Boundary Condition for the Distribution Function of a Gas of Linear Molecules

J. Halbritter

Institut für Theoretische Physik der Universität Erlangen-Nürnberg, Erlangen

(Z. Naturforsch. **29 a**, 1723—1735 [1974]; received October 9, 1974)

The scattering of linear molecules by a potential wall is studied. It is assumed that the interaction potential between the molecule and the wall depends on the distance of the center of mass of the molecule from the wall and on the orientation of the molecular axis. From the wave function of the reflected molecule an expression for the transition probability for scattering into the various final molecular states is obtained. Together with a modification of Maxwell's assumption for the interaction of atoms with solid surfaces, this transition probability is used to derive a boundary condition for the distribution function of a gas of linear rotating molecules. This also takes into account the change of rotational angular momentum in the collision with the wall.

Introduction

The kinetic theory of non-equilibrium phenomena in dilute molecular gases is based on the Waldmann-Snider equation[1, 2]. For rarefied gases where collisions of the molecules with the walls are of importance this kinetic equation has to be supplemented by a boundary condition for the distribution function. In this paper such a boundary condition for linear molecules is presented. Special emphasis is laid on the phenomena associated with the change of internal rotational angular momentum of the molecule in the collision with the wall. This point is relevant for the Knudsen corrections to the Senftleben-Beenakker effect[3] which have been calculated by Vestner[4], and for the thermomagnetic pressure difference[4, 5]. The latter effect, predicted by Waldmann[5], has been measured by Hulsman et al.[6] in Leiden. The influence of the wall collisions on the molecular rotational angular momentum also plays an important role for the explanation of the "Scott-effect"[7] by Waldmann[5]. In the theoretical treatment of these effects phenomenological boundary conditions for a set of moments of the distribution function have been used[4, 5]. They are derived from irreversible thermodynamics by a method invented by Waldmann[8]. On the other hand, the coefficients occurring in these phenomenological boundary conditions can also be calculated from a boundary condition for the distribution function. This particular point will be treated in a subsequent paper, whereas this paper is concerned with the derivation of the boundary condition for the distribution function itself.

A boundary condition for the distribution function of a monatomic gas had already been given by Maxwell[9]. He assumed that one part of the molecules which hit the wall is specularly reflected and the other part is re-emitted thermally. Because of its simplicity, Maxwell's boundary condition is often used in kinetic theory of rarefied gases. For references confer the book of Cercignani[10] or the article of Grad[11]. In Maxwell's boundary condition the energy exchange between gas and solid is described by a single accommodation coefficient. An extension of Maxwell's boundary condition which includes more than one accommodation coefficient has been given by Cercignani and Lampis[12]. A rigorous microscopic derivation of a boundary condition requires the knowledge of the molecule-wall interaction as well as the solution of the corresponding many-body scattering problem. A formal boundary condition for the distribution function of a monatomic gas has been derived by Kuščer[13]. It contains the interaction of the gas atom with the wall through a many-body scattering operator which also includes the degrees of freedom of the wall. Such a boundary condition is, however, only useful for applications if the corresponding scattering problem can be solved at least in some approach. This is a practically hopeless attempt, the more so as one is not only interested in the change of velocity of the molecule but also in the influence of the collision on the rotational angular momentum. The scattering of atoms by solid surfaces is, however, until now not well understood, neither experimentally nor theoretically. For a discussion of this topic (gas-sur-

Reprint requests to Dr. J. Halbritter, Institut für Theoretische Physik der Universität Erlangen-Nürnberg, *D-8520 Erlangen*, Glückstraße 6.

face interaction) confer e. g. a paper of Goodman[14], where also further references can be found. It is clear that the basis of any complete theory of atom-surface scattering must be a quantum theory of inelastic scattering. Since such a theory is not yet fully developed the molecule-wall interaction must be treated with some model.

In this paper a generalization of Maxwell's assumption is used to derive a boundary condition for the distribution function of a gas of linear molecules. It will be assumed that a fraction α of the incident molecules is thermalized and is re-emitted in an isotropic Maxwell distribution with the temperature of the solid. The molecules of the remaining fraction $(1-\alpha)$ are scattered in such a way as if the solid could be represented by an infinitely high potential wall. Therefore the quantum theory for the scattering of a rotating molecule by a potential wall is studied in some detail. For numerical calculations of boundary coefficients, which will be described in a subsequent paper, further approximations have to be made, whereas a formal boundary condition for the distribution function is derived without such restrictions. In the applications the molecule-wall interaction potential is split into a part which depends on the distance of the center of mass of the molecule from the potential wall ("spherical" part) and a part which depends on the orientation of the molecular axis as well ("nonspherical" part). In connection with molecule-molecule scattering a distorted wave Born approximation (DWBA) has been performed by Köhler, Hess, and Waldmann[15] to investigate the angular momentum dependence of the scattering amplitude. This can be done if the nonspherical part of the intermolecular potential is small compared with the spherical one. A similar approximation is made here for the molecule-wall collisions.

This paper proceeds as follows: First the scattering of linear molecules by a potential wall is investigated. From the asymptotic form of the wave function of the reflected molecules a "transition matrix" is obtained which contains, in particular, the transition probabilities for scattering into the various final free-molecular states. For the special case where the density operator of the molecules incident on the wall is diagonal with respect to the magnetic quantum numbers, the appropriate boundary condition follows immediately. It can be generalized without difficulties to the case of an arbitrary initial density matrix. The boundary condition obtained is in accordance with two general requirements: conservation of the number of particles at the wall (i. e. equality of incident and reflected flux of molecules) and preservation of thermal equilibrium between gas and wall if the incoming particles are already in equilibrium with the wall. It will be shown that these two requirements follow from the unitarity of the S-matrix which describes the scattering of the molecules by the potential wall. The kernel of the boundary condition obtained is calculated explicitly for a simple interaction potential in a distorted wave Born approximation. It should be remarked that the boundary condition for the distribution function can also be used to describe the scattering of a molecular beam by a solid surface.

§1. Scattering of Linear Molecules by a Potential Wall

a) Wave Function of the Scattered Molecules

The axis of the linear molecule will be characterized by the unit vector $\boldsymbol{u}$. The direction of the normal $\boldsymbol{n}$ of the potential wall is chosen as x-axis. It will be assumed that the interaction potential between the molecule and the potential wall depends not only on the x-coordinate of the molecular center of mass but also on the orientation of the axis $\boldsymbol{u}$ relative to the normal $\boldsymbol{n}$. The projection of the momentum of the molecule parallel to the wall will be conserved in the scattering process. The molecular internal angular momentum is denoted by $\boldsymbol{J}$ (in units of $\hbar$), the moment of inertia of the linear molecule is Θ, and the molecular mass is μ. The operator for the rotational energy

$$H_{\text{int.}} = \hbar^2 J^2/2\,\Theta \tag{1.1}$$

has eigenvalues

$$E(j) = \hbar^2 j(j+1)/2\,\Theta \tag{1.2}$$

in states $|jm\rangle$ with rotational quantum numbers j and magnetic quantum numbers m. The total molecular energy is denoted by E, the kinetic energy by $K = p^2/2\,\mu$, where $\boldsymbol{p}$ is the momentum of the molecule. The motion parallel to the potential wall can be separated from the total wave function. Only the wave function describing the motion perpendicular to the wall and the internal motion must be determined. It is a solution of Schrödinger's equation

$$(E' - H_0)\,|\psi\rangle = V\,|\psi\rangle\,, \tag{1.3}$$

with

$$H_0 = H_{\text{int.}} + p_n{}^2/2\,\mu\,,$$
$$E' = E - \hbar^2\, k_{\|}{}^2/2\,\mu\,. \tag{1.4}$$

The interaction potential is denoted by V, $p_n = \boldsymbol{p}\cdot\boldsymbol{n}$ is the projection of $\boldsymbol{p}$ along the normal to the wall, $\boldsymbol{k}_{\|}$ is the component of the wave vector $\boldsymbol{k} = (1/\hbar)\,\boldsymbol{p}$ parallel to the wall. The potential V tends to zero as $x \to +\infty$ and to $+\infty$ as $x \to -\infty$. The solution of Eq. (1.3) therefore has to satisfy the following boundary condition: For $x \to +\infty$ it must be expressible as a sum of two plane waves, one for the incident molecule and the other for the reflected molecule. For $x \to -\infty$ the wave function must vanish. It will be shown that the solution of Eq. (1.3) which satisfies these boundary conditions fulfills the integral equation (Lippmann-Schwinger-equation)

$$|\,\psi^{(+)}\rangle = |\,\Phi^{(-)}\rangle + (E' - H_0 + i\,\eta)^{-1}\, V\,|\,\psi^{(+)}\rangle\,. \tag{1.5}$$

