EFFECT OF INELASTIC COLLISIONS ON TRANSPORT PHENOMENA IN HOT GASES

V. M. Dubner and N. V. Komarovskaya

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The contribution of nonresonance inelastic collisions of atoms or molecules to the transport coefficients is examined within the framework of the classical approximation of collision theory. Attention is concentrated on transitions between upper levels adjacent to the continuous spectrum. A general estimate is obtained for the total inelastic collision cross section, and certain limiting cases are investigated.

The kinetic theory of gases with internal degrees of freedom [1, 2] permits expression of the transport coefficients in terms of the so-called collision integrals, which take inelastic processes into account. For the collision of a structured and a structureless particle (we confine ourselves to this case), the following two integrals are the most important:

$$\Omega^{(1,1)} = \left(\frac{T}{2\pi M^*}\right)^{1/2} \left\langle \frac{M^*(w^2 - \vec{w}\vec{w}')}{2T} \right\rangle,$$
$$\Omega^{(2,2)} = \left(\frac{T}{2\pi M^*}\right)^{1/2} \left\langle \left(\frac{M^*}{2T}\right)^2 \times \right.$$
$$\left. \times \left[w^4 - (\mathbf{w}\mathbf{w}')^2 - \frac{1}{6}\,(w^2 - w'^2) \right] \right\rangle, \qquad (1)$$

where

$$\langle \ldots \rangle =$$
$$= \frac{1}{4}\left(\frac{\pi M^*}{2T}\right)^{1/2} \int \sum_{ik} (\ldots)\, W_{ik} \exp\left(-\frac{E_i}{T}\right) f_0(\mathbf{w})\, d\mathbf{w} \times$$
$$\times \left[\sum_i \exp\left(-\frac{E_i}{T}\right)\right]^{-1} \qquad (2)$$

Here, E_i are the energy levels of the structured particle of mass M_0; T is the temperature in energy units; **w** and **w'** are the relative velocities of the colliding particles before and after collision; $M^* = m_2M_0/(m_2 + M_0)$ is the reduced mass; m_2 is the mass of the structureless particle; W_{ik} is the probability of a transition accompanied by a change of relative velocity $\mathbf{w} \to \mathbf{w}'$ and internal state $E_i \to E_k$;

$$f_0 = \left(\frac{M^*}{2\pi T}\right)^{3/2} \exp\left(-\frac{M^* w^2}{2T}\right)$$

is the normalized Maxwellian relative velocity distribution.

Clearly, the quantities Ω depend importantly on the entire set of inelastic collision probabilities W_{ik}, which, as a rule, are only approximately known, and, even in this case, finding sums of type (2) involves cumbersome computations. Therefore, we have attempted to find quantities (1) directly on the basis of the classical approximation of collision theory [3, 4]. This method permits us to make certain estimates of the role of inelastic collisions of atoms and electrons with atoms.

1. The classical approach to the structured particle implies that its "simple" component particles with masses m and m_0($m + m_0 = M_0$) have classical velocities **v**, $\mathbf{v}_0$ and coordinates **R**, $\mathbf{R}_0$; their interaction is described by the effective potential V ($\mathbf{r} \equiv \mathbf{R} - \mathbf{R}_0$). The motion of the structured particle as a whole is characterized by the distribution function $F_0(\mathbf{G}_0)$ of the velocity of the center of inertia $\mathbf{G}_0 = m\mathbf{v} + m_0\mathbf{v}_0/M_0$, while the internal state with negative energy $0 \geq -E \geq$ $\geq \min V(r)$ is given by the distribution

$$\delta\left\{-E - \frac{\mu_0 g_0^2}{2} - V(r)\right\}, \qquad (3)$$

where $\mathbf{g}_0 = \mathbf{v} - \mathbf{v}_0$ is the relative velocity of the particles m and m_0, and $\mu_0 = mm_0/M_0$ is their reduced mass.

In the classical approximation, the interaction of a structured and an impinging particle m_2 (with velocity $\mathbf{v}_2$ distributed according to the law $f_2(\mathbf{v}_2)$) is treated as the scattering of a particle m (or m_0) at m_2, accompanied by an instantaneous change of velocity $\mathbf{g} = \mathbf{v} - \mathbf{v}_2$ by $\mathbf{g}'$, as a result of which there is a change in the energy of relative motion in the structured particle. "Instantaneity" of collision means that the characteristic dimensions of the region of interaction of the particles m (or m_0) and m_2 must be much less than the characteristic dimension of the structured particle in the state with binding energy $-E$.

