular cross sections describing the production of a tensor polarization of the molecular rotational angular momenta. These orientation cross sections depend essentially on the nonspherical part of the intermolecular potential. For small nonsphericity of the interaction, valid in the case of H_2, it is sufficient to take into account only energetically elastic collisions For a simple potential model (nearly spherical rigid ellipsoids of revolution) the scattering amplitude is analytically evaluated in first order DWBA. The relevant collision integral which describes the coupling between the rotational heat flux and the Kagan polarization is calculated for room temperature. The comparison with the experimental value shows a good agreement.

Introduction

The influence of homogeneous magnetic and electric fields on the thermal conductivity of polyatomic gases — Senftleben-Beenakker effect — has been the subject of intensive experimental investigations during the last decade [1–6]. The first theoretical explanations of the effect go back to Kagan and Maksimov [7] and to Knaap and Beenakker [8] who started with a generalized classical Boltzmann equation which took into account the internal rotational degrees of freedom of a molecule. In their treatment the effect is caused by a special type of non-equilibrium velocity-angular velocity correlation, the so called Kagan polarization [7]. The shape of the experimental curves which showed the change in the heat conductivity versus the ratio magnetic field strength/pressure could satisfactorily be explained but not the magnitude of the saturation values.

The internal rotational degrees of freedom should, however, be treated quantum mechanically rather than classically, in particular for molecules with widely spaced rotational levels, such as H_2, HD, D_2. An adequate treatment of the heat conductivity problem based on the quantum mechanical Waldmann-Snider equation [9, 10] was first performed by McCourt and Snider [11]. This was followed by Levi and McCourt [12] and later by Raum and Köhler [13] for mixtures. The results for the shape of the (H/p) dependent curve $\Delta\lambda/\lambda(H=0)$ remained the same as in the classical case because also in the quantum mechanical treatment the corresponding Kagan polarization had been taken as the decisive rotational angular momentum anisotropy term in the molecular distribution function. This assumption is in good agreement with experiments for all diamagnetic gases. On the other hand, there has been no attempt to explain the magnitude of the saturation value of $[\Delta\lambda^{\parallel}/\lambda(H=0)]$, e. g., from the quantum mechanics of molecular collision: This magnitude depends essentially on the ratio of certain collision integrals of the linearized Waldmann-Snider collision term. Recently, a number of classical collision models, viz. rough spheres [14, 15], loaded spherocylinders [16] and ellipsoids [17] have been used to calculate the corresponding collision integrals.

It is the purpose of this paper to evaluate the Waldmann-Snider collision integral relevant for the Senftleben-Beenakker effect of the heat conductivity for p-H_2 at room temperature. While n-H_2 should be treated with the theory for gas mixtures [13], for p-H_2 the pure gas kinetic theory can be applied.

The starting point for the calculation of the magnitude of the Senftleben-Beenakker effect is a given nonspherical intermolecular potential. The desired collision integrals are proportional to certain temperature dependent effective cross sections which, in turn, are determined by molecular cross sections which describe the production of a second rank ten-

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sor polarization of the molecular rotational angular momenta in a collision. These "orientation cross sections" are related to the nonspherical part of the binary scattering amplitude and thus to the nonsphericity of the intermolecular potential [18, 19]. Since the calculation of the scattering amplitude from a potential is, in general, a difficult task, approximations have to be made. First, a simple model for the nonspherical H_2-H_2 interaction is introduced which consists in regarding the molecules as nearly spherical rigid ellipsoids of revolution. The gas H_2 has been chosen since in this case potential parameters are more easily available than in the other cases and the nonspherical part of the potential is especially small compared with the spherical part. The scattering amplitude (matrix with respect to magnetic quantum numbers) can therefore be calculated analytically in a first order distorted wave Born approximation. It proves sufficient to take into account only energetically elastic collisions for which the pertaining orientation cross sections are linear in the nonsphericity (the inelastic cross sections would be quadratic). The model is strictly valid only for temperatures above room temperature because an attractive part of the interaction has been neglected.

In this paper first the kinetic theory results for the Senftleben-Beenakker effect of the thermal conductivity are briefly reviewed. Then the relevant collision integrals are discussed. A simple potential model is introduced for which the DWBA scattering amplitude and the orientation cross section $\sigma_{\mathrm{q\,rot,K}}$ (which describes a coupling between the rotational heat flux and the Kagan polarization) is evaluated for 300 K and compared with the experimental value obtained by Hermans [3].

I. The Heat Conductivity Tensor

In the presence of a magnetic field the heat conductivity of a polyatomic gas becomes a field dependent second rank tensor [1] (Senftleben-Beenakker effect). For a dilute gas of linear diamagnetic molecules the form of this tensor can be derived from the linearized Waldmann-Snider equation using a Chapman-Enskog procedure [11] or the moment method [13]. The distribution function which obeys the Waldmann-Snider equation is a matrix with respect to the degenerate rotational states of the molecule. That is to say, it depends as well on $\boldsymbol{J}$ which is the dimensionless operator for the rotational angular momentum. The Senftleben-Beenakker effect is caused by this rotational angular momentum anisotropy of the distribution function. For linear molecules, the comparison between theory [11–13] and experiments [2–5] yields the result that the relevant moments in the distribution function are given by (the irreducible parts of) the third rank tensor ("flux of the tensor polarization")

$$a_{\mu\nu,\lambda} = (15\,m/2\,k_{\mathrm{B}}\,T_0\langle J^2(J^2-3/4)\rangle_0)^{1/2}\,\langle c_\lambda\,\overline{J_\mu\,J_\nu}\rangle, \tag{1}$$

where $\boldsymbol{c}$ is the molecular velocity, $\overline{\boldsymbol{J}\,\boldsymbol{J}}$ is the irreducible second rank tensor built up from the components of $\boldsymbol{J}$, and $\langle\ldots\rangle_0$ denotes an equilibrium average (equilibrium temperature T_0). The appropriately normalized vector part of (1) is called the "Kagan-vector"

$$a_\mu = \sqrt{\tfrac{5}{3}}\,a_{\mu\lambda,\lambda}\,, \tag{2}$$

which expresses a special kind of nonequilibrium correlation between molecular velocity and rotational angular momentum. The Kagan polarization couples (by means of the collisions) with the translational and rotational heat flux vectors. This coupling gives rise to a change of the total heat flux compared with the monatomic case where the distribution function does not depend on magnetic quantum numbers. In an external homogeneous magnetic field the polarization is partially destroyed because of the precession of the magnetic moment which is connected with the rotational angular momentum. This process leads to a decrease in heat conductivity with increasing field strength.