As is well known, the positiv quantity η gives the desired boundary condition $(\eta \to +0)$. The wave function of the incident molecule is denoted by $|\,\Phi^{(-)}\rangle$. It satisfies

$$(E' - H_0)\,|\,\Phi^{(-)}\rangle = 0\,. \tag{1.6}$$

Its coordinate representation

$$\langle x\,|\,\Phi^{(-)}\rangle = e^{ik'x}\,|\,j'\,m'\rangle \tag{1.7}$$

is defined in the whole space. The internal rotational state of the incident molecule is $|\,j'\,m'\rangle$. The x-component of the wave vector of the incident molecule is $k'\,(k' < 0)$. Hence

$$k' = (\mu/\hbar)\,\boldsymbol{c}'\cdot\boldsymbol{n} = (\mu/\hbar)\,c_n{}'\,, \tag{1.8}$$

where $\boldsymbol{c}'$ is the velocity of the incident molecule. In scattering theory a T operator is defined by

$$T\,|\,\Phi^{(-)}\rangle = V\,|\,\psi^{(+)}\rangle\,, \tag{1.9}$$

which obeys the equation

$$T = V + V\,(E' - H_0 + i\,\eta)^{-1}\,T\,. \tag{1.10}$$

In order to determine the wave function for $x \to \pm\infty$, the coordinate representation of the state vector $|\,\psi^{(+)}\rangle$ is used. It will be written as

$$\psi^{(+)}(x, \boldsymbol{u}) = \langle x\,\boldsymbol{u}\,|\,\psi^{(+)}\rangle = \sum_{jm} Y_{jm}(\boldsymbol{u})\,\psi^{(+)}_{jm}(x)\,, \tag{1.11}$$

where the spherical harmonics

$$Y_{jm}(\boldsymbol{u}) = \langle \boldsymbol{u}\,|\,j\,m\rangle \tag{1.12}$$

are the wave functions for the internal rotational states of the linear molecule. The eigenfunctions of H_0, defined by

$$H_0\,|\,k\,j\,m\rangle = \left[\frac{\hbar^2\,k^2}{2\,\mu} + E(j)\right]|\,k\,j\,m\rangle \tag{1.13}$$

describe the free motion of the molecule. They are normalized according to

$$\langle k\,j\,m\,|\,k'\,j'\,m'\rangle = 2\,\pi\,\delta\,(k - k')\,\delta^{jj'}\,\delta_{mm'} \tag{1.13 a}$$

$$\frac{1}{2\,\pi}\sum_{jm}\int_{-\infty}^{+\infty} \mathrm{d}k\,|\,k\,j\,m\rangle\langle k\,j\,m\,| = 1\,, \tag{1.13 b}$$

where "1" is the unit operator in molecular configuration space. It is convenient to use the projection operator on the j-subspace, defined by [16]

$$P^j = \sum_m |\,j\,m\rangle\,\langle j\,m\,|\,. \tag{1.14}$$

It has the following properties:

$$P^j\,J^2 = J^2\,P^j = j\,(j+1)\,P^j$$
$$P^j\,P^{j'} = \delta^{jj'}\,P^j\,,\quad \sum_j P^j = 1\,. \tag{1.15}$$

The coordinate representation of Eq. (1.5) gives the desired wave function $\psi^{(+)}_{jm}(x)$. Using Eqs. (1.7), (1.9,) (1.11) – (1.13) one obtains

$$\psi^{(+)}_{jm}\,(x) = e^{ik'x}\,\delta^{jj'}\,\delta_{mm'}$$
$$+ \frac{1}{2\,\pi}\int_{-\infty}^{+\infty} \frac{\mathrm{d}\varkappa\, e^{i\varkappa x}\, T\,(\varkappa, k')^{jj'}_{mm'}}{E' - \left[\dfrac{\hbar^2\,\varkappa^2}{2\,\mu} + E\,(j)\right] + i\,\eta}\,. \tag{1.16}$$

The quantity $T\,(\varkappa, k')^{jj'}_{mm'}$ in Eq. (1.16) is a matrix element of the T-operator between free particle states

$$T\,(\varkappa, k')^{jj'}_{mm'} = \langle \varkappa\,j\,m\,|\,T\,|\,k'\,j'\,m'\rangle\,. \tag{1.17}$$

The first term on the right of Eq. (1.16) is the projection of the state vector of the incident molecule [given by Eq. (1.7)] on the internal state $|\,j\,m\rangle$, the second term represents the "scattered" molecules. It will be shown that for $x \to +\infty$ this term describes the molecules reflected from the potential wall. As $x \to +\infty$ it reduces to a plane wave propogating away from the potential wall. The amplitude of this plane wave turns out to be proportional to a T-matrix element on the energy shell. As $x \to -\infty$ it will be exactly the negative of the first term, so that $\psi^{(+)}_{jm}(x) \to 0$ as $x \to -\infty$ for all j and m.

Now the behaviour of $\psi^{(+)}_{jm}$ for $x \to +\infty$ will be investigated. As $x \to +\infty$, one can close the contour of integration by a large semicircle in the upper half of the complex $\varkappa$-plane, since the contribution of this semicircle tends to zero as $x \to +\infty$. The poles of the integrand are given by the poles of the T-matrix in the upper half plane and by that zero of the denominator which lies above the real $\varkappa$-axis. The contributions of the poles of the T-matrix tend to zero as $x \to +\infty$. The zero of the denominator which lies above the real $\varkappa$-axis is given by $+\{(2\mu/\hbar^2)[E'-E(j)+i\eta]\}^{1/2}$. Using Cauchy's integral formula, one obtains

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{\mathrm{d}\varkappa\, e^{i\varkappa x}\,T(\varkappa,k')^{jj'}_{mm'}}{E'-\left[\dfrac{\hbar^2\varkappa^2}{2\mu}+E(j)\right]+i\eta} = -\left(\frac{i\mu}{\hbar^2 k_j}\right)e^{ik_jx}\,T(k_j,k')^{jj'}_{mm'}\,, \qquad (1.18)$$

where the quantity k_j is given by

$$k_j=\left[\frac{2\mu}{\hbar^2}\,(E'-E(j))\right]^{1/2}, \qquad (1.19)$$

expressing the conservation of energy in the scattering:

$$\frac{\hbar^2 k_j^2}{2\mu}+E(j)=\frac{\hbar^2 k'^2}{2\mu}+E(j')=E'\,. \qquad (1.20)$$

With the abbreviation

$$R(k_j,k')^{jj'}_{mm'}=-\left(\frac{i\mu}{\hbar^2 k_j}\right)T(k_j,k')^{jj'}_{mm'}\,, \qquad (1.21)$$

the asymptotic form of the wave function can also be written as

$$\psi^{(+)}_{jm}(x)\underset{x\to+\infty}{=}e^{ik'x}\,\delta^{jj'}\,\delta_{mm'}+e^{ik_jx}\,R(k_j,k')^{jj'}_{mm'}\,. \qquad (1.22)$$

The second term on the right of Eq. (1.22) represents the asymptotic form of the wave function of the reflected molecule. Its amplitude is proportional to a T-matrix element on the energy shell since the reflected molecule has the same energy as the incident molecule. A reflection is not possible into all rotational states j, but only into those states, for which k_j, defined by Eq. (1.19), is real. The quantity $R(k_j,k')^{jj'}_{mm'}$ determines the transition probabilities for scattering into the various final free molecular states. It appears, as will be shown later, in the boundary condition for the distribution function. The "transition matrix" $R(k_j,k')^{jj'}_{mm'}$ fulfills two conditions which follow from the unitarity of the S matrix, as will be shown in the next section. It remains to investigate the wave function $\psi^{(+)}_{jm}(x)$ for $x\to-\infty$. In this case one can close the contour of integration by a large semicircle in the lower half of the complex $\varkappa$-plane. That zero of the denominator in Eq. (1.16) which lies below the real $\varkappa$-axis is given by

$$-\left\{\frac{2\mu}{\hbar^2}\,[E'-E(j)+i\eta]\right\}^{1/2}.$$

As $x\to-\infty$ the only contribution to the integral stems from this zero. Using Cauchy's integral formula, one obtains

$$\frac{1}{2\pi}\int_{-\infty}^{+\infty}\frac{\mathrm{d}\varkappa\, e^{i\varkappa x}\,T(\varkappa,k')^{jj'}_{mm'}}{E'-\left[\dfrac{\hbar^2\varkappa^2}{2\mu}+E(j)\right]+i\eta} = -\left(\frac{i\mu}{\hbar^2 k_j}\right)e^{-ik_jx}\,T(-k_j,k')^{jj'}_{mm'}\,. \qquad (1.23)$$

