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TRANSPORT PHENOMENA IN DIATOMIC GASES AT LOW TEMPERATURES AND IN A MAGNETIC FIELD

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The thermal conductivity and viscosity of light diatomic molecules in the presence of a constant magnetic field are investigated on the basis of a quantum-kinetic equation in which the identity of the particles is taken into account. It is shown that in the transition from high to low temperatures, the behavior of the kinetic coefficients does not change in a magnetic field. The observed quantitative difference in the Senftleben effect for ortho- and para-hydrogen can be explained by taking into account the difference in the statistical weights of states with rotational momenta of different parity.

1. INTRODUCTION

THE change in the transport coefficients of molecular gases in an external field was discovered in O_2 by Senftleben[1] and confirmed to date by a series of experimental researches carried out in O_2 and well as in other gases.[2–4] The theory of this phenomenon[5,6] is based on the classical kinetic equation of Boltzmann and is not directly applicable to the effect in light gases (H_2, HD, D_2), for which the quantum character of the rotational motion is significant even at room temperature. However, the method developed earlier,[6] which was based on the introduction of a small parameter ϵ (the nonsphericity parameter) responsible for the effect, and on the use of the symmetry properties of the collision operator, can also be applied to this case if the Boltzmann equation is replaced by the equation for the single-particle density matrix. Our research is devoted to this purpose.

Of greatest interest to the problem referring to the effect in light gases is the question of the effect of nuclear spin. We shall assume the coupling of the nuclear spin to the axis to be broken (which is already true at $H > 10$ Oe); therefore, the spin of the nucleus affects only the statistics of the molecule. The requirement of quantum-mechanical symmetry leads to the result that in the normal term of the hydrogen molecule, $^1\Sigma_g^+$, the levels with even (odd) values of the rotational angular momentum l exist only for even (odd) total spin of both nuclei and, consequently possess different nuclear multiplicities of degeneracy. Since the probability of change in the spin of H_2 is very small, the hydrogen exists in two different modifications (para and ortho), which do not change into one another (in the absence of a catalyst). The same also applies to deuterium.

We are interested in the following experimental fact: the viscosities of para and normal hydrogen are different.[7] This difference can be explained by interference effects, which lead to the result that the integral scattering cross sections are different for different and identical particles. The calculations, which are carried out under the assumption that the interaction between the molecules is purely central,[8] gave a result much lower than the experiment (at least for $T > 20°K$). This allows us to assume that the difference in the viscosities of para and normal hydrogen is chiefly the result of the noncentral interaction of the molecules. Therefore, the maximum change in the viscosity in the presence of a field[4] should be of the same order of magnitude as the difference in the viscosities of para- and normal hydrogen. Unfortunately, the experiments[4,5] were conducted in different temperature ranges, which excludes the possibility of their comparison.

In connection with the problem of the change in the kinetic coefficients in the field, one must call attention to the experiments of sound dispersion,[9–11] which determine the frequency of rotational relaxation f_{RDF} (RDF = rotational degree of freedom). Since $\epsilon \sim f_{RDF}/f_{TDF}$ (TDF = translational degree of freedom; $f_{TDF} \sim 10^3$ MHz/atm), the results[9–11] make it possible to estimate the nonsphericity parameter.

For H_2, frequency $f_{RDF} = 10$ MHz/atm, for D_2, $f_{RDF} = 15$ MHz/atm, for HD, $f_{RDF} \sim 10^2$ MHZ/atm. Therefore for H_2 and D_2 we have $\epsilon \sim 10^{-2}$, while for HD we have $\epsilon \sim 10^{-1}$. Inasmuch as the relative change in the transfer coefficients is of second order in ϵ,[6] the resultant order of magnitude for the hydrogen isotopes agrees with experiment.[3,4]