The detailed kinetic theory which is described in Refs. [11–13] yields the following expression for the heat conductivity tensor:

$$\lambda_{\mu\nu}(\boldsymbol{H}) = \lambda(H=0)\,[\delta_{\mu\nu} + A^{(\lambda)}\,f_{\mu\nu}(\varphi)]\,, \tag{3}$$

where $\lambda(H=0)$, $A^{(\lambda)}$ and φ can be expressed in terms of collision integrals of the linearized Waldmann-Snider collision term in the following way:

$$\lambda(H=0) = \frac{p_0\,k_{\mathrm{B}}}{m}\left[\frac{5}{2\,\omega_{\mathrm{qtr}}} + \frac{c_{\mathrm{rot}}}{k_{\mathrm{B}}\,\omega_{\mathrm{qrot}}}\right]\cdot[1 + A^{(\lambda)}], \tag{4}$$

$$A^{(\lambda)} = \left[\sqrt{\frac{5}{2}}\,\frac{\omega_{\mathrm{qtr,K}}}{\omega_{\mathrm{qtr}}} + \sqrt{\frac{c_{\mathrm{rot}}}{k_{\mathrm{B}}}}\,\frac{\omega_{\mathrm{qrot,K}}}{\omega_{\mathrm{qrot}}}\right]^2 \Big/ \omega_{\mathrm{K}}\left[\frac{5}{2\,\omega_{\mathrm{qtr}}} + \frac{c_{\mathrm{rot}}}{k_{\mathrm{B}}\,\omega_{\mathrm{qrot}}}\right], \tag{5}$$

$$\varphi = \omega_{\mathrm{H}}/\omega_{\mathrm{K}}\,, \qquad \omega_{\mathrm{H}} = \gamma\, H\,. \tag{6}$$

The angle φ is the angle of precession during a time $\tau = 1/\omega_{\mathrm{K}}$; $\boldsymbol{H} = H\,\boldsymbol{h}$ is the homogeneous magnetic field with direction $\boldsymbol{h}$, γ is the gyromagnetic ratio and p_0 is the equilibrium pressure.

The field dependent second rank tensor $f_{\mu\nu}(\varphi)$ is given by [11–13]

$$f_{\mu\nu}(\varphi) = -\frac{3}{10}\left[\left(\frac{\varphi^2}{1+\varphi^2} + \frac{8\,\varphi^2}{1+4\,\varphi^2}\right)\delta_{\mu\nu} + \left(\frac{\varphi^2}{1+\varphi^2} - \frac{8\,\varphi^2}{1+4\,\varphi^2}\right) h_\mu\, h_\nu + \left(\frac{\varphi}{1+\varphi^2} + \frac{4\,\varphi}{1+4\,\varphi^2}\right)\varepsilon_{\mu\lambda\nu}\, h_\lambda\right], \tag{7}$$

where $\varepsilon_{\mu\lambda\nu}$ is the total antisymmetric isotropic third rank tensor.

In Eqs. (3) – (6), the quantities $\omega_{\mathrm{q\,tr}}$, $\omega_{\mathrm{q\,rot}}$, and ω_{K} are the relaxation coefficients of the translational and rotational heat fluxes and of the Kagan vector; $\omega_{\mathrm{q\,tr,K}}$ and $\omega_{\mathrm{q\,rot,K}}$ are the coupling coefficients of the Kagan vector with the respective heat fluxes and c_{rot} is the rotational heat capacity per molecule at the equilibrium temperature T_0. In deriving Eq. (3) from the set of moment equations [13] use has been made of the fact that for linear molecules with small nonsphericity the coupling between the translational and rotational heat fluxes can be neglected [18], and that the relaxation coefficients of the irreducible parts of the flux of tensor polarization can be put equal to the common value ω_{K}.

According to results of the following chapters (cf. also Ref. [18]) for homonuclear molecules with a small nonsphericity of their interaction, such as H_2, D_2, the coupling coefficient $\omega_{\mathrm{q\,tr,K}}$ (which is mainly determined by energetically inelastic collisions) can be neglected compared to $\omega_{\mathrm{q\,rot,K}}$ (which is mainly determined by energetically elastic collisions). Thus Eq. (5) can be simplified in this case to give

$$A_{\mathrm{el}}^{(\lambda)} = \frac{2\,c_{\mathrm{rot}}\,\omega_{\mathrm{qtr}}\,\omega^2_{\mathrm{qrot,K}}}{\omega_{\mathrm{qrot}}\,\omega_{\mathrm{K}}(5\,k_{\mathrm{B}}\,\omega_{\mathrm{qrot}} + 2\,c_{\mathrm{rot}}\,\omega_{\mathrm{qtr}})}, \tag{8}$$

i. e. the coupling between the rotational heat flux and the Kagan vector is decisive for the Senftleben-Beenakker effect. This can be understood as the quantum mechanical analogue to the classical elastic Kagan-Maksimov [7, 8] collision model. The relaxation coefficients $\omega_{\mathrm{q\,tr}}$, $\omega_{\mathrm{q,rot}}$ and ω_{K} can, up to terms quadratic in the nonsphericity, be expressed in terms of Chapman-Cowling [20] integrals $\Omega^{(l,r)}$ (see the following chapter!). Then Eq. (8) becomes approximately

$$A_{\mathrm{el}}^{(\lambda)} = \left[c_{\mathrm{rot}}\Big/\left(\frac{25}{4}\,k_{\mathrm{B}}\,\frac{\Omega^{(1,1)}}{\Omega^{(2,2)}} + c_{\mathrm{rot}}\right)\right] \cdot \left[\omega_{\mathrm{qrot,K}}\Big/\frac{8\,n_0}{3}\,\Omega^{(1,1)}\right]^2. \tag{9}$$

Since the Chapman-Cowling integrals can be inferred from the literature, the only unknown quantity in the expression Eq. (9) is the coupling coefficient $\omega_{\mathrm{q\,rot,K}}$. In the Appendix, some remarks are made on the low-temperature behaviour of (9).