As can be seen from Eqs. (1.16), (1.23), the requirement $\psi^{(+)}_{jm}(x)=0$ for $x\to-\infty$ is equivalent to

$$T(-k_j,k')^{jj'}_{mm'}=i\left(\frac{\hbar^2 k'}{\mu}\right)\delta^{jj'}\,\delta_{mm'}\,. \qquad (1.24)$$

This equivalence can also be established from Schrödinger's equation Eq. (1.3), and from the definition of the T-matrix Eq. (1.9), which are combined to give

$$T\,|\,\Phi^{(-)}\rangle=(E'-H_0)\,|\,\psi^{(+)}\rangle\,. \qquad (1.25)$$

By using Eqs. (1.7), (1.13), the T-matrix element of interest can be expressed as

$$\frac{2\mu}{\hbar^2}\,T(-k_j,k')^{jj'}_{mm'} = \int_{-\infty}^{+\infty} e^{ik_jx}\left[k_j^2\,\psi^{(+)}_{jm}(x)+\frac{\mathrm{d}^2\psi^{(+)}_{jm}(x)}{\mathrm{d}x^2}\right]\mathrm{d}x\,. \qquad (1.26)$$

By partial integration this can be written as

$$\frac{2\mu}{\hbar^2}\,T(-k_j,k')^{jj'}_{mm'} = -\left[\psi^{(+)}_{jm}\,\frac{\mathrm{d}}{\mathrm{d}x}\,(e^{ik_jx})-e^{ik_jx}\,\frac{\mathrm{d}}{\mathrm{d}x}\,(\psi^{(+)}_{jm})\right]_{x=-\infty}^{x=+\infty}. \qquad (1.27)$$

From Eq. (1.27) follows Eq. (1.24) by using the requirement $\psi^{(+)}_{jm}(x)=0$ for $x\to-\infty$, and Eq. (1.22) for the wave function for $x\to+\infty$. Thus it is shown that Eq. (1.5) is equivalent to Schrödinger's equation, but contains the desired boundary condition via the small positive quantity η. This is well known for scattering in three dimensions.

b) Two Properties of the Transition Matrix which Follow from the Unitarity of the S Matrix

The unitarity formulae for the S matrix are different from those which are familiar from the three-dimensional case. This results from the fact that the states of the molecule incident on the potential wall are all different from the states of the reflected molecule (an incident molecule always has $k'<0$, while for a reflected molecule $k>0$). The states representing the reflected molecule do not form a complete set, so that the relation $S S^{\dagger}=1$ is not valid here) in three-dimensional scattering this relation follows from the completeness of the set of free-particle states). To derive the unitarity equations one can proceed in the following way. The S matrix will be defined by

$$S=1-2\pi i\,\delta(E'-H_0)\,T \tag{1.28}$$

as in the three-dimensional case. The state $S|\Phi^{(-)}\rangle$ is investigated, where $|\Phi^{(-)}\rangle$ represents the incident molecule and is defined by Equations (1.6), (1.7). It is convenient to express the δ-function in Eq. (1.28) by the eigenstates of H_0, which are defined by Eq. (1.13). The relation thus obtained

$$\delta(E'-H_0)=\sum_{jm}\int_{-\infty}^{+\infty}\frac{\mathrm{d}\varkappa}{2\pi}\,\delta\left[\frac{\hbar^2\varkappa^2}{2\mu}+E(j)-E'\right]\cdot|\varkappa\,j\,m\rangle\langle\varkappa\,j\,m| \tag{1.29}$$

is used to calculate the state $S|\Phi^{(-)}\rangle$. By using Eqs. (1.21), (1.24) the relation

$$S|\Phi^{(-)}\rangle=\sum_{jm}{}'\,|k_j\,j\,m\rangle\,R(k_j,k')^{jj'}_{mm'}, \tag{1.30}$$

is derived, since the integration over the δ-function can be performed. The prime in Eq. (1.30) and in the following equations indicates that only such rotational quantum numbers j occur for which k_j, defined by Eq. (1.19), is real. One infers from a comparison of Eq. (1.30) with Eq. (1.22) that the S matrix transforms the incident state $|\Phi^{(-)}\rangle$ into the reflected state $S|\Phi^{(-)}\rangle$. The incident states $|\Phi^{(-)}\rangle$ are a complete set on the half space characterized by the projection operator

$$P^{(-)}=\sum_{jm}\int_{-\infty}^{0}\frac{\mathrm{d}k}{2\pi}\,|k\,j\,m\rangle\langle k\,j\,m|, \tag{1.31}$$

whereas the reflected states $S|\Phi^{(-)}\rangle$ form a complete set on the half space with projection operator

$$P^{(+)}=\sum_{jm}\int_{0}^{\infty}\frac{\mathrm{d}k}{2\pi}\,|k\,j\,m\rangle\langle k\,j\,m|. \tag{1.32}$$

The projection operators $P^{(+)}$ and $P^{(-)}$ have the following properties:

$$P^{(+)}P^{(-)}=P^{(-)}P^{(+)}=0, \tag{1.33}$$
$$P^{(+)}P^{(+)}=P^{(+)},\ P^{(-)}P^{(-)}=P^{(-)},\ P^{(+)}+P^{(-)}=1.$$

Since $|\Phi^{(-)}\rangle$ is contained in the half space $P^{(-)}$ and $S|\Phi^{(-)}\rangle$ lies in the half space $P^{(+)}$, one can rewrite Eq. (1.30) as

$$S^{(+-)}|k'\,j'\,m'\rangle=\sum_{jm}{}'\,|k_j\,j\,m\rangle\,R(k_j,k')^{jj'}_{mm'}, \tag{1.34}$$

where $S^{(+-)}$ is defined as

$$S^{(+-)}=P^{(+)}\,S\,P^{(-)}. \tag{1.35}$$

The states $S^{(+-)}|\Phi^{(-)}\rangle$ are complete on the half space characterized by $P^{(+)}$, so that the relation

$$S^{(+-)}\,S^{(+-)\dagger}=P^{(+)} \tag{1.36}$$

must be valid. This is the desired equation replacing $S S^{\dagger}=1$. It leads to an important relation for the transition matrix which will now be derived. The matrix elements of the operator $S^{(+-)}$ are given according to Eqs. (1.13 a), (1.34) by

$$\langle k\,j\,m|S^{(+-)}|k'\,j'\,m'\rangle=2\pi\,\delta(k-k_j)\;R(k_j,k')^{jj'}_{mm'} \tag{1.37}$$

A matrix element of Eq. (1.36) is considered between free molecular states with the same j. By using Eq. (1.37) one obtains the following relation

$$\delta_{mm''}=\sum_{j'}\int_{-\infty}^{0}\mathrm{d}k'\,\delta(k-k_j)\sum_{m'}[R(k,k')^{jj'*}_{mm'}]^*\,R(k,k')^{jj'}_{m''m'} \tag{1.38}$$

with a fixed wave number $k>0$. In performing the integration over the δ-function, the formula

$$\delta[\Phi(k')]=\sum_i\delta(k'-k_i')/|\Phi'(k_i')| \tag{1.39}$$

is used. The quantities k_i' are the roots of the equation $\Phi(k')=0$, and $\Phi'(k_i')$ denotes the derivative of Φ at the point $k'=k_i'$. The sum is taken over all the roots. To the integral in Eq. (1.38) only the root $\Phi(k')=k-k_j(k')$ with the negative sign contributes. This root is given by

$$k_{j'}'=-[k^2+(2\mu/\hbar^2)(E(j)-E(j'))]^{1/2}. \tag{1.40}$$

For a final state with fixed k and j it gives the wave number for the incident molecule in rotational state j' with the same total energy. Performing the integration one obtains the relation

$$\sum_{j'}{}' \frac{k}{[-k_{j'}{}']} \{R(k, k_{j'}{}')^{jj'} R^{\dagger}(k, k_{j'}{}')^{jj'}\}_{mm'} = \delta_{mm'} , \tag{1.41}$$

where a transition operator (an operator with respect to the magnetic quantum numbers) has been defined by

$$\begin{aligned} R(k, k')^{jj'} &= \sum_{m m'} R(k, k')^{jj'}_{mm'} \, | j\, m \rangle \langle j'\, m' | \\ R^{\dagger}(k, k')^{j'j}_{m'm} &= [R(k, k')^{jj'}_{mm'}]^* . \end{aligned} \tag{1.42}$$