It follows that the classical approximation, in which the discrete character of the spectrum of the structured particle is disregarded, can be used to calculate means of type (2) when: a) the chief contribution to these means is made by transitions between highly excited states; b) the density of these states

$$\rho(E) = \int \delta\left\{-E - \frac{\mu_0 g_0^2}{2} - V(r)\right\} \frac{\mu_0^3\, d\mathbf{g}_0\, d\mathbf{r}}{h^3} \qquad (4)$$

is such that the distances between neighboring levels are small in comparison with the mean particle energy m_2T : $\rho T \gg 1$; and c) the total number of these states is large:

$$\int \rho(E)\, dE \gg 1.$$

2. Thus, we will consider the collision of a stationary structured particle $[F_0(\mathbf{G}_0) = \delta(\mathbf{G}_0)]$ in a state with

energy $-E$ and a particle m_2. For the present we confine ourselves to the interaction of m_2 and m, which we characterize by the differential cross section for elastic scattering $d\sigma(g)$. Then, the probability of a transition with change of velocity $\mathbf{w} \to \mathbf{w}'$ is $g d\sigma$. Multiplication of $g d\sigma$ by the delta function (3) and integration over the scattering angles, $d\mathbf{w}$, and phase space $\mu_0^3 d\mathbf{g}_0 d\mathbf{r}/h^3$ is equivalent to the summation over all end states E_k in (2). The subsequent integration over all permissible values of E corresponds to summation over the initial states. Introducing the notation $M = m + m_2$, $\mu = mm_2/M$ and going over to the new integration variables $\mathbf{g}$ and $\mathbf{u} = (\mu/M^*)\mathbf{g}_0 + (m_2/M)\mathbf{v}_2$, we arrive at the expression

$$\left(\frac{2\pi M^*}{T}\right)^{1/2} \Omega^{(1,1)} = \frac{1}{4\pi Q}\left(\frac{M^*\mu_0}{2hT}\right)^3 \int \left\{\left(\frac{\mu g}{M^*}\right)^2 + \frac{\mu m_0}{M^* M_0}(\mathbf{ug}' - \mathbf{ug}) - \frac{\mu^2}{M^{*2}}\mathbf{gg}'\right\} \times$$
$$\times \exp\left\{\frac{E}{T} - \frac{M^*}{2T}\left[\left(\frac{m_0 u}{M_0}\right)^2 - 2\frac{m_0\mu}{M_0 M^*}\mathbf{ug} + \left(\frac{\mu g}{M^*}\right)^2\right]\right\} \delta\left\{(E+V) - \frac{\mu_0}{2}\left[u^2 + 2\frac{m_2}{M}\mathbf{ug} + \left(\frac{m_2}{M}g\right)^2\right]\right\} \times$$
$$\times g\, d\sigma(g)\, d\mathbf{g}\, d\mathbf{u}\, d\mathbf{r},$$

where

$$Q = \int_0^{E_{\max}} \exp\left(\frac{E}{T}\right)\rho\, dE.$$

The integral $\Omega^{(2,2)}$, which we henceforth leave out of consideration, has a similar, but more unwieldy form.

If $d\sigma$ does not depend on the azimuthal scattering angle, integration over all directions of $\mathbf{g}'$ permits a transformation of the first factor of the integrand to

$$\left(\frac{\mu g}{M^*}\right)^2 - \frac{\mu m_0}{M^* M_0}\mathbf{ug},$$

and the replacement of $d\sigma$ in (5) with

$$\sigma_1(g) = \int (1 - \cos\vartheta)\, d\sigma(g, \vartheta)$$

the effective cross section for momentum transfer. After integration over the angles, Eq. (5) takes the form

$$\frac{2\pi M}{\mu_0 m_2 Q}\left(\frac{M^*\mu_0}{2hT}\right)^3 \int u g^2 \sigma_1(g)\, dE\, d\mathbf{r}\, dg\, du \times$$
$$\times \left\{\left(\frac{\mu}{M^*} + \frac{\mu\mu_0}{2m^2}\right) g^2 + \frac{E+V}{\mu} + \frac{\mu_0}{2\mu}u^2\right\} \times$$
$$\times \exp\left\{\frac{E}{T} - \frac{M^*}{2T} \times \left[\frac{\mu_0}{\mu}u^2 + \frac{2(E+V)}{M^*} + \frac{\mu}{M^*}g^2\right]\right\},$$