2. EQUATION FOR THE DENSITY MATRIX. GENERAL PROBLEM

For the description of the kinetic properties of a gas with rotational degrees of freedom (RDF) at low temperatures ($T \lesssim \hbar^2/2I$) we must consider the single-particle density matrix

$$f^L_{MM'} \equiv f_{LM;\,LM'}(t, \mathbf{r}, \mathbf{p}).$$

in place of the distribution function f(t, r, u, L). Here L, M are the magnitude and projection of the rotational angular momentum L on the fixed axis Z; the translation degrees of freedom are described classically as usual. The nondiagonal (in L) elements of the density matrix are small

$$f_{LL'}/f_{LL} \sim \Omega_{\mathrm{RDF}}/\omega_{LL'} \tag{2.1}$$

(Ω_{RDF} is the inverse of the relaxation time of the RDF),

$$\hbar\omega_{LL'} = \frac{\hbar^2}{2I}[L(L+1) - L'(L'+1)]$$

and cannot be taken into account. The kinetic equation for $f^L_{MM'}$ was obtained by Snider[12] and by Waldman.[13]

In the presence of the magnetic field H, it has the form

$$\frac{\partial \hat{f}}{\partial t}+\frac{\mathbf{p}}{m}\nabla\hat{f}+\frac{i\mu}{\hbar}[\hat{\mathbf{L}}\mathbf{H},\hat{f}]=\left[\frac{\partial\hat{f}}{\partial t}\right]_{\text{coll}},$$

$$\left[\frac{\partial \hat{f}}{\partial t}\right]^{L}_{\text{coll }MN}=16\pi^4\hbar^2\sum_{\substack{L'L_1\ L_1'M_1\\ NN_1\ N'N_1'}}\iint d\mathbf{p}_1\,d\mathbf{p}'\cdot$$
$$\times\langle LML_1M_1(\mathbf{p}\mathbf{p}_1)\,|t|\,L'NL_1'N_1(\mathbf{p}_,'\,\mathbf{p}+\mathbf{p}_1-\mathbf{p}')\rangle_{\text{av}}\cdot$$
$$\times f^{L'}_{NN'}(\mathbf{r},\mathbf{p},t)f^{L_1'}_{N_1N_1'}(\mathbf{r},\mathbf{p}+\mathbf{p}_1-\mathbf{p}',t)\cdot$$
$$\times\langle L'N'L_1N_1'(\mathbf{p}',\mathbf{p}+\mathbf{p}_1-\mathbf{p}')\,|t^*\delta(E)|\,LM'L_1M_1(\mathbf{p}\mathbf{p}_1)\rangle$$
$$+\frac{(2\pi\hbar)^3}{i\hbar}\sum_{L_1M_1NN_1}\int d\mathbf{p}_1[\langle LML_1M_1(\mathbf{p}\mathbf{p}_1)\,|t|\,LNL_1N_1(\mathbf{p}\mathbf{p}_1)\rangle_{\text{av}}\cdot \tag{2.2}$$
$$\times f^{L}_{NM'}(\mathbf{r},\mathbf{p},t)f^{L_1}_{N_1M_1}(\mathbf{r},\mathbf{p}_1,t)-f^{L}_{MN}(\mathbf{r},\mathbf{p},t)f^{L_1}_{M_1N_1}(\mathbf{r},\mathbf{p}_1,t)\cdot$$
$$\times\langle LNL_1N_1(\mathbf{p}\mathbf{p}_1)\,|t^*|\,LM'LM_1(\mathbf{p}\mathbf{p}_1)\rangle_{\text{av}}],$$

where $(\mathbf{p}\cdot\mathbf{p}_1) = {}^1\!/_2(\mathbf{p}-\mathbf{p})$,

$$\langle LML_1M_1(\mathbf{p}\mathbf{p}_1)\,|t|\,L'NL_1'N_1(\mathbf{p}'\mathbf{p}_1')\rangle_{\text{av}}=\langle LML_1M_1(\mathbf{p}\mathbf{p}_1)\,|t|\,L'NL_1'N_1(\mathbf{p}'\mathbf{p}_1')\rangle$$
$$\pm\ g_L^{-1}\langle LML_1M_1(\mathbf{p}\mathbf{p}_1)\,|t|\,L_1'N_1L'N(\mathbf{p}_1'\mathbf{p}')\rangle,$$

$\langle\ldots|t|\ldots\rangle$ is the scattering matrix introduced by Snider.[12]

In contrast with Snider,[12] the identity of particles was taken into account in (2.2) and (2.3), while in contrast with Waldman[13] transitions with change in L are considered. The sign +(–) in (2.3) corresponds to Bose (Fermi) statistics, $g_L = \sum_i (2S^i_L + 1)$ is the number of spin states possible for a given L. In the derivation of (2.2) and (2.3) it was assumed that the spin states of the molecules do not change in the collisions.