The sum in Eq. (1.41) is taken over those quantum numbers j' which give a real $k'_{j'}$. Equation (1.41) is the first desired relation for the transition matrix. The second follows from the requirement that the total flux of the reflected molecules must be equal to the incident flux. The wave function of the reflected molecules is given by the second term on the right of Equation (1.22). If the incident molecules are not in a rotational state $| j'\, m' \rangle$ but in a state $| \chi^{(-)j'} \rangle$ then Eq. (1.22) is changed into

$$\psi^{(+)}_{jm}(x) \underset{x \to +\infty}{=} e^{ik'x} \, \delta jj' \, \chi^{(-)j'}_{m} + e^{ik_j x} \sum_{m'} R(k_j, k')^{jj'}_{mm'} \, \chi^{(-)j'}_{m'} . \tag{1.43}$$

where

$$\chi^{(-)j'}_{m'} = \langle j'\, m' | \chi^{(-)j'} \rangle , \tag{1.44}$$

is the spin function of the incident molecules. The probability current density for the reflected molecules is given by

$$\begin{aligned} J^{(+)} = \frac{\hbar}{\mu} \sum_{m'm''} (\chi^{(-)j'}_{m'})^* \, \chi^{(-)j'}_{m''} \\ \cdot \{\sum_{j}{}' k_j \, R^{\dagger}(k_j, k')^{j'j} R(k_j, k')^{jj'}\}_{m'm''} , \end{aligned} \tag{1.45}$$

where the summation is over all possible rotational quantum numbers j into which a scattering can occur i. e. for which k_j is real. The current density of the incident molecules is

$$J^{(-)} = \frac{(-\hbar\, k')}{\mu} \sum_{m'} | \chi^{(-)j'}_{m'} |^2 . \tag{1.46}$$

Equating Eq. (1.45) and Eq. (1.46), the relation

$$\sum_{j}{}' \frac{k_j}{(-k')} \{R^{\dagger}(k_j, k')^{j'j} \, R(k_j, k')^{jj'}\}_{mm'} = \delta_{mm'} \tag{1.47}$$

is obtained. Because the transition matrix occurs in the boundary condition for the distribution function, as will be shown later, Eq. (1.47) and Eq. (1.41) guarantee the two general requirements: conservation of particle number and preservation of thermal equilibrium between gas and surface. This particular point will be discussed later. It should be mentioned that Eq. (1.47) can also be derived from

$$S^{(+-)\dagger} \, S^{(+-)} = P^{(-)} \tag{1.48}$$

in the same way as Eq. (1.41) was obtained from Eq. (1.36). Equations (1.36), (1.48) expresse the unitarity of the S matrix in scattering by an infinitely high potential wall.

§2. The Transition Matrix in DWBA Approximation

The transition matrix, defined by Eq. (1.21), is related through the Lippmann-Schwinger-equation, Eq. (1.10), with the interaction potential between a molecule and the potential wall. It is assumed that this interaction potential can be split up into a part which depends only on the distance of the center of mass of the molecule from the potential wall (called "spherical" part, in analogy with the terminology used in Ref. [15]), and a part which depends on the orientation of the molecular axis $\boldsymbol{u}$ relative to the normal $\boldsymbol{n}$ of the wall as well (called "nonspherical" part). For the interaction of a homonuclear diatomic molecule with a potential wall one has in good approximation

$$V(x, \boldsymbol{u} \cdot \boldsymbol{n}) = V_0(x) + \varepsilon \, v_1(x) \, P_2(\boldsymbol{u} \cdot \boldsymbol{n}) , \tag{2.1}$$

where ε is a small parameter ($\varepsilon \ll 1$) characterizing the nonspherical interaction; $P_2(\boldsymbol{u} \cdot \boldsymbol{n})$ is a Legendre polynomial with argument $\boldsymbol{u} \cdot \boldsymbol{n} = \cos \vartheta$, ϑ being the angle between $\boldsymbol{u}$ and $\boldsymbol{n}$. For small ε the T matrix can be expanded in powers of ε. The term linear in ε is known as distorted wave Born approximation (DWBA). For the scattering between molecules this approximation has been used by Köhler, Hess, and Waldmann [15] to investigate the angular momentum dependence of the scattering amplitude. In his Thesis, Köhler [17] also performed numerical calculations in view of the Senftleben-Beenakker effect of viscosity and heat conduction. This chapter is an extension of the ideas developed in these papers to the scattering of molecules by a potential wall.

a) Formal Expression for the T matrix in DWBA Approximation

The Lippmann-Schwinger-equation is written in the form

$$T = V + V\, G^{(+)}\, V\,, \tag{2.2}$$

where

$$G^{(+)} = (E' - H + i\,\eta)^{-1} \tag{2.3}$$

is the Green's function for outgoing plane waves pertaining to the full Hamiltonian $H = H_0 + V$. The interaction potential is written as

$$V = V_0 + \varepsilon\, V_1\,, \tag{2.4}$$

which, when inserted in Eq. (2.3), results in an expansion of the operator $G^{(+)}$ of the form

$$G^{(+)} = G_0{}^{(+)} + \varepsilon\, G_0{}^{(+)}\, V_1\, G_0{}^{(+)} + \dots\,, \tag{2.5}$$

where

$$G_0{}^{(+)} = [E' - (H_0 + V_0) + i\,\eta]^{-1} \tag{2.6}$$

belongs to the "spherical" part V_0 alone. An expansion of the T operator in powers of ε is given by

$$T = T_0 + \varepsilon\, T_1 + \dots\,, \tag{2.7}$$

with

$$T_0 = V_0 (1 + G_0{}^{(+)}\, V_0) \tag{2.8 a}$$

$$T_1 = (1 + V_0\, G_0{}^{(+)}) V_1 (1 + G_0{}^{(+)}\, V_0)\,. \tag{2.8 b}$$

Using these equations one can write down the general expressions for the T matrix elements or, with use of Eq. (1.21), the transition matrix in order ε. Using the fact that the states $|j'\,m'\rangle$ are eigenstates of $H_{\text{int.}}$ with eigenvalues $E(j')$, expressed by

$$H_{\text{int.}}\,|j'\,m'\rangle = E(j')\,|j'\,m'\rangle\,, \tag{2.9}$$

one obtains from Eq. (2.8)

$$\begin{aligned} T_0(k,k')^{jj'}_{mm'} &= \langle k\,j\,m\,|\,V_0(1 + G_0{}^{(+)}\,V_0)\,|\,k'\,j'\,m'\rangle \\ &= \delta^{jj'}\,\delta_{mm'}\,\langle k\,|\,V_0 \qquad\qquad (2.10) \\ &\cdot \left[1 + \left(\frac{\hbar^2\,k'^2}{2\,\mu} - \frac{p_n{}^2}{2\,\mu} - V_0 + i\,\eta\right)^{-1} V_0\right] |\,k'\rangle\,. \end{aligned}$$

The energy E' appearing in the preceding equations is given by Equation (1.4). The states $|\,\tilde{\chi}_{k'}^{(\pm)}\rangle$, defined by

$$\left[1 + \left(\frac{\hbar^2\,k'^2}{2\,\mu} - \frac{p_n{}^2}{2\,\mu} - V_0 \pm i\,\eta\right)^{-1} V_0\right] |\,k'\rangle = |\,\chi_{k'}^{(\pm)}\rangle\,, \tag{2.11}$$

are called "distorted waves" and represent the solution of the scattering problem with the potential V_0 alone. In terms of these states the contribution to the T matrix from the first term on the right side of Eq. (2.7) is given by

$$T_0(k,k')^{jj'}_{mm'} = \delta^{jj'}\,\delta_{mm'}\,\langle k\,|\,V_0\,|\,\tilde{\chi}_{k'}^{(+)}\rangle\,. \tag{2.12}$$