II. Collision Integrals

In this section the collision integrals occurring in the expressions for the Senftleben-Beenakker effect of the heat conductivity are investigated. Instead of the ω..'s effective cross sections σ.. (temperature dependent and not necessarily positive) are used. They are defined by

$$\omega_{\,..} = n_0\, v_0\, \sigma_{\,..}\,, \tag{10}$$

where $v_0 = (8\,k_{\mathrm{B}}\,T_0/\pi\,m_{\mathrm{red}})^{1/2}$ is a mean thermal velocity and n_0 is the equilibrium particle density. The effective cross sections of the relaxation coefficients are positive. They can, in the "spherical approximation" (the nonspherical part of the intermolecular potential being neglected) be expressed in terms of Chapman-Cowling integrals [20, 21] which can be taken from the literature, viz.

$$\sigma_{\mathrm{qtr}} \approx (16/15)\; v_0^{-1}\,\Omega^{(2,2)}\,, \tag{11}$$

$$\sigma_{\mathrm{qrot}} \approx \sigma_{\mathrm{K}} \approx (8/3)\; v_0^{-1}\,\Omega^{(1,1)}\,. \tag{12}$$

For the coupling coefficients the "spherical approximation" cannot be made since it would yield zero values of the effective cross sections which are essentially determined by the nonspherical part of the potential (see below). They can be written as [19]

$$\sigma_{\mathrm{qtr,K}} = \frac{2}{5}\left|\frac{2}{3\langle J^2(J^2-\frac{3}{4})\rangle_0}\right|^{1/2} [\![\gamma^2\,\sigma^{(1)}_{\mathrm{ee}} - \gamma'^2\,\sigma^{(1)}_{\mathrm{e'e'}}]\!]\,, \tag{13}$$

$$\sigma_{\mathrm{qrot,K}} = 2\left|\frac{k_{\mathrm{B}}}{15\,c_{\mathrm{rot}}\langle J^2(J^2-\frac{3}{4})\rangle_0}\right|^{1/2} \cdot [\![\gamma^2(\varepsilon_1-\varepsilon_2)\,\sigma^{(1)}_{\mathrm{ee}} - \gamma\,\gamma'(\varepsilon_1'-\varepsilon_2')\,\sigma^{(1)}_{\mathrm{ee'}}]\!]\,. \tag{14}$$

For convenience, the connection with the notation used by McCourt[12] et al. is indicated[21a]

$$\sigma_{\text{qtr}} \equiv \sigma\binom{1010}{1010}, \quad \sigma_{\text{qrot}} \equiv \sigma\binom{1001}{1001}, \quad \sigma_{\text{K}} \equiv \sigma\binom{1200}{1200}, \tag{15 a}$$

$$\sigma_{\text{qtr, K}} \equiv -\sqrt{5/3}\,\sigma\binom{1010}{1200}, \qquad \sigma_{\text{qrot, K}} \equiv +\sqrt{5/3}\,\sigma\binom{1001}{1200}. \tag{15 b}$$

In Eqs. (13), (14), γ' and γ are the magnitudes of the dimensionless relative velocities before and after the collision (unit vectors $\boldsymbol{e}'$ and $\boldsymbol{e}$ of their respective directions). They are connected by energy conservation

$$\gamma^2 + \varepsilon_1 + \varepsilon_2 = \gamma'^2 + \varepsilon_1' + \varepsilon_2',$$

where $\varepsilon(j) = \hbar^2 j(j+1)/2\,\Theta\,k_{\text{B}}\,T_0$

is the dimensionless rotational energy and $\varepsilon_1 \equiv \varepsilon(j_1)$, $\varepsilon_1' \equiv \varepsilon(j_1')$, etc. The bracket symbol $[\![\ldots]\!]$ denotes a weighted averaging over γ and the postcollisional rotational quantum numbers j_1, j_2 as well as an integration over the angle of deflection $\vartheta = \arccos(\boldsymbol{e}\cdot\boldsymbol{e}')$ and a summation over the precollisional rotational quantum numbers j_1', j_2' as follows:

$$[\![F]\!] = 2\,\pi\,Q^{-2} \sum_{j_1 j_2 j_1' j_2'} \iint (2\,j_1+1)(2\,j_2+1)\exp\{-\varepsilon(j_1)-\varepsilon(j_2)\} \times \exp(-\gamma^2)\,\gamma^3\,F(\gamma,\vartheta\,|\,j_1\,j_2,j_1'\,j_2')\,\sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\gamma\,. \tag{16}$$

In Eq. (16), F may be any function of γ, ϑ and the rotational quantum numbers, and Q is the rotational partition sum. The decisive quantities in Eqs. (13), (14) are the "orientation cross sections" $\sigma^{(1)}_{\text{ee}}$, $\sigma^{(1)}_{\text{e}'\text{e}'}$, $\sigma^{(1)}_{\text{ee}'}$. They are defined by

$$\sigma^{(1)}_{\text{ee}} = (2\,j_1+1)^{-1}\,(2\,j_2+1)^{-1}\,\frac{\gamma'}{\gamma}\,\mathrm{tr}_1\,\mathrm{tr}_2\left\{a^{j_1 j_2,\,j_1' j_2'}\,a^{\dagger\,j_1' j_2',\,j_1 j_2}\sqrt{15/2}\,\overline{\boldsymbol{J}_1\boldsymbol{J}_1} : \boldsymbol{e}\,\boldsymbol{e}\right\}, \tag{17}$$