The density matrix is normalized, so that the particle density of the gas is

$$n(\mathbf{r},t)=\sum_{LM}\int d\mathbf{p}f^L_{MM}=\mathrm{Sp}\int d\mathbf{p}\hat{f}. \tag{2.4}$$

Equation (2.2) is identically satisfied by the equilibrium density matrix

$$f^{(0)L}_{MM'}=n\delta_{MM'}f^{(0)}(p)f^{(0)}_L,$$
$$f^{(0)}_p=(2\pi mT)^{-3/2}\exp(-p^2/2m),$$
$$f^{(0)}_L=g_LZ^{-1}\exp(-\hbar^2L(L+1)/2IT),$$
$$Z=\sum_L g_L(2L+1)\exp(-\hbar^2L(L+1)/2IT). \tag{2.5}$$

Linearization of Eq. (2.2) relative to a small departure $\hat{\chi}$ from equilibrium

$$\hat{f}=n\hat{f}^{(0)}(1+\hat{\chi}) \tag{2.6}$$

takes the form (the Z axis is directed along the magnetic field):

$$n\sum_{lm}a_{lm}{}^*\hat{A}_{lm}+i\mu H[L_Z,\hat{\chi}]=-n\hat{I}\hat{\chi},$$

$$[\hat{A}_{1m}]^L_{MM'}=\sqrt{\frac{m}{2T}}\,Y_{1m}(\mathbf{u})\left[\frac{mu^2}{2T}-\frac{5}{2}+\frac{\hbar^2L(L+1)}{2IT}-T\frac{\partial\ln Z}{\partial T}\right]\delta_{MM'}, \tag{2.7}$$

$$[\hat{A}_{00}]^L_{MM'}=\left[\left(\frac{2}{3}-\frac{1}{c_v}\right)\left(\frac{mu^2}{2T}-\frac{3}{2}\right)-\frac{\hbar^2L(L+1)}{2ITc_v}+\frac{T}{c_v}\frac{\partial\ln Z}{\partial T}\right]\delta_{MM'}$$

$$[\hat{A}_{2m}]^L_{MM'}=\frac{m}{2T}Y_{2m}(\mathbf{v})\,\delta_{MM'}. \tag{2.7}$$

The explicit form of the a_{lm} is given in[6]; the term $n\hat{I}\hat{\chi}$ is obtained by linearization of $n^{-1}f^{(0)-1}[\partial f/\partial t]_{\text{coll}}$.

As in the classical case,[5,6] the linearized collision operator is divided into two parts:

$$\hat{I}=\hat{I}^{(0)}+\varepsilon\hat{I}^{(1)},\quad \varepsilon\ll 1. \tag{2.8}$$

Here $\hat{I}^{(0)}$ is the Maxwell collision operator for molecules, and the second term, which is assumed to be small, describes processes related to the noncentral interaction of the molecules.

The sought function $\hat{\chi}$ can be expanded in a series in the eigenfunctions of the operator $\hat{I}^{(0)}$. In the quantum case, the role of the spherical harmonics $Y_{lm}(\mathbf{M})$ is played by the irreducible tensors $[Y_{lm}(\hbar\hat{L}/\sqrt{2IT})]^L_{MM'}$, the matrix elements of which differ from zero only if $M - M' = m$. These tensors go over into the normalized spherical harmonics of **M** in the quasiclassical limit if they are normalized by the condition

$$\sum_{M'}[Y_{lm}]^L_{MM'}[Y_{l'm'}]^L_{M'M''}=\left[\frac{\hbar^2L(L+1)}{2IT}\right]^l\delta_{ll'}\delta_{mm'}\delta_{MM''}. \tag{2.9}$$