As can be seen from Eq. (2.12), the potential V_0 cannot induce changes of the rotational and magnetic quantum numbers. In the case of homonuclear diatomic molecules where the potential is written in the form of Eq. (2.1), the contribution to the T matrix linear in ε is given by

$$T_1(k,k')^{jj'}_{mm'} = P^{jj'}_{2mm'}\,\langle \tilde{\chi}_k^{(-)}\,|\,v_1\,|\,\tilde{\chi}_{k'}^{(+)}\rangle\,, \tag{2.13}$$

with

$$P^{jj'}_{2mm'} = \langle j\,m\,|\,P_2(\boldsymbol{u}\cdot\boldsymbol{n})\,|\,j'\,m'\rangle\,. \tag{2.14}$$

An explicit expression for the operator P_2 in a spin representation is given in Reference[18]. If the distorted waves are known, the transition matrix in order ε can be calculated from Eqs. (2.12), (2.13) and Equation (1.21). For a simple interaction potential an explicit solution of the Schrödinger equation for the distorted waves can be given and the transition matrix can be calculated in order ε. This will be done in the following.

b) Calculation of the Transition Matrix for a Simple Interaction Potential

The size of a homonuclear diatomic molecule is determined by its electron cloud. It can be approximated by an ellipsoid of revolution, where the molecular axis $\boldsymbol{u}$ is the symmetry axis of the ellipsoid. The scattering of a diatomic homonuclear molecule by a potential wall (the plane $x = 0$) is shown in Figure 1. It will be assumed that the interaction potential has the value V_0 if the distance x of the center of mass C of the molecule from the potential wall is smaller than $r(\vartheta)$, and is zero if x is greater than $r(\vartheta)$; the meaning of $r(\vartheta)$ is seen from Fig-

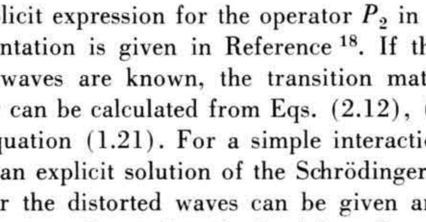

Fig. 1. Scattering of a diatomic homonuclear molecule at an infinite high potential wall. The quantity $r(\vartheta)$ is the distance of the molecular center of mass C from the tangential plane. This plane coincides with the plane $x = 0$ at the moment of contact.

ure 1. The potential $V(x,\vartheta)$ can thus be written as

$$V(x,\vartheta) = V_0\, H[r(\vartheta) - x]\,, \tag{2.15}$$

where H is the Heaviside step function. In the final result the limit $V_0 \to +\infty$ is performed, so that the molecule is certainly reflected from the potential wall. If the ellipsoid deviates only slightly from a sphere, the distance $r(\vartheta)$ is given by

$$r(\vartheta) \approx b\,(1 + \tfrac{1}{2}\,\varepsilon_{\mathrm{E}}^2 \cos^2\vartheta)\,, \tag{2.16}$$

where ε_{E} is the numerical excentricity of the ellipsoid given by $\varepsilon_{\mathrm{E}} = (1 - b^2/a^2)^{1/2}$; a and b are the semiaxes of the ellipsoid. If one inserts Eq. (2.16) into Eq. (2.15) and expands the step function in order $\varepsilon_{\mathrm{E}}^2$, one obtains

$$V(x,\vartheta) = V_0\, H(a-x) + \varepsilon\, V_0\, a\, \delta(a-x)\, P_2(\cos\vartheta)\,, \tag{2.17}$$

which has the form of Eq. (2.1). The parameter ε in Eq. (2.17) is given by $\varepsilon = \frac{1}{3}\,\varepsilon_{\mathrm{E}}^2$.

In order to calculate the T_0 matrix one must solve Schrödinger's equation with the interaction potential $V_0\, H(a-x)$. Figure 2 shows this potential together with the incident and reflected plane waves. The energy $\hbar^2 k'^2/2\mu$ of the incident wave can be taken smaller than V_0, because in the final result the limit $V_0 \to +\infty$ is performed. The amplitude of the reflected wave is denoted by $A_{k'}^{(+)}$. The solution of Schrödinger's equation

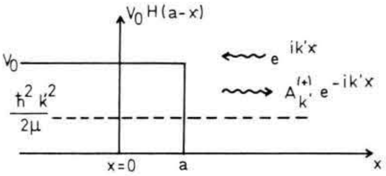

Fig. 2. Scattering by the potential $V(x) = V_0 H(a-x)$.

$$\left[\frac{\hbar^2 k'^2}{2\mu} + \frac{\hbar^2}{2\mu}\frac{\mathrm{d}^2}{\mathrm{d}x^2} - V_0\, H(a-x)\right] \tilde{\chi}_{k'}^{(+)}(x) = 0 \tag{2.18}$$

is written in the form

$$\tilde{\chi}_{k'}^{(+)} = \begin{cases} e^{ik'x} + A_{k'}^{(+)}\, e^{-ik'x} & \text{for } x > a\,, \\ B_{k'}^{(+)}\, e^{\varkappa(k')(x-a)} & \text{for } x < a\,, \end{cases} \tag{2.19}$$

where

$$\varkappa(k') = \left[\frac{2\mu}{\hbar^2}\left(V_0 - \frac{\hbar^2 k'^2}{2\mu}\right)\right]^{1/2} \tag{2.20}$$

is positive and real according to the assumption made above. The amplitudes $A_{k'}^{(+)}$ and $B_{k'}^{(+)}$ are determined from the boundary condition for the wave function at $x = a$ and are given by

$$A_{k'}^{(+)} = -\frac{\varkappa(k') - i\,k'}{\varkappa(k') + i\,k'}\, e^{2ik'a}\,,$$
$$B_{k'}^{(+)} = \frac{2\,i\,k'}{\varkappa(k') + i\,k'}\, e^{ik'a}\,. \tag{2.21}$$

With Eq. (2.21) the solution of Eq. (2.18) is known and the T matrix can be calculated according to Equations (2.12), (2.13). One finds

$$\langle k\,|\,V_0\, H(a-x)\,|\,\tilde{\chi}_{k'}^{(+)}\rangle = 2\,i\,k'\, e^{i(k'-k)a}\, V_0/\,[\varkappa(k') - i\,k]\,[\varkappa(k') + i\,k']\,, \tag{2.22}$$

which in the limit $V_0 \to \infty$ reduces to

$$\lim_{V_0\to\infty} \langle k\,|\,V_0\, H(a-x)\,|\,\tilde{\chi}_{k'}^{(+)}\rangle = \frac{i\,k'\,\hbar^2}{\mu}\, e^{i(k'-k)a}\,. \tag{2.23}$$

Using the relation

$$\tilde{\chi}_k^{(\pm)}(x) = \tilde{\chi}_{-k}^{(\mp)}(x)^*\,, \tag{2.24}$$

which can be derived from time-reversal-invariance, one obtains for the matrix element in Eq. (2.13) the following expression

$$\langle \tilde{\chi}_k^{(-)}\,|\,a\, V_0\, \delta(a-x)\,|\,\tilde{\chi}_{k'}^{(+)}\rangle = 4\,a\,k\,k'\, e^{i(k'-k)a}\, V_0/\,[\varkappa(k) - i\,k]\,[\varkappa(k') + i\,k']\,, \tag{2.25}$$

which in the limit $V_0 \to \infty$ reduces to

$$\lim_{V_0\to\infty} \langle \tilde{\chi}_k^{(-)}\,|\,a\, V_0\, \delta(a-x)\,|\,\tilde{\chi}_{k'}^{(+)}\rangle = (2\,a\,\hbar^2/\mu)\, k\, k'\, e^{i(k'-k)a}\,. \tag{2.26}$$

Thus, for the simple potential described above, the T matrix has been calculated explicitly in order ε. For the transition matrix, defined by Eq. (1.21), one obtains:

$$R(k_j, k')_{mm'}^{jj'} = -e^{i(k'-k_j)a}\,[\delta^{jj'}\,\delta_{mm'} + \varepsilon\, 2\, i\, a\, k'\, P_{2mm'}^{jj'}]\,. \tag{2.27}$$

In Eq. (2.27) the wave numbers k_j and k' are connected by energy conservation according to Equation (1.20). The first term on the right side of Eq. (2.27) represents the scattering by the spherical potential alone. The second term stems from the spin-dependent part of the interaction. As can be seen from the spin-representation of the operator P_2 (cf. Ref. [18]), this term has non-zero matrix elements only of $\Delta j = j' - j = \pm 2$ (inelastic collisions) or if $\Delta j = 0$ (elastic collisions). In an inelastic collision the component of the velocity of the molecule perpendicular to the potential wall is changed because of energy conservation. In the applications of the theory the transition matrix Eq. (2.27) will be used for the calculation of coefficients occurring in the boundary conditions for the mean tangential velocity and the tensor polarization.