and for $\sigma^{(1)}_{\text{e}'\text{e}'}$ and $\sigma^{(1)}_{\text{ee}'}$, $\boldsymbol{e}\,\boldsymbol{e}$ has to be replaced by $\boldsymbol{e}'\,\boldsymbol{e}'$ and $\boldsymbol{e}\,\boldsymbol{e}'$ in Equation (17). The quantity $a^{j_1 j_2,\,j_1' j_2'}$ is the single channel scattering amplitude (matrix with respect to the magnetic quantum numbers) on the energy shell for a collision process $j_1' + j_2' \rightarrow j_1 + j_2$. It depends on $\boldsymbol{e}$, $\boldsymbol{e}'$ and the magnitude of the relative velocity. The trace over magnetic quantum numbers is denoted by "tr". The quantities $\sigma^{(1)}_{\text{ee}}$ ... etc. are called "orientation cross sections" for the tensor polarization because they are a measure for the production of the $\overline{\boldsymbol{e}\,\boldsymbol{e}}$ ... etc. components of the 2-nd rank tensor polarization of the molecular rotational angular momenta (j_1) in a collision. They vanish in the case of a purely spherical potential since then the scattering amplitude is independent of magnetic quantum numbers and can be taken outside the trace in (17); the remaining trace of an ireducible tensor is zero.

In order to obtain the orientation cross sections, the scattering amplitude matrix has to be calculated from a nonspherical intermolecular potential. If the nonsphericity is small, this calculation can be done in first order distorted wave Born approximation (DWBA)[22] if the Schrödinger equation for scattering by the spherical part of the potential can be solved exactly. The corresponding scattering solutions are the "distorted waves". The nonspherical part of the potential is then treated in first order perturbation theory. The DWBA scattering amplitude matrix is written as

$$a^{j_1 j_2,\,j_1' j_2'} = a_{\text{sph}}\,P^{j_1 j_2}\,P^{j_1' j_2'} + a^{j_1 j_2,\,j_1' j_2'}_{\text{nonsph}}\,, \tag{18}$$

where a_{sph} is the part of the scattering amplitude due the scattering by the spherical part of the potential and $P^{j_1 j_2}$ is a two particle operator projecting on rotational angular momentum states[18]. If the nonspherical DWBA scattering amplitude $a^{j_1 j_2,\,j_1' j_2'}_{\text{nonsph}}$ possesses an elastic part (which is always true for homonuclear diatomic molecules) then the orientation cross sections (17) are linear in the nonsphericity because of the interference of the spherical and nonspherical part of the scattering amplitude, viz.

$$\mathrm{tr}_1\,\mathrm{tr}_2\left\{a^{j_1 j_2,\,j_1 j_2}\,a^{\dagger\,j_1 j_2,\,j_1 j_2}\,\overline{\boldsymbol{J}_1\boldsymbol{J}_1}\right\} \approx 2\,\mathrm{Re}\left\{a^*_{\text{sph}}\,\mathrm{tr}_1\,\mathrm{tr}_2\left[a^{j_1 j_2,\,j_1 j_2}_{\text{nonsph}}\,\overline{\boldsymbol{J}_1\boldsymbol{J}_1}\right]\right\}. \tag{19}$$

On the other hand, for linear molecules, all energetically inelastic cross sections are quadratic in the nonsphericity. Furthermore, it can be shown[18, 19] that in the elastic case $(\gamma' = \gamma)$ one has

$$_{\text{el}}\sigma^{(1)}_{\text{ee}} = {}_{\text{el}}\sigma^{(1)}_{\text{e}'\text{e}'} \mp {}_{\text{el}}\sigma^{(1)}_{\text{ee}'}\,, \tag{20}$$

so that the effective cross section $\sigma_{\mathrm{q\,tr,K}}$ is at least quadratic in the small nonsphericity whereas $\sigma_{\mathrm{q\,rot,K}}$ is linear. This is the reason why for the gases H_2 and D_2 the collision cross section $\sigma_{\mathrm{q\,tr,K}}$ can be neglected in the expression for the Senftleben-Beenakker effect. The validity of this statement has also been proved experimentally by Hermans [5]. In the elastic case, Eq. (14) can thus be simplified to give

$$\sigma_{\mathrm{qrot,K}} = 2\,[k_{\mathrm{B}}/15\,c_{\mathrm{rot}}\langle J^2(J^2-\tfrac{3}{4})\rangle_0]^{1/2}\,[\![\gamma^2(\varepsilon_1-\varepsilon_2)\,(\sigma_{\mathrm{ee}}^{(1)}-\sigma_{\mathrm{ee}'}^{(1)})]\!]_{\mathrm{el}}\,. \tag{21}$$

The subscript "el" on the bracket denotes that $\gamma'=\gamma$ in (21) and the sum over rotational quantum numbers goes only over j_1 and j_2 $(j_1'=j_1,\ j_2'=j_2)$.

A simple nonspherical model potential for H_2 (D_2) will be introduced in the following chapter for which the first order DWBA scattering amplitude matrix, the orientation cross sections $\sigma_{\mathrm{ee}}^{(1)}$, $\sigma_{\mathrm{ee}'}^{(1)}$, and, finally, the effective cross section $\sigma_{\mathrm{q\,rot,K}}$ can be evaluated.

III. A Simple Model for the Nonspherical Potential
The Resulting Scattering Amplitude and Orientation Cross Sections

In order to calculate the DWBA scattering amplitude Eq. (18) from a given nonspherical potential in an analytic way, the following simple model for a potential between H_2 molecules is used: Let $\boldsymbol{u}$ be a unit vector in the direction of the molecular axis. The molecule (i. e. its electron cloud) is, in our model, approximated by a nearly spherical ellipsoid of revolution with axis $\boldsymbol{u}$ the surface of which can be approximated by the first two terms of a Legendre polynomial series

$$R_{\mathrm{s}}(\boldsymbol{u},\hat{\boldsymbol{x}}) \approx (R_0/2)\,[1+2\,\beta\,P_2(\boldsymbol{u}\cdot\hat{\boldsymbol{x}})]\,. \tag{22}$$