the integration with respect to u being confined to the region

$$\left|\sqrt{-\frac{2(E+V)}{\mu_0}} - \frac{m_2}{M}g\right| \leqslant u \leqslant \sqrt{-\frac{2(E+V)}{\mu_0}} + \frac{m_2}{M}g,$$

so that

$$\left(\frac{2\pi M^*}{T}\right)^{1/2} \Omega^{(1,1)} = \frac{4\pi m T}{\mu_0^3 M^* Q}\left(\frac{M^*\mu_0}{2hT}\right)^3 \times$$
$$\times \int g^2 \left[\left(g^2 + \frac{T}{M^*}\right)\operatorname{sh}\left(\frac{M^* v g}{T}\right) - v g \operatorname{ch}\left(\frac{M^* v g}{T}\right)\right] \times$$
$$\times \exp\left\{\frac{E}{T} - \frac{M^*}{2T}(g^2 + v^2)\right\} \sigma_1(g)\, dg\, d\mathbf{r}\, dE,$$

where

$$v(\mathbf{r}) = \frac{m_0}{M_0}\sqrt{-\frac{2(E+V)}{\mu_0}}$$

is the velocity of the particle with mass m for finite motion of the pair $m + m_0$ with energy $-E$.

Expression (6) takes into account, in the classical approximation, all the elastic and inelastic collisions of the particle m_2 with the particle M_0 in all bound states, including the lower ones for which the continuous spectrum approximation is known to be incorrect. Therefore, in (6) the integration with respect to E should be confined to the region of highly excited states, while quantum calculations must be used to take inelastic collisions with lower states into account. We note, however, that owing to the large distances between these levels and their small populations (as compared with the ground state), the part played by nonresonance collisions with atoms and molecules in lower states should evidently be very small.

3. In certain cases, a further simplification of integral (6) is possible. If the mean velocity of particle m is small in comparison with $(T/M^*)^{1/2}$, i.e.,

$$\langle v^2 \rangle = \left(\frac{m_0}{M_0}\right)^2 \int g_0^2\, \delta\left\{-E - \frac{\mu_0 g_0^2}{2} - V\right\} \times \exp\left(\frac{E}{T}\right)\frac{\mu_0^3 d\mathbf{g}_0 d\mathbf{r}\, dE}{h^3} \times \left[\int_0^{E_{\max}} \exp\left(\frac{E}{T}\right)\rho(E)\, dE\right]^{-1} \ll T/M^* \qquad (7)$$

(in the numerator, the integration with respect to E is confined to the highly excited states), then, expanding $\operatorname{sh} x$, $\operatorname{ch} x$, and $\exp(x)$ in series, we obtain under the integral sign

$$\frac{M^* g^5 v}{T}\left(1 - \frac{5M^* v^2}{6T} + \ldots\right)$$

and, retaining only the first term, we find

$$\langle \sigma_{\text{in}} \rangle = \left(\frac{2\pi M^*}{T}\right)^{1/2} \Omega_{\text{in}}^{(1,1)} \sim \frac{1}{Q}\int \exp\left(\frac{E}{T}\right)\rho(E)\, dE \times \left(\frac{M^*}{2T}\right)^3 \int_0^\infty \sigma_1(g)\, g^5 \exp\left(-\frac{M^* g^2}{2T}\right) dg.$$

It is easy to see that the first factor in (8) is simply the relative number of atoms (molecules) in excited states, while the second

$$\left(\frac{M^*}{2T}\right)^3 \int_0^\infty \sigma_1 g^5 \exp\left(-\frac{M^* g^2}{2T}\right) dg =$$

$$= \left(\frac{2\pi\mu}{\mu T/M^*}\right)^{1/2} \Omega_{mm_2}^{(1,1)} \left(\frac{\mu T}{M^*}\right)$$

reduces to the ordinary elastic collision integral for the particles m and m_2.