§3. Boundary Condition for the Distribution Function of a Gas of Linear Molecules

In § 1 and § 2 of this paper the scattering of molecules by a potential wall has been discussed. The transition matrix, defined by Eq. (1.21), determines the transition probabilities for scattering into free molecular states. In order to determine the boundary condition for the distribution function of a gas at a solid surface, one would have to know the transition probabilities for scattering by a real surface, where each of the surface atoms while oscillating about its equilibrium position interacts with the incident molecule. Unfortunately, however, no generally satisfactory methods are available for treating the scattering of an atom or molecule by a system of bound particles (see e. g. Chapter 11 in Reference [19]). For the interaction potential between the molecule and the surface certain models have to be used. For a more detailed discussion of the interaction between atoms and molecules with solid surfaces confer e. g. a paper of Goodman [14], where also further references can be found.

The model for the gas-surface-interaction used in this paper consists in a generalization of Maxwell's assumption about the reflection of gas atoms by a solid surface. It is assumed that a fraction $(1-\alpha)$ of the molecules which hit the solid surface are scattered so as if the solid would act as an infinite high potential wall, while the remaining fraction α of the incident molecules is thermalized by the surface and re-emitted in an isotropic Maxwell distribution with the temperature of the surface. The parameter α is the accommodation coefficient for the total energy. The boundary condition for the distribution function is first derived for a special case (§ 3a). The general case follows then in a unique way (§ 3b).

a) A Special Case: The Incident Distribution Function is Diagonal in the Magnetic Quantum Numbers

If the velocity of a molecule incident on the surface is denoted by $\boldsymbol{c}'$, then $c_n' = \boldsymbol{c}' \cdot \boldsymbol{n} < 0$, if $\boldsymbol{n}$ is the outer normal of the surface at the point considered. The distribution function of the incident molecules is defined in such a way that $f_-^{j'}(\boldsymbol{c}')_{m'm'}\,\mathrm{d}^3c'$ gives the number of molecules per unit volume with velocity $\boldsymbol{c}'$ in the range d^3c' in a state with rotational quantum number j' and magnetic quantum number m'. The number of molecules leaving the unit area of the surface per unit time with velocity $\boldsymbol{c}$ in d^3c $(c_n = \boldsymbol{c} \cdot \boldsymbol{n} > 0)$ in a rotational state j with magnetic quantum number m is given by $c_n\, f_+^j(\boldsymbol{c})_{mm}\,\mathrm{d}^3c$. If one denotes with $K(\boldsymbol{c}'\,j'\,m \to \boldsymbol{c}\,j\,m)$ the transition probability for a transition from the incident free-particle state $|\boldsymbol{c}'\,j'\,m'\rangle$ into the final free-particle state $|\boldsymbol{c}\,j\,m\rangle$, then the boundary condition for the distribution function is expressed by

$$f_+^j(\boldsymbol{c})_{mm} = \sum_{j'\,m'} \int_{c_n'<0} \mathrm{d}^3c'\, K(\boldsymbol{c}'\,j'\,m' \to \boldsymbol{c}\,j\,m)\, f_-^{j'}(\boldsymbol{c}')_{m'm'}\,. \tag{3.1}$$

The integration and summation in Eq. (3.1) is extended over all incident molecules. If one takes into account the model described above for the interaction of the molecules with the surface, then the transition probability $K(\ldots)$ can be expressed in terms of the transition matrix of Eq. (1.22) and is given by

$$K(\boldsymbol{c}'\,j'\,m' \to \boldsymbol{c}\,j\,m) = (1-\alpha)\, K_{\mathrm{S}}(\boldsymbol{c}'\,j'\,m' \to \boldsymbol{c}\,j\,m) + \alpha\, K_{\mathrm{M}}(\boldsymbol{c}'\,j'\,m' \to \boldsymbol{c}\,j\,m)\,, \tag{3.2}$$

with

$$K_{\mathrm{S}}(\boldsymbol{c}'\,j'\,m' \to \boldsymbol{c}\,j\,m) = |R(c_n, c_n')_{mm'}^{jj'}|^2\, \mu\, c_n\, \delta\left[\frac{\mu}{2}\, c_n^2 + E(j) - \frac{\mu}{2}\, c_n'^2 - E(j')\right] \delta(\boldsymbol{c}'_{\mathrm{tg.}} - \boldsymbol{c}_{\mathrm{tg.}})\,, \tag{3.3}$$

and

$$K_{\mathrm{M}}(\boldsymbol{c}'\,j'\,m' \to \boldsymbol{c}\,j\,m) = (-c_n') \exp\left\{-\beta_{\mathrm{w}}\left[\frac{\mu}{2}\, c^2 + E(j)\right]\right\} [2\,\pi\, Q\,(k_{\mathrm{B}}\, T_{\mathrm{W}}/\mu)^2]^{-1}\,. \tag{3.4}$$

The wave numbers in the transition matrix have been replaced by the velocity according to Equation (1.8). The transition probability K is written as a sum of two terms: the first one represents the scattering by the potential wall (denoted by a subscript "S") and the second one gives the transition probability caused by the thermalization of the incident molecules by the surface (the subscript "M" denotes a Maxwell distribution of the re-emitted molecules). The two δ-functions in Eq. (3.3) indicate the conservation of the total energy of a molecule and of the momentum tangential to the potential wall in the scattering process. In Eq. (3.4) the quantity Q is the rotational partition function

$$Q = \sum_j (2\,j+1)\ \exp\{-\beta_{\mathrm{W}}\,E(j)\}\,, \tag{3.5}$$

where $\beta_{\mathrm{W}} = (k_{\mathrm{B}}\,T_{\mathrm{W}})^{-1}$; k_{B} is Boltzmann's constant and T_{W} is the temperature of the surface. The transition probability K is normalized according to

$$\sum_{j\,m}\ \int_{c_n>0} \mathrm{d}^3c\; c_n\, K(\mathbf{c}'\,j'\,m' \rightarrow \mathbf{c}\,j\,m) = (-c_n')\,. \tag{3.6}$$

The same equation is valid for the quantities K_{S} and K_{M} alone. The factors c_n, $(-c_n')$, and Q in Eqs. (3.3), (3.4) are determined from Eq. (3.6) and from the requirement Equation (1.47).

Equation (3.1) is a boundary condition for the diagonal elements of the distribution functions f_+ and f_- (diagonal with respect to the magnetic quantum numbers), because the transition probability K can connect only occupation probabilities which are diagonal elements. By a generalization of Eq. (3.1) one obtains a boundary condition which also relates non-diagonal elements of both f_+ and f_-. The transition probability K is then replaced by a superoperator $\mathcal{K}$ which contains now four magnetic quantum numbers, one pair of them for the incident distribution matrix and the other pair for the outcoming distribution matrix. Equation (3.1) fulfills the conservation of the particle number and the preservation of thermal equilibrium between gas and surface. This will be shown with the generalized boundary condition which naturally contains Eq. (3.1) as a special case.

b) General Boundary Condition

Equation (3.1) can be generalized in the following way. The summation over the magnetic quantum numbers of the incident distribution function in Eq. (3.1) is of the form

$$\sum_{m'} \left| R(c_n, c_n')^{jj'}_{mm'} \right|^2 f^{j'}_{-}\,(\mathbf{c}')_{m'm'}\,. \tag{3.7}$$

Because f_- is diagonal, this can also be written as

$$\sum_{m''\,m'''} \{R(c_n, c_n')^{jj'}_{mm''}\ \mathrm{R}^\dagger(c_n, c_n')^{j'j}_{m'''m}\}\, f^{j'}_{-}\,(\mathbf{c}')_{m''m'''}\,, \tag{3.8}$$

where the adjoint of the transition matrix is defined by

$$R^\dagger(c_n, c_n')^{j'j}_{m'm} = [R(c_n, c_n')^{jj'}_{mm'}]^*\,. \tag{3.9}$$

From the structure of Eq. (3.8) it is seen that the generalization is achieved by the replacement of the transition probability K by a superoperator