In Eq. (22), $\hat{\boldsymbol{x}}$ is a unit vector pointing from the center of the molecule to the surface point under consideration, R_0 is the mean diameter of the nearly spherical molecule and $\beta \ll 1$ (which is certainly valid for H_2 and D_2) is the nonsphericity parameter denoting the deviation of the molecule from spherical symmetry. If the lengths of the principal axes of the ellipsoid are $R_0 \pm a/2$, respectively, then $\beta = 2\,a/3\,R_0$. Consider now two colliding H_2 molecules each of them being represented by an ellipsoid of revolution with surface described by Equation (22). The intermolecular potential is, in our model, taken to be $V_0=\mathrm{const}$ if the ellipsoids touch or penetrate each other and zero if they are separate. In the limit $V_0 \to \infty$ (which will be performed later) this model corresponds to "nearly spherical rigid bodies". This type of scattering has also been studied by Curtiss and coworkers [23] but with a method and aim different from the following. The intermolecular potential can then be expressed as

$$V(\boldsymbol{u}_1,\boldsymbol{u}_2,\boldsymbol{r}) = V_0\,\Theta\,(R(\boldsymbol{u}_1,\boldsymbol{u}_2,\hat{\boldsymbol{r}})-r)\,, \tag{23}$$

where

$$R(\boldsymbol{u}_1,\boldsymbol{u}_2,\hat{\boldsymbol{r}}) = |\,\boldsymbol{R}_{\mathrm{s}1}(\boldsymbol{u}_1,\hat{\boldsymbol{x}}_1) - \boldsymbol{R}_{\mathrm{s}2}(\boldsymbol{u}_2,\hat{\boldsymbol{x}}_2)|$$

(for $\boldsymbol{u}_1$, $\boldsymbol{u}_2$, $\hat{\boldsymbol{r}}$, $\boldsymbol{R}_{\mathrm{s}1}$, $\boldsymbol{R}_{\mathrm{s}2}$ and R see Figure 1), Θ is the Heaviside step function, $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$ are unit vectors in the directions of the respective molecular axes and $\boldsymbol{r}=r\,\hat{\boldsymbol{r}}=\boldsymbol{r}_1-\boldsymbol{r}_2$ is the vector connecting the centers of mass of both molecules, pointing from molecule 2 to molecule 1.

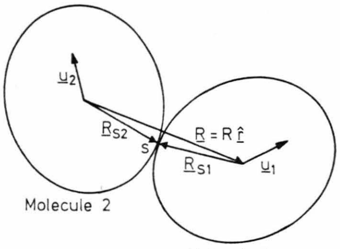

Fig. 1. Two colliding molecules which are represented by nearly spherical ellipsoids of revolution. The unit vectors in the directions of the respective molecular axes are $\boldsymbol{u}_1$ and $\boldsymbol{u}_2$; the vector connecting their centers of mass is denoted by $\boldsymbol{R}$.

From Eq. (22) and with simple geometrical considerations one obtains for $\beta \ll 1$

$$R(\boldsymbol{u}_1,\boldsymbol{u}_2,\hat{\boldsymbol{r}}) = R_0[1+\beta\,(P_2(\boldsymbol{u}_1\cdot\hat{\boldsymbol{r}}) + P_2(\boldsymbol{u}_2\cdot\hat{\boldsymbol{r}}))] + O(\beta^2)\,. \tag{24}$$

With the use of Eq. (24) and the smallness of β, an expansion of Eq. (23) in powers of β up to linear terms yields

$$V(\boldsymbol{u}_1,\boldsymbol{u}_2,\boldsymbol{r}) = V_{\mathrm{sph}}(r) + V_2(r)\,\,[P_2(\boldsymbol{u}_1\cdot\hat{\boldsymbol{r}}) + P_2(\boldsymbol{u}_2\cdot\hat{\boldsymbol{r}})]\,, \tag{25}$$

where $$V_{\mathrm{sph}}(r) = V_0\,\Theta\,(R_0-r)\,, \tag{26 a}$$

$$V_2(r) = V_0\,R_0\,\beta\,\delta\,(r-R_0)\,. \tag{26 b}$$

Equations (25), (26 a, b) represent the nonspherical H_2-H_2 potential to be used in the following for the analytic calculation of the first order DWBA scattering amplitude.

Next, the value of β has to be estimated. This can be done by calculating the electronic quadrupole moment Q_0 of the H_2 molecule and by comparing the result with the experimental value obtained by Harrick and Ramsey[24]. For this calculation a negative charge distribution is used which is constant within the volume of the ellipsoid and zero outside. The result for small nonsphericity is

$$-(Q_0/e) = (6/5)\,\beta\,R_0^2. \tag{27}$$

With $-(Q_0/e)_{\text{exp}} = 0.33\ \text{Å}^2 \pm 10\%$ and a molecular diameter of $R_0 = 2.72$ Å (which was taken from the hard sphere viscosity cross section[21]) one obtains $\beta = 0.037 \pm 10\%$. Since this estimate for β is rough, we take the value $\beta = 0.04$ for our calculations. The order of magnitude of β is certainly correct.

Because in the above potential only the repulsive interaction has been taken into account, Eqs. (26 a) and (26 b) should not be used for calculations with temperatures below room temperature for which in the calculation of collision integrals also the attractive interaction is important.

Next, the elastic scattering amplitude, Eq. (18), is calculated from the nonspherical potential, Equations (25), (26). The spherical part, a_{sph}, is written in the usual partial wave expansion form[22] (the symmetrization of the scattering amplitude because of Bose-Einstein statistics has not been taken into account)

$$a_{\text{sph}}(k, \boldsymbol{e}'\cdot\boldsymbol{e}) = \frac{4\pi}{k} \sum_{l=0,1,\dots}^{\infty} \{e^{i\delta_l} \sin\delta_l \sum_m Y^*_{lm}(\boldsymbol{e})\, Y_{lm}(\boldsymbol{e}')\}, \tag{28}$$

where $\hbar k = \sqrt{m\,k_B T_0}\,\gamma$ is the magnitude of the relative wave vector and $\delta_l(k)$ are the phase shifts with respect to the scattering problem governed by the spherical potential $V_{\text{sph}}(r)$. In the hard sphere limit $V_0 \to \infty$ the phase shifts are given by the well known expression

$$\delta_l(k) = \arctan\big(j_l(k R_0)/n_l(k R_0)\big), \tag{29}$$

where j_l and n_l are the respective spherical Bessel- and Neumann functions, defined e. g. in Abramowitz and Stegun[25].