In the other limiting case ($M^* v^2 \gg T$), when the relative motion of particles m and m_2 is chiefly determined by the finite motion of the particle m, in integral (6) we can replace sh x and ch x with exp (x)/2 and integrate with respect to g, expanding near the point g = v:

$$\sigma_1(g) = \sigma_1(v) + \sigma_1'(g - v) + \ldots$$

Retaining the first term of this expansion, after simple transformations we obtain

$$\langle \sigma_{\text{in}} \rangle \sim \frac{1}{4} \left(\frac{2\pi M^*}{T}\right)^{1/2} \times$$
$$\times \frac{1}{Q} \int \exp\left(\frac{E}{T}\right) \left(\frac{m_0}{M_0} g_0\right) \sigma_1 \left(\frac{m_0 g_0}{M_0}\right) \times \tag{9}$$
$$\times \delta\left(-E - \frac{\mu_0 g_0^2}{2} - V\right) \frac{\mu_0^3 d g_0 d\mathbf{r} dE}{h^3}.$$

At first glance it might appear that, by analogy with (8), this expression should contain the averaging over the finite motion of the quantity $(m_0 g_0/M_0)^3 \sigma_1$. However, this is not so, since in this case the change of velocity of the particle m_2 (in the system of the center of inertia of the particle M_0) is chiefly related to the change of the velocity of the center of inertia of the structured particle after scattering of the fast particle m on the almost stationary particle m_2, as distinct from the case $M^* v^2 \ll T$, when the change of velocity of the fast particle m_2 is determined by scattering on a stationary particle and the center of inertia of the system, m + m_0, remains fixed.

4. We use the results obtained to estimate the role of inelastic processes in the collision of various particles with single-electron atoms. The Coulomb potential describing the interaction of a valence electron and a nucleus leads to the divergence of Q and other quantities of type (8), (9). To eliminate this effect, it is possible to use the screened Coulomb potential

$$V = -\frac{e^2}{r} \exp\left(-\frac{r}{R}\right),$$

selecting the screening radius R in accordance with the state of the gas mixture in question. For example, in a slightly nonideal plasma, R is the ordinary Debye radius, and $R \gg e^2/T$. The statistical sum over the bound states and the number of these states in the screened Coulomb field [5] are, respectively, equal (without regard for spin) to

$$Q \approx \exp\left(\frac{I}{T}\right) + N; \quad N \approx \frac{5\pi^{1/2}}{2^{9/2}} \left(\frac{R}{a_0}\right)^{3/2},$$

where I is the ionization potential of the atom, and a_0 is the Bohr radius.

Simple calculations, perfectly analogous to those made in (5), give

$$\langle v^2 \rangle = \frac{12}{5} \left(\frac{m_0}{M_0}\right)^2 \frac{e^2}{\mu_0 R}, \tag{10}$$

and inequality (7) takes the form

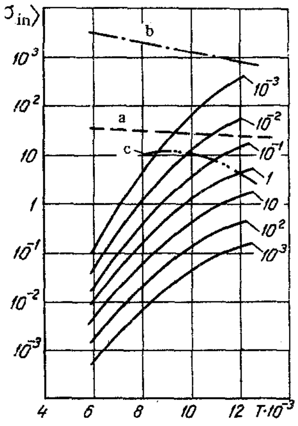
$$\frac{12}{5} \left(\frac{m^0}{M_0}\right)^2 \frac{e^2}{RT} \gg \frac{\mu_0}{M^*}. \tag{11}$$

In the event of the collision of an atom and an electron ($\mu_0 = M^* = m_e$), criterion (11) of the immobility of the finite electron (and, a fortiori, the nucleus) is satisfied, owing to the smallness of the parameter e^2/RT. In this case $\sigma_1 = 2\pi e^4 \Lambda/\mu^2 g^4$, where Λ is the Coulomb logarithm, and the contribution of inelastic collisions of the electron with the atomic electron or nucleus is

$$\langle \sigma_{\text{in}} \rangle \sim \frac{N}{Q} \left(\frac{M^*}{2\mu}\right)^2 \frac{\pi e^4 \Lambda}{T^2}. \tag{12}$$

Thus, the inelastic collision of a free electron with an excited atom reduces to scattering of the electron on almost stationary, weakly interacting charges, the scattering on the nucleus being smaller by a factor of 4 than that on the finite electron. In integral (1), the quantity (12) is combined with the averaged diffusion cross section for elastic scattering on an atom in the ground state:

$$\langle \sigma_{\text{el}} \rangle = \left(\frac{M^*}{2T}\right)^3 \int_0^\infty g^5 \exp\left(-\frac{M^* g^2}{2T}\right) \sigma_{ea}(g) dg.$$



Total cross section for inelastic collisions $\langle \sigma_{\text{in}} \rangle$ between electrons (πa_0^2 units) and hydrogen atoms (solid lines, the figures denote the pressure in atm). For comparison: a – $\langle \sigma_{\text{el}} \rangle$ [6], b) the quantity $\pi e^4/T^2$, which determines the order of the Coulomb cross sections; the line c intersects the isobars at the points where the degree of ionization is equal to 10%.