---

$\mathcal{K}^{jj'}(\mathbf{c}, \mathbf{c}')_{mm',m''m'''}$ given by the following expressions:

$$\mathcal{K}^{jj'}(\mathbf{c}, \mathbf{c}')_{mm',m''m'''} = (1-\alpha)\,\mathcal{K}^{jj'}_{\mathrm{S}}\,(\mathbf{c}, \mathbf{c}')_{mm',m''m'''} + \alpha\,\mathcal{K}^{jj'}_{\mathrm{M}}\,(\mathbf{c}, \mathbf{c}')_{mm',m''m'''}\,, \tag{3.10}$$

$$\mathcal{K}^{jj'}_{\mathrm{S}}\,(\mathbf{c}, \mathbf{c}')_{mm',m''m'''} = R(c_n, c_n')^{jj'}_{mm''}\ R^\dagger(c_n, c_n')^{j'j}_{m'''m'} \times \mu\, c_n\, \delta\left[\frac{\mu}{2}\, c_n^{\,2} + E(j) - \frac{\mu}{2}\, c_n'^{\,2} - E(j')\right] \delta(\mathbf{c}'_{\mathrm{tg.}} - \mathbf{c}_{\mathrm{tg.}})\,, \tag{3.11}$$

$$\mathcal{K}^{jj'}_{\mathrm{M}}\,(\mathbf{c}, \mathbf{c}')_{mm',m''m'''} = (-c_n')\, e^{-\beta_{\mathrm{W}}[(\mu/2)\,c^2 + E(j)]} \left[2\,\pi\, Q \left(\frac{k_{\mathrm{B}}\,T_{\mathrm{W}}}{\mu}\right)\right] \delta_{mm'}\,\delta_{m''m'''}\,. \tag{3.12}$$

The diagonal elements of the superoperator $\mathcal{K}$ are identical with the transition probabilities

$$\mathcal{K}^{jj'}(\mathbf{c}, \mathbf{c}')_{mm,m'm'} = K(\mathbf{c}'\,j'\,m' \rightarrow \mathbf{c}\,j\,m)\,, \tag{3.13}$$

as it should be. Thus one obtains the following boundary condition:

$$f^{j}_{+}\,(\mathbf{c})_{mm'} = \sum_{j'}\ \sum_{m''\,m'''}\ \int_{c_n'<0} \mathrm{d}^3c'\, \mathcal{K}^{jj'}(\mathbf{c}, \mathbf{c}')_{mm',m''m'''}\, f^{j'}_{-}\,(\mathbf{c}')_{m''m'''}\,. \tag{3.14}$$

If the distribution matrix of the incoming molecules is known, Eq. (3.14) allows in principle the calculation of the distribution function of the outcoming molecules. Equation (3.14) can be written in operator form, if the action of the superoperator $\mathcal{K}$ on the incoming distribution matrix is defined by

$$[\mathcal{K}^{jj'}(\mathbf{c},\mathbf{c}')\, f_-^{j'}(\mathbf{c}')]_{mm'} = \sum_{m''m'''} K^{jj'}(\mathbf{c},\mathbf{c}')_{mm',m''m'''}\, f_-^{j'}(\mathbf{c}')_{m''m'''}\,. \tag{3.15}$$

Equation (3.14) then becomes

$$f_+^{j}(\mathbf{c}) = \sum_{j'} \int_{c_n'<0} \mathrm{d}^3c' [\mathcal{K}^{jj'}(\mathbf{c},\mathbf{c}')\, f_-^{j'}(\mathbf{c}')]\,. \tag{3.16}$$

c) Conservation of the Number of Patricles at the Surface. Thermal Equilibrium Between Gas and Surface

The number of molecules incident on unit area of the surface per unit time must be equal to the number of molecules leaving the unit area of the surface in unit time. This is expressed by

$$\sum_{jm} \int_{c_n>0} c_n\, f_+^{j}(\mathbf{c})_{mm}\, \mathrm{d}^3c = \sum_{j'm'} \int_{c_n'<0} (-c_n')\, f_-^{j'}(\mathbf{c}')_{m'm'}\, \mathrm{d}^3c\,. \tag{3.17}$$

The boundary condition must satisfy this equation. By substituting Eq. (3.14) into Eq. (3.17) one obtains for the left side of Eq. (3.17)

$$\sum_{j'} \sum_{m''m'''} \int_{c_n'<0} \mathrm{d}^3c'\, f_+^{j'}(\mathbf{c}')_{m''m'''} \sum_{jm} \int_{c_n>0} \mathrm{d}^3c\, \mathcal{K}^{jj'}(\mathbf{c},\mathbf{c}')_{mm,m''m'''}\, c_n\,. \tag{3.18}$$

It can be shown, however, that the superoperator has the property

$$\sum_{jm} \int_{c_n>0} \mathrm{d}^3c\, \mathcal{K}^{jj'}(\mathbf{c},\mathbf{c}')_{mm,m''m'''}\, c_n = \delta_{m''mm'''}\, (-c_n')\,, \tag{3.19}$$

so that Eq. (3.17) is satisfied identically. Equation (3.19) is a consequence of Equation (1.47). To see this, let us substitute Eqs. (3.10), (3.12) into Eq. (3.19) and perform the integrations over the δ-functions of $\mathcal{K}_\mathrm{S}$, using also Eq. (3.6):

$$\frac{1}{(-c_n')} \sum_{jm} \int_{c_n>0} \mathrm{d}^3c\, \mathcal{K}^{jj'}(\mathbf{c},\mathbf{c}')_{mm,m''m'''}\, c_n$$

$$= (1-a) \sum_{j}{}' \frac{k_j}{(-k')} \{R^\dagger(k_j,k')^{j'j}\, R(k_j,k')^{jj'}\}_{m''m'''} + a\, \delta_{m''m'''}\,. \tag{3.20}$$

With Eq. (1.47) the desired Eq. (3.19) now follows immediately. It is not surprising that Eq. (1.47) guarantees the particle conservation, as that equation was derived from the conservation of the probability current density in the scattering at the potential wall.

The boundary condition must preserve thermal equilibrium between the gas and the surface. This means that, if the incident distribution function is a Maxwell distribution corresponding to the temperature of the surface, the outgoing one must also be a Maxwellian with the same temperature. The incoming distribution is assumed to be of the form

$$f_-^{j'}(\mathbf{c}')_{mm'} \propto \delta_{mm'}\, e^{-\beta_\mathrm{W}[(\mu/2)c'^2+E(j')]}\,. \tag{3.21}$$

If one inserts Eq. (3.21) into the right side of Eq. (3.14) one obtains

$$f_+^{j}(\mathbf{c})_{mm'} \propto e^{-\beta_\mathrm{W}[(\mu/2)c^2+E(j)]}\, \{(1-a) \sum_{j'm''} \int_{c_n'<0} \mathrm{d}^3c'\, \mathcal{K}_\mathrm{S}^{jj'}(\mathbf{c},\mathbf{c}')_{mm',m''m''} + a\, \delta_{mm'}\}\,, \tag{3.22}$$

since the superoperator $\mathcal{K}_\mathrm{S}$ contains a δ-function which expresses the conservation of the total energy of a molecule in the scattering process. It will instantly be shown that the superoperator $\mathcal{K}_\mathrm{S}$ fulfills the condition

$$\sum_{j'm''} \int_{c_n'<0} \mathrm{d}^3c'\, \mathcal{K}_\mathrm{S}^{jj'}(\mathbf{c},\mathbf{c}')_{mm',m''m''} = \delta_{mm'}\,. \tag{3.23}$$

The distribution function of the outcoming molecules is then proportional to $\delta_{mm'}\, e^{-\beta_\mathrm{W}[(\mu/2)c^2+E(j)]}$, i. e. it is proportional to a Maxwell function with the temperature of the surface, as required. The proof of

Eq. (3.23) is quite analogous to the corresponding proof of Equation (3.19). One inserts Eq. (3.11) into Eq. (3.23) and performs the integrations over the δ-functions. The result is:

$$\sum_{j' m''} \int_{c_n' < 0} \mathrm{d}^3 c' \, \mathcal{K}_{\mathrm{S}}^{jj'} (\mathbf{c}, \mathbf{c}')_{mm', m'' m''} = \sum_{j'}{}' \frac{k}{(-k'_{j'})} \{ R(k, k'_{j'})^{jj'} R^{\dagger}(k, k'_{j'})^{j'j} \}_{mm'} \,. \tag{3.24}$$

Using Eq. (1.41), the desired Eq. (3.23) follows imediately.