The first order DWBA scattering amplitude matrix $a_{\text{nonsph}}^{j_1 j_2, j_1' j_2'}$ which is connected with the nonspherical potential Eq. (25), (26 b) can be written as follows[19]:

$$a_{\text{nonsph}}^{j_1 j_2, j_1' j_2'}(k, \boldsymbol{e}, \boldsymbol{e}') = -\frac{m_{\text{red}}}{2\pi\hbar^2} \frac{\sqrt{4\pi}}{5} \Big[\sqrt{2 j_1 + 1}\,(j_1\,0, 2\,0 \mid j_1'\,0) \sum_M T_{2M}^{j_1 j_1'}\, P^{j_2} P^{j_2'} \cdot \langle \chi_{\boldsymbol{k}}^{(-)} \mid V_2(r)\, Y_{2M}(\hat{\boldsymbol{r}}) \mid \chi_{\boldsymbol{k}'}^{(+)} \rangle + (1,2)\,\text{interchanged} \Big]. \tag{30}$$

In Eq. (30), the operator $T_{2M}^{j_1 j_1'}$ is a second rank spherical tensor operator which is a particular case of the general spherical tensor operators $T_{LM}^{jj'}$ (cf. Ref. [18])

$$T_{LM}^{jj'} = \sum_{mm'} (-1)^{j-m} (j'\,m', j\,{-m} \mid L\,M)\, \lvert j\,m \rangle \langle j'\,m' \rvert, \tag{31}$$

which transform under rotations like adjoint spherical harmonics and have the trace property

$$\text{tr}[T_{LM}^{jj'}\,(T_{L'M'}^{jj'})^\dagger] = \delta_{LL'}\,\delta_{MM'}. \tag{32}$$

The states $\lvert \chi^{(\pm)} \rangle$ represent the "distorted waves", i. e. $\langle \boldsymbol{r} \mid \chi_{\boldsymbol{k}}^{(+)} \rangle \equiv \chi_{\boldsymbol{k}}^{(+)}(\boldsymbol{r})$ are the scattering solutions of the Schrödinger equation

$$\big((-\hbar^2/2\,m_{\text{red}})\,\Delta_{\boldsymbol{r}} + V_{\text{sph}}(r)\big)\,\chi_{\boldsymbol{k}}^{(+)}(\boldsymbol{r}) = (\hbar^2 k^2/2\,m_{\text{red}})\,\chi_{\boldsymbol{k}}^{(+)}(\boldsymbol{r}), \tag{33}$$

with the boundary condition of plane waves plus outgoing (incoming for "$-$") spherical waves at infinity. The distorted waves can be expanded in spherical harmonics, viz. (for $|\boldsymbol{k}| = |\boldsymbol{k}'|$)

$$\chi_{\boldsymbol{k}'}^{(+)}(\boldsymbol{r}) = 4\pi \sum_l \Big\{ i^l \chi_l^{(+)}(k, r) \sum_m Y_{lm}(\boldsymbol{e}')\, Y^*_{lm}(\hat{\boldsymbol{r}}) \Big\}; \quad \chi_l^{(-)*} = \chi_l^{(+)}. \tag{34}$$

With (34) and after performing the angular integrations explicitly one obtains

$$\langle \chi_{\boldsymbol{k}}^{(-)} | V_2(r)\, Y_{2M}(\hat{\boldsymbol{r}}) | \chi_{\boldsymbol{k}'}^{(+)} \rangle = \frac{8\,\pi^{3/2}}{\sqrt{5}} \sum_{l l'} \Big\{ i^{(l-l')} \sqrt{(2\,l+1)\,(2\,l'+1)} \cdot (l\,0, l'\,0 \,|\, 2\,0)\, F_{l l'}(k) \sum_{m m'} (l\,m, l'\,m' \,|\, 2\,M)\; Y_{lm}(\boldsymbol{e}')\; Y_{l'm'}(\boldsymbol{e}) \Big\}\,. \tag{35}$$

The quantities $F_{ll'}(k)$ occurring in (35) are radial integrals defined by

$$F_{ll'}(k) = \int_0^\infty \chi_l^{(+)}(k,r)\; V_2(r)\; \chi_{l'}^{(+)}(k,r)\; r^2\,\mathrm{d}r\,. \tag{36}$$

The radial solutions $\chi_l^{(\pm)}(k,r)$ of the spherical scattering problem can easily be obtained for a step potential Equation (26 a) [22]. With the simple form of $V_2(r)$, Eq. (26 b), the radial integral (36) can immediately be evaluated. In the limit $V_0 \to \infty$ one finds for the $F_{ll'}$ the expression

$$F_{ll'}(k) \;=\; -\,(\hbar^2\,\beta/m\,k^2\,R_0)\,\big(h_l^{(1)}(k\,R_0)\;h_{l'}^{(1)}(k\,R_0)\big)^{-1}\,, \tag{37}$$

where the $h_l^{(1)} = j_l + i\,n_l$ are spherical Hankel functions of the first kind. Because one has $F_{ll'}(k) = F_{l'l}(k)$ in the elastic case $(k' = k)$, Eq. (20) of Chapter II is valid.