We compare this quantity, which is tabulated in [6], with $\langle\sigma_{in}\rangle$. Using calculations of the degree of ionization of atomic hydrogen [7] and the formulas for N, Q, and $\langle\sigma_{in}\rangle$, we arrive at the results given in the figure. Clearly, there are regions of temperatures and pressures, where the fraction of atoms in excited states is large, and the contribution of inelastic collisions to the integrals Ω exceeds that of elastic collisions. However, in these regions, the degree of ionization is so large that electron-atom collisions have almost no effect on the transport phenomena.

We now consider the collisions of two atoms, one of which is in the ground state and transitions in which are not taken into account. The interaction of this atom and the nucleus should be taken into account in accordance with (8), and since in this case the quantity σ_1 is on the order of the gas-kinetic cross sections, $\langle\sigma_{in}\rangle$ is approximately a factor N/Q smaller than the cross section for elastic collision of two atoms in the ground state.

The interaction with the finite electron of the excited atom under the same conditions as considered above should be estimated in accordance with (9). Assuming, for simplicity, that $\sigma_1 = \sigma_{ea}$ is constant, we have

$$\langle \sigma_{in} \rangle \sim \frac{1}{4Q}\left(\frac{2\pi M^*}{T}\right)^{1/2}\frac{32\pi^2 me^2\sigma_{ea}}{h^3}\times$$
$$\times\int e^{E/T}\left[\exp\left(-\frac{r}{R}\right)-\frac{Er}{e^2}\right] r dr dE.$$

Neglecting exp (E/T), extending the integration with respect to E to ∞ and going over to the new variable τ: $\exp(-\tau) = \tau ER/e^2$, we obtain

$$8\pi^2\left(\frac{2\pi M^*}{T}\right)^{1/2}\frac{me^4R\,\sigma_{ea}}{h^3}\times$$
$$\times\int_0^\infty d\tau\int_0^1 x dx(1+\tau)e^{-\tau}(e^{-\tau x}-xe^{-\tau})$$

and, finally,

$$\langle \sigma_{in} \rangle \sim \frac{2}{hQ}\frac{R}{a_0}\left(\frac{2\pi M^* e^4}{T}\right)^{1/2}(\ln 2+1/8)\sigma_{ea} =$$
$$=\frac{N}{Q}\frac{2^4(1/8+\ln 2)}{5\pi}\left(\frac{M^*}{m_e}\frac{e^2}{RT}\right)^{1/2}\sigma_{ea}.$$

Under the conditions considered above, owing to the smallness of N/Q, the quantity (13) is small in comparison with the cross section for elastic scattering of hydrogen atoms. For atoms with a smaller ionization potential and greater masses, and at $M^*e^2/m_eRT \gg 1$, the opposite situation is clearly possible but the analysis of such cases lies outside the scope of this article.

The case of collision between a heave charged particle and an atom is also of interest. The interaction with the nucleus is found from (8) and is exactly equal to (12). The interaction with the finite electron should be found from (9), but in view of the Coulomb nature of σ_1 the corresponding integrals with respect to E diverge at the lower limit, which is due to the assumption, made in deriving (9), that the free particle is stationary. Therefore, noting that (9) is the averaging of σ_1 over the finite motion, we replace $\langle g_0^{-3}\rangle$ with $(\langle g_0\rangle)^{-3}$, after which

$$\langle \sigma_{in} \rangle \sim \frac{2\pi}{Q}\left(\frac{2\pi M^*}{T}\right)^{1/2}\left(\frac{R}{a_0}\right)^{3/2}\frac{e^2}{h}\,\pi a_0^2\sim$$
$$\sim\frac{N}{Q}\left(\frac{M^*}{m_e}\,\frac{e^2}{a_0T}\right)^{1/2}\pi a_0^2. \qquad (14)$$

In a number of cases, this quantity may be quite large; however, a more accurate estimate is possible only if the integral (6) is correctly evaluated.

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Institute of High Temperatures AS USSR, Moscow