If we take it into account that in (2.7)

$$[L_ZY_{lm}]^L_{MM'}=(M-M')[Y_{lm}]^L_{MM'}=m[Y_{lm}]^L_{MM'}, \tag{2.10}$$

it then becomes evident that all the contributions of the research of[6] are directly transferred to the quantum case by means of the simple replacement of the spherical harmonics of the rotational angular momentum by the corresponding irreducible tensors, and the integrations over dM by taking the trace. In particular, the scalar product of the two quantities $\hat{A}$ and $\hat{B}$ should be taken in the sense

$$\langle\hat{A},\hat{B}\rangle=\int d\mathbf{p}\,\mathrm{Sp}\,\hat{f}^{(0)}A^*B. \tag{2.11}$$

Then a change in the kinetic coefficients in the magnetic field will be given by the expressions (see[6])

$$\Delta c_{lm;\,l'm}=\varepsilon^2\sum_n\langle\hat{I}^{(1)+}\hat{K}^+\hat{A}_{lm},\hat{\psi}_n\rangle\Delta K_{nn}\langle\hat{\psi}_n\hat{I}^{(1)}\hat{K}\hat{A}_{l'm}\rangle,$$

$$\Delta K_{nn}=-\lambda_n{}^{-1}\sum_{m_1+m_2=m}C^{lm}_{l_1m_1;\,l_2m_2}C^{l'm}_{l_1m_1;\,l_2m_2}\frac{m_2{}^2\gamma^2+im_2\gamma\lambda_n}{\lambda_n{}^2+m_2{}^2\gamma^2} \tag{2.12}$$

$$\gamma=\mu H/pT,\qquad n=(lm;\ l_1l_2.\ r_1r_2).$$

We recall that in the index n which characterizes the eigenfunction of the operator $\hat{I}^{(0)}$, the numbers lm describe the tensor character of the functions, l_1 and l_2 (r_1 and r_2) its dependence on the direction (magnitude) of the velocity and rotational angular momentum. The eigenvalues λ_n depend actually only on l_1 and r_1 ($\lambda_n = \lambda_{r_1 l_1}$).

Equations (2.12) show that the behavior of the transfer coefficients in a magnetic field does not change on going from high to low temperatures, for which quantum effects are substantial.

3. ACCOUNT OF IDENTITY OF PARTICLES

Experiment[4] shows that at room temperature the change in the first viscosity in a magnetic field for para hydrogen exceeds by a factor of two the corresponding value for normal hydrogen. This difference can be explained if we assume that the interference effects, which arise from the identity of the particles in the nonspherical part of the interaction, is large. We limit ourselves to the consideration of first viscosity and the thermal conductivity. Since the principal role in these phenomena is played by transitions without change in L in the collisions, we shall assume that the matrix t is diagonal in the rotational angular momenta of the colliding molecules. Therefore the linearized collision operator has the form

$$[\hat{I}\hat{\chi}]^{L}_{MN} = \sum_{L_1} f^{(0)}_{L_1} (\hat{I}_{LL_1}\hat{\chi})_{MN} + \frac{f^{(0)}_{L}}{g_L} [\Delta \hat{I}_{LL}\hat{\chi}]_{MN}, \tag{3.1}$$

where the first term describes the collisions of molecules with angular momenta L and L_1, considered as non-identical, while the second term is the correction to the collision integral for the identity factor in collisions of particles with angular momentum L (see (2.3)).

For the collision integral $\hat{I}^{(0)}$, it is natural to assume that the interference effects play practically no role. Therefore, the difference in the effects for para- and ortho-modifications enter in only because of the difference in their matrix elements $\hat{I}^{(1)}\hat{K}\hat{A}_{lm}$. For a description of the properties of the nonspherical part of the interaction, we have used the simplest model:

$$[\hat{I}_{LL_1}\hat{K}\hat{A}_{lm}]_{MN} = a^{l} [\psi_n]_{MN}{}^{L} (2L_1 + 1),$$

$$[\Delta\hat{I}_{LL}\hat{K}\hat{A}_{lm}]_{MN} = b^{l} [\psi_n]_{MN}{}^{L} (2L + 1),$$

$$\psi_n = \sum_{m_1+m_2=m} C^{lm}_{lm_1;\,2m_2} Y_{lm_1}\left(\sqrt{\frac{m}{2T}}\,\mathbf{u}\right) Y_{2m_2}\left(\frac{\hbar \mathbf{L}}{\sqrt{2IT}}\right), \tag{3.2}$$

a^{l} and b^{l} depend only on l.