With the help of Eqs. (17), (19), (28) – (37) together with some Racah algebra and by use of the following identities for scalar products

$$P^j\,\overline{J_\mu\,J_\nu}\;P^j\,\overline{e_\mu\,e_\nu} = (4\sqrt{\pi}/15)\;[(2\,j+1)\;j(j+1)\;(j(j+1)-\tfrac{3}{4})]^{1/2} \sum_M Y_{2M}(\boldsymbol{e})\;T_{2M}^{jj}\,, \tag{38 a}$$

$$P^j\,\overline{J_\mu\,J_\nu}\;P^j\,\overline{e_\mu\,e_\nu'} = (4\,\pi/3)\,\sqrt{2/15}\;[(2\,j+1)\;j(j+1)\;(j(j+1)-\tfrac{3}{4})]^{1/2} \cdot \sum_{m,m'} (1\,m, 1\,m' \,|\, 2\,M)\; Y_{1m}(\boldsymbol{e})\; Y_{1m'}(\boldsymbol{e}')\; T_{2M}^{jj}\,, \tag{38 b}$$

the orientation cross sections $\sigma_{\mathrm{ee}}^{(1)}$, $\sigma_{\mathrm{ee}'}^{(1)}$ can be expressed in terms of a Legendre polynomial series (wherein the argument is the cosine of the scattering angle). We refrain from writing down these expressions because only the cross sections integrated over the scattering angle $\vartheta = \sphericalangle(\boldsymbol{e}, \boldsymbol{e}')$ are needed in the expression for $\sigma_{\mathrm{q\,rot,\,K}}$. Using explicit formulae for the Racah and Clebsch-Gordan coefficients occurring we obtain after some labour:

$$\begin{aligned} 2\,\pi \int_0^\pi \sin\vartheta\;\sigma_{\mathrm{ee}}^{(1)}\,\mathrm{d}\vartheta = &-12\,\pi\,\sqrt{2/15}\;(m/\hbar^2\,k)\;(j_1\,0, 2\,0\,|\,j_1\,0)\;[j_1(j_1+1)\;(j_1(j_1+1)-\tfrac{3}{4})]^{1/2} \\ &\cdot \sum_{l=0}^{\infty} \frac{(l+1)\,(l+2)}{2\,l+3} \Big\{ \frac{2\,(2\,l+3)^2}{3\,(2\,l+1)\,(2\,l+5)}\; \mathrm{Re}[e^{-i\,\delta_{l+1}} \sin\delta_{l+1}\,F_{l+1,\,l+1}] \\ &- \mathrm{Re}[(e^{-i\,\delta_l} \sin\delta_l + e^{-i\,\delta_{l+2}} \sin\delta_{l+2})\;F_{l,\,l+2}] \Big\}\,, \end{aligned} \tag{39}$$

and

$$\begin{aligned} 2\,\pi \int_0^\pi \sin\vartheta\;\sigma_{\mathrm{ee}'}^{(1)}\,\mathrm{d}\vartheta = &-4\,\pi\,\sqrt{2/15}\;(m/\hbar^2\,k)\;(j_1\,0, 2\,0\,|\,j_1\,0)\;[j_1(j_1+1)\;(j_1(j_1+1)-\tfrac{3}{4})]^{1/2} \\ &\cdot \sum_{l=0}^{\infty} \frac{(l+1)\,(l+2)}{2\,l+3} \Big\{ \frac{2\,l+3}{2\,l+1}\; \mathrm{Re}[e^{-i\,\delta_l} \sin\delta_l\,F_{l+1,\,l+1}] \\ &+ \frac{2\,l+3}{2\,l+5}\; \mathrm{Re}[e^{-i\,\delta_{l+2}} \sin\delta_{l+2}\,F_{l+1,\,l+1}] - 6\;\mathrm{Re}[e^{-i\,\delta_{l+1}} \sin\delta_{l+1}\,F_{l,\,l+2}] \Big\}\,. \end{aligned} \tag{40}$$

The expressions (39), (40) have to be inserted into Equation (21). The j_1- and j_2-summations can be factored out and must be performed numerically. Finally, the l-summation and the γ-integration have to be done numerically as well. For the latter a Gauss-Hermite integration procedure [25] has been used. The convergence of the j-series is rapid so that the first four j-values (0, 2, 4, 6) are sufficient. On the other hand, at room temperature 30 l-values have to be taken into account in order to obtain an accuracy of better than 1%.

IV. Comparison of Theoretical and Experimental Results

For the calculation of $\sigma_{\mathrm{q\,rot,K}}$ for p-H_2 at 300 K according to Eq. (21) the values $\hbar^2/2\,k_B\,\Theta = 85.4$ K, $R_0 = 2.72$ Å, and $\beta = 0.04$ have been used. Because R_0 has been taken from the classical hard sphere viscosity cross section and the β value from the electronic quadrupole moment of the H_2 molecule, no adjustable parameter appears in the calculation. The value of the rotational heat capacity per molecule at 300 K is $c_{\mathrm{rot}}/k_B = 1.0885$. The result of the calculation is

$$(\sigma_{\mathrm{q\,rot,K}})_{\mathrm{th}} = 0.286\ \text{Å}^2.$$

A theoretical value for σ_K, in spherical approximation according to Eq. (12), can be inferred from the literature [21]. For the Lennard-Jones potential used in Ref. [21] one obtains $\sigma_K = 13.9$ Å^2 while for the simple classical hard sphere model with the above molecular diameter the value

$$\sigma_K = \tfrac{2}{3}\,\pi\,R_0^2 = 15.5\ \text{Å}^2$$

is found.

The experimental value of σ_K and the magnitude (not the sign!) of $\sigma_{\mathrm{q\,rot,K}}$ can be extracted from Hermans' [3] measurements of the saturation values of the parallel and perpendicular magnetic Senftleben-Beenakker effects, respectively. For the parallel effect, e. g., Eqs. (3) – (9) yield

$$\left[\frac{\sigma_{\mathrm{qrot,K}}}{\sigma_K}\right]^2_{\mathrm{exp}} = -\frac{3}{5}\,\frac{c_{\mathrm{rot}}}{\frac{25}{4}\,k_B\,\Omega^{(1,1)}/\Omega^{(2,2)} + c_{\mathrm{rot}}}\left(\frac{\Delta\lambda_{\parallel}}{\lambda(H=0)}\right)_{\mathrm{sat}}. \tag{41}$$

The theoretical value for the ratio $\Omega^{(1,1)}/\Omega^{(2,2)}$ is 0.456 for a Lennard-Jones potential and 0.5 for hard spheres [21]. The experimental value for σ_K is extracted from Hermans' (see Ref. [3]) $(H/p_0)_{1/2}$-value and is given by $(\sigma_K)_{\mathrm{exp}} = 15.0$ Å^2 not much different from the theoretical value mentioned before. The saturation value $[\Delta\lambda_{\parallel}/\lambda(H=0)]_{\mathrm{sat}}$ found by Hermans [3] was -7.0×10^{-5}. With these experimental data Eq. (41) gives us the magnitude of the coupling cross section between rotational heat flux and Kagan vector

$$|\sigma_{\mathrm{q\,rot,K}}|_{\mathrm{exp}} = 0.31\ \text{Å}^2\ (\pm 10\%).$$

Hence the agreement of theoretical and experimental values for the effective cross section $\sigma_{\mathrm{q\,rot,K}}$ for p-H_2 at room temperature is astonishingly good despite of the simplicity of the potential used.