With Eq. (3.14) a consistent boundary condition for the distribution matrix of a gas of linear molecules has been obtained. It is less general than the boundary condition of Kuščer [13], which includes in principle the full complexity of the many body problem, but is only for monatomic gases. Equation (3.14) with Eqs. (3.10) – (3.12) is useful for establishing boundary conditions for the average gas velocity and the tensor polarization. This will be shown in a subsequent paper. It can also be used to study the scattering of a molecular beam by a solid surface.

d) Reciprocity Relation

The phases of the free-particle states are chosen here in such a way that the relation

$$\vartheta \, | k \, j \, m \rangle = (-)^m \, | -k \, j - m \rangle \tag{3.25}$$

holds, where ϑ is the operator of time-reversal (confer Reference [19]). Time-reversal invariance is expressed by the equation

$$T(k, k')^{jj'}_{mm'} = (-)^{m'-m} \, T(-k', -k)^{j'j}_{-m'-m} \tag{3.26}$$

for the matrix elements of the T operator. According to Eq. (1.21), the relation

$$k_j \, R(k_j, k')^{jj'}_{mm'} = (-)^{m'-m} (-k') \;\; R(-k', -k_j)^{j'j}_{-m'-m} \tag{3.27}$$

for the transition matrix follows from Equation (3.26). If one multiplies Eq. (3.27) with its complex conjugate, one gets

$$\frac{k_j}{(-k')} \left| R(k_j, k')^{jj'}_{mm'} \right|^2 = \frac{(-k')}{k_j} \left| R(-k', -k_j)^{j'j}_{-m'-m} \right|^2 \tag{3.28}$$

which relates the transition probabilities for the direct transition and the time-reversed one. Equation (3.27) leads to an equation for the transition probability P or the superoperator $\mathcal{K}$, which is known as "reciprocity relation". According to Eq. (3.27) the following relation is obtained for the superoperator K_{S}:

$$(-c_n') \mathcal{K}_{\mathrm{S}}^{jj'} (\mathbf{c}, \mathbf{c}')_{mm', m'' m'''} = (-)^{m-m'+m'''-m''} \; c_n \mathcal{K}_{\mathrm{S}}^{j'j} (-\mathbf{c}', -\mathbf{c})_{-m''-m''', -m-m'} \,. \tag{3.29}$$

Taking into account Eq. (3.10) and Eq. (3.12), one gets the relation

$$\begin{aligned} &(-c_n') e^{-\beta_{\mathrm{W}} [(\mu/2) c'^2 + E(j')]} \mathcal{K}^{jj'} (\mathbf{c}, \mathbf{c}')_{mm', m'' m'''} \\ &\qquad = (-)^{m-m'+m'''-m''} \, c_n \, e^{-\beta_{\mathrm{W}} [(\mu/2) c^2 + E(j)]} \, \mathcal{K}^{j'j} (-\mathbf{c}', -\mathbf{c})_{-m''-m''', -m-m'} \end{aligned} \tag{3.30}$$

for the superoperator $\mathcal{K}$. For the special case $m = m', m'' = m'''$ Eq. (3.30) reduces to an equation for the transition probability K of the form

$$(-c_n') e^{-\beta_{\mathrm{W}} [(\mu/2) c'^2 + E(j')]} \, K(\mathbf{c}' \, j' \, m' \to \mathbf{c} \, j \, m) = (c_n) \, e^{-\beta_{\mathrm{W}} [(\mu/2) c^2 + E(j)]} K(-\mathbf{c} \, j - m \to -\mathbf{c}' \, j' - m') \,. \tag{3.31}$$

From Eq. (3.29) one recovers Eq. (3.23) by integration and summation and using Equation (3.19). But the strong reciprocity relation is not necessary for preservation of thermal equilibrium between gas and wall, already the integral relation Eq. (3.23), which follows from unitarity of the S matrix, is sufficient. The same must be true in the general case, when the matrix elements of the scattering operator T also contain the internal states of the surface. This is in contrast to Kuščer [13], who used a reciprocity relation similar to the above one for the proof of thermal equilibrium. Finally it should be noted that a reciprocity relation for the interaction of an atomic beam with a solid surface had been verified experimentally by Miller and Subbarao[20]. More detailed information can be found in a paper by Wenaas[21] and in the book by Cercignani[10].

The boundary condition for the distribution function of a gas of linear molecules derived in this paper will be used in a following one for the calculation of boundary conditions for the average gas velocity and tensor polarization. The knowledge of the transition matrix even for a very simple interaction potential (§ 2b) allows a calculation of coefficients appearing in these boundary conditions and a comparison with experimental data.

Acknowledgement

I thank Prof. L. Waldmann for stimulating this work and for many helpful comments. Thanks are due also to Dr. W. E. Köhler, Dr. H. Vestner, and Dr. S. Hess for numerous discussions.

---

[1] L. Waldmann, Z. Naturforsch. **12 a**, 660 [1957]; **13 a**, 609 [1958], and in "Handbuch der Physik", ed. S. Flügge, Vol. 12, Springer-Verlag, Berlin 1958.

[2] R. F. Snider, J. Chem. Phys. **32**, 1051 [1960].

[3] A summary is given by J. J. M. Beenakker in "Festkörperprobleme VIII", ed. O. Madelung, Vieweg, Braunschweig 1968; J. J. M. Beenakker and R. F. McCourt, Ann. Rev. Phys. Chem. **21**, 47 [1970].

[4] H. Vestner, "Transporterscheinungen und Randbedingungen in verdünnten mehratomigen Gasen im Magnetfeld", Thesis Erlangen 1973; Z. Naturforsch. **28 a**, 869 [1973]; Z. Naturforsch. **29 a**, 663 [1974].

[5] L. Waldmann, Z. Naturforsch. **22 a**, 1678 [1967]; Communications at A. P. S. Meeting, Dallas, March 1970.

[6] H. Hulsman, F. G. van Kuik, H. F. P. Knaap, and J. J. M. Beenakker, Physica **57**, 522 [1972]; H. Hulsman, G. F. Bulsing, G. E. Eggermont, L. J. F. Hermans, and J. J. M. Beenakker, Physica **72**, 287 [1974].

[7] G. G. Scott, H. W. Sturner, and R. M. Williamson, Phys. Rev. **158**, 117 [1967]; Phys. Letters **25 A**, 573 [1967].

[8] L. Waldmann, Z. Naturforsch. **22 a**, 1269 [1967].

[9] J. C. Maxwell, Phil. Trans. Royal Soc. I, Appendix (1879); reprinted in: "The Scientific Papers of J. C. Maxwell", Dover Publication (1965).

[10] C. Cercignani, Mathematical Methods in Kinetic Theory, Plenum Press, New York 1969.

[11] H. Grad, in: "Handbuch der Physik", ed. S. Flügge, Vol. 12, Springer-Verlag, Berlin 1958.

[12] a) C. Cercignani and M. Lampis, Trans. Theory Stat. Phys. **1**, 101 [1971]. b) C. Cercignani and M. Lampis, International Symposium on Rarefied Gas Dynamics, Academic Press, New York, London 1974.

[13] I. Kuščer, Surface Science **25**, 225 [1971].

[14] F. O. Goodman, Surface Science **26**, 327 [1971].

[15] W. E. Köhler, S. Hess, and L. Waldmann, Z. Naturforsch. **25 a**, 336 [1970].

[16] S. Hess, Springer Tracts in Modern Physics, Vol. **54**, 135 [1970], Springer-Verlag, Berlin 1970.

[17] W. E. Köhler, Transporterscheinungen in Gasen aus linearen Molekülen im äußeren Magnetfeld und nichtsphärische Wechselwirkung, Thesis Erlangen 1970; Z. Naturforsch. **26 a**, 1926 [1971]; Z. Naturforsch., to be published.

[18] S. Hess and W. E. Köhler, Z. Naturforsch. **23 a**, 1903 [1968].

[19] M. L. Goldberger and K. M. Watson, "Collision Theory", John Wiley, New York 1964.

[20] D. R. Miller and R. B. Subbarao, J. Chem. Phys. **55**, 1478 [1971].

[21] E. P. Wenaas, J. Chem. Phys. **54**, 376 [1971].