The factor $(2L_1 + 1)$ in (3.2) arises because of summation in $[\hat{I}_{LL_1}\hat{K}\hat{A}_{lm}]_{MN}$ over the projections of the angular momentum matrix which describes a molecule with rotational angular momentum L_1. At high temperatures, the model (3.2) transforms into that used in[6].

In this model,

$$\langle \hat{I}^{+}_{1} \hat{K}^{+} \hat{A}_{lm}, \hat{\psi}_n \rangle = a^{l} \left(\frac{\hbar^2}{2IT}\right)^2 \overline{L^2 (L+1)^2} + b^{l} \left(\frac{\hbar^2}{2IT}\right)^2 \overline{g_L^{-1} f_L^{(0)} (L+1)^2 L^2 (2L+1)}. \tag{3.3}$$

Here we have introduced the notation

$$\overline{\omega(L)} = \sum_{L} f_L^{(0)} \omega(L) (2L+1). \tag{3.4}$$

It is clear that the term with b^{l} in (3.3) must be taken into account only when a small number of levels are excited. At room temperatures, such a situation takes place only for para- and ortho-hydrogen. So far as the different modifications of deuterium and normal hydrogen are concerned, we have for them, without great error,

$$\langle \hat{I}^{+}_{1} \hat{K}^{+} \hat{A}_{lm}, \hat{\psi}_n \rangle = \overline{(\hbar^2/2IT)^2 L^2 (L+1)^2}. \tag{3.5}$$

Therefore the effects on deuterium and its modifications must be identical, and the ratio of the effects on H_2 and D_2 is given by the formula

$$\frac{\Delta_{H_2}}{\Delta_{D_2}} = \left(\frac{\varepsilon_{H_2}}{\varepsilon_{D_2}}\right)^2 \left[\left(\frac{I_{D_2}}{I_{H_2}}\right)^2 \overline{l^2 (l+1)^2_{H_2}} / \overline{l^2 (l+1)^2_{D_2}}\right]^2. \tag{3.6}$$

This ratio is equal to ½, in accord with experiment,[3,4] which gives the difference of ϵ_{H_2} and ϵ_{D_2}: $\epsilon_{D_2} \sim 1.4\, \epsilon_{H_2}$. Such a result is not unexpected, since

$$\frac{\varepsilon_{D_2}}{\varepsilon_{H_2}} \sim \frac{(f_{RDF})_{D_2}}{(f_{RDF})_{H_2}} \frac{(f_{TDF})_{H_2}}{(f_{TDF})_{D_2}} \tag{3.7}$$

(f_{RDF} is the frequency of rotational relaxation).

Upon decrease in temperature $\Delta_{H_2}/\Delta_{D_2}$ tends to zero, because of the smaller value of the moment of inertia of hydrogen.

For the ratio of the effects in parahydrogen and normal hydrogen, we have

$$\frac{\Delta_{pH_2}}{\Delta_{nH_2}} = \frac{[a^{l}\overline{L^2 (L+1)^2}_{pH_2} + b^{l}\overline{L^2 (L+1)^2 g_L{}^{-1} f_L{}^{(0)} (2L+1)}_{pH_2}]^2}{(a^{l})^2 \overline{L^2 (L+1)^2}_{nH_2}}. \tag{3.8}$$

At room temperature, $\Delta_{pH_2}/\Delta_{nH_2} \sim 2$ (see[4]), which is achieved for $b^{l} \sim a^{l}$. For a decrease in temperature, $\Delta_{pH_2}/\Delta_{nH_2}$ tends to zero, and as $T \to \infty$, to unity.

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163