Finally the neglect of $\sigma_{\mathrm{q\,tr,K}}$ compared with $\sigma_{\mathrm{q\,rot,K}}$ can be justified as follows: From the Waldmann-Snider collision integrals the equality of two important coupling cross sections can be derived [19]

$$\sqrt{3}\,\sigma_{\mathrm{qtr,K}} = \sigma_{\eta,\mathrm{T}} \tag{42}$$

where $\sigma_{\eta,\mathrm{T}}$ is the coupling cross section of the friction pressure tensor and the tensor polarization. It can be extracted from the saturation value of the Senftleben-Beenakker effect for the viscosity which has been measured by Korving [26], and which gives $|\sigma_{\eta,\mathrm{T}}| \approx 0.02$ Å^2. Thus one has $|\sigma_{\mathrm{q\,tr,K}}| \approx 0.0116$ Å^2 and the ratio $|\sigma_{\mathrm{q\,tr,K}}/\sigma_{\mathrm{q\,rot,K}}|$ is 0.037 which is indeed of the order of magnitude of the nonsphericity parameter β.

For an amended nonspherical potential which takes into account also the attractive part of the interaction, e. g. in the form of a square well in the spherical potential, the DWBA scattering amplitude could still be evaluated analytically. But the expressions for the phase shifts and the radial integrals would become much more complicated and two adjustable parameters (depth and range of the well) would appear. This generalization has not yet been tried.

Appendix

Remarks on the Low Temperature Behaviour of the Senftleben-Beenakker Effect

The low temperature behaviour of the saturation values of the longitudinal and perpendicular effects and of the maximum value of the transverse effect for p-H_2 is briefly discussed. For this purpose the temperature dependence of the expression (9) has to be investigated. At temperature $T_0 \lesssim \hbar^2/2\,k_B\,\Theta \approx 85$ K it is sufficient to take into account only the first two rotational levels $j = 0, 2$ of the p-H_2 molecule. In this approximation c_{rot} is given by

$$c_{\mathrm{rot}}/k_B \approx 5\,\varepsilon(j=2)^2\exp\{-\varepsilon(j=2)\};\ \varepsilon(j) = \hbar^2\,j(j+1)/2\,\Theta\,k_B\,T_0\,, \tag{A 1}$$

and varies strongly with temperature. In the same approximation, the expression for $\sigma_{\mathrm{q\,rot,K}}$, Eq. (21), can be written as

$$\sigma_{\mathrm{qrot,K}} \approx (4\pi/3)\ \sqrt{2/105} \iint \exp\{-\gamma^2\}\,\gamma^5 [\sigma_{\mathrm{ee}}^{(1)}(2,0) - \sigma_{\mathrm{ee}'}^{(1)}(2,0)] \sin\vartheta\, \mathrm{d}\vartheta\, \mathrm{d}\gamma\,, \tag{A 2}$$

where $\sigma_{\mathrm{ee}}^{(1)}(2,0) \equiv \sigma_{\mathrm{ee}}^{(1)}(j_1=2,\ j_2=0,\ \gamma\sqrt{T_0}, \vartheta)$ etc.; i. e. only the $2+0 \rightarrow 2+0$ collisions contribute to the cross section $\sigma_{\mathrm{q\,rot,K}}$. So, the decisive ratio in expression (9) is, for low temperatures, approximately given by $(\sigma_0 = |a_{\mathrm{sph}}|^2)$

$$\frac{3\,\omega_{\mathrm{qrot,K}}}{8\,n_0\,\Omega^{(1,1)}} \approx \sqrt{\frac{2}{105}}\ \frac{\iint \exp\{-\gamma^2\}\,\gamma^5 [\sigma_{\mathrm{ee}}^{(1)}(2,0) - \sigma_{\mathrm{ee}'}^{(1)}(2,0)] \sin\vartheta\, \mathrm{d}\vartheta\, \mathrm{d}\gamma}{\iint \exp\{-\gamma^2\}\,\gamma^5 (1-\cos\vartheta)\,\sigma_0 \sin\vartheta\, \mathrm{d}\vartheta\, \mathrm{d}\gamma}\,. \tag{A 3}$$

The cross sections σ_0, $\sigma_{\mathrm{ee}}^{(1)}$, $\sigma_{\mathrm{ee}'}^{(1)}$ should not be strongly γ-dependent (for classical rigid spheres, e. g., σ_0 is a constant) so that also the ratio Eq. (A 3) can be expected to vary only slowly with temperature. Then the temperature dependence of $A_{\mathrm{el}}^{(\lambda)}$ between 20 and 100 K is mainly determined by the temperature dependence of the factor

$$B_{\mathrm{rot}} = c_{\mathrm{rot}} / [(25\,k_{\mathrm{B}}/4)\ \Omega^{(1,1)}/\Omega^{(2,2)} + c_{\mathrm{rot}}] \tag{A 4}$$

with c_{rot} being given by Equation (A 1).

Measurements performed by Hermans et al. [5] for the transverse heat conductivity of p-H_2 at various temperatures between 22 K and 110 K showed good proportionality of $|\lambda_{\mathrm{trans}}/\lambda(H=0)|_{\max}$ with B_{rot} in agreement with the above considerations.

The author thanks Prof. Dr. L. Waldmann for discussions.

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