

EVALUATION OF THE CONTRIBUTION OF INELASTIC COLLISIONS TO THE KINETIC COEFFICIENTS; USING THE CORRELATION FUNCTION METHOD

L. I. PODLUBNYĬ

Moscow Power Engineering Institute

Submitted June 12, 1969

Zh. Eksp. Teor. Fiz. 57, 1778-1789 (November, 1969)

For slow electrons ($\bar{\epsilon} < \omega$) in a weakly ionized molecular plasma, we evaluate the distribution function, the average energy, the average energy losses, the mobility, and the heat conductivity, taking inelastic processes into account. We use the correlation function method to take into account vibrational and rotational transitions of the molecules when they collide with electrons. We obtain the quasi-classical rotational correlation functions for linear molecules and symmetric top type molecules.

1. INTRODUCTION

THE correlation function method (or the temperature-time Green function method) has been extensively applied in the kinetics of condensed media. To describe non-equilibrium processes one uses in the first approximation in the density the normal method for evaluating distribution functions and kinetic coefficients which is based upon solving a Boltzmann equation with a collision integral in the traditional form. All the same, even for rarefied systems (gaseous plasma, molecular mixtures) there are problems for the solution of which one must use the correlation function formalism.

In particular, the correlation function method makes it appreciably easier to take into account the contribution of inelastic collisions to kinetic coefficients (mobility, relaxation time tensor, and so on) and to the distribution function. One can obtain a simple expression for the inelastic collision integral if we restrict ourselves to the first (Born) approximation in the integral equation for the two-particle temperature-time Green function G_{12}

$$(1 - iG_1G_2V)G_{12} = G_1G_2 \tag{1.1}$$

We shall assume that G_2 is the propagator of simple structureless particles, and G_1 the propagator of particles which are "dressed" by an internal potential. The integral equation (1.1) describes a two-component non-equilibrium mixture of simple and compound particles. To linearize the problem we consider the simplest case when we may consider a small non-equilibrium admixture of simple particles in a thermostat of compound particles which is in local equilibrium with respect to the internal degrees of freedom (temperature T) and the translational degrees of freedom (temperature T_1).

Substituting G_{12} into the equation of motion for G_2 and using the standard technique (for instance, [1]) we find for the integral for the collisions of the simple (mass m and distribution function $f(p)$) and compound (mass M , density n_0) particles (everywhere in the following $\hbar = k = e = 1$)

$$\hat{I}_{12}f(p) = n_0 \int_{-\infty}^{\infty} dt \int d^3p' |V(q)|^2 \Phi_{T_1}(q, t) \Phi_T(q, t)$$

$$\times [e^{it(p'^2 - p^2)/2m} f(p') - e^{it(p'^2 - p^2)/2M} f(p)]. \tag{1.2}$$

Here $q = p' - p$, and the Fourier transform $\Phi_T(q, t)$ of the correlation function (two-particle Green function with pairwise identical spatial arguments) is equal to

$$\begin{aligned} \Phi_T(q, t) &= \frac{1}{Z} \sum_{n, n'} \exp \left\{ -\frac{E_n}{T} + it(E_n - E_{n'}) \right\} | \langle e^{iqr} \rangle_{nn'} |^2 \\ &= \frac{1}{Z} \int d^3r_1 d^3r_2 e^{iq(r_1 - r_2)} G \left(r_1, r_2 - t - \frac{i}{T} \right) G^*(r_1, r_2, -t), \\ Z &= \sum_n e^{-E_n/T}, \quad G(r_1, r_2, t) = \sum_n e^{-itE_n} \psi_n^*(r_1) \psi_n(r_2). \end{aligned} \tag{1.3}$$

Using the Heisenberg representation $e^{it\hat{H}} e^{iqr} e^{-it\hat{H}} = e^{iqr(t)}$ (\hat{H} is the internal Hamiltonian of the compound particles) we find instead of (1.3)

$$\Phi_T(q, t) = \langle e^{iqr(t)} e^{-iqr(0)} \rangle_T. \tag{1.4}$$

The correlation function $\Phi_{T_1}(q, t)$ describing the translational motion of the compound particles (momentum p_1 , position operator $R_1(t) = R_1(0) + (t/M)p_1$) is similarly defined:

$$\begin{aligned} \Phi_{T_1}(q, t) &= \langle e^{iqR_1(t)} e^{-iqR_1(0)} \rangle_{T_1} \\ &= \exp \{ -q^2(it + t^2 T_1) / 2M \}. \end{aligned} \tag{1.5}$$

Substituting (1.3) to (1.5) into (1.2) we obtain the linearized collision integral in the usual form

$$\hat{I}_{12}f(p) = \sum_{n, n'} \int d^3p' \{ W_{p'p}^{n'n} f(p') - W_{pp'}^{n'n} f(p) \}. \tag{1.2a}$$

Correlation functions such as (1.4) were introduced by Van Hove [2] but have as yet apparently not been used to solve actual gas-kinetic problems. Meanwhile the collision integral in the form (1.2) has appreciable advantages as compared to the collision integral (1.2a) as it enables us to manage without evaluating the inelastic rate constants for different transitions and the subsequent summation over all channels.

Solving the Boltzmann equation with the collision integral in the form (1.2) we can directly express the kinetic coefficients (mobility, viscosity, thermal conductivity, average energy losses, and so on) taking inelastic collisions into account in terms of the interparticle collisional potentials and the internal potentials of the compound particles.

2. DISTRIBUTION FUNCTION AND KINETIC COEFFICIENTS FOR ELECTRONS IN A MOLECULAR PLASMA

As an example of an application of the correlation function method to a description of transfer processes, taking inelastic collisions into account, we study the procedure of evaluating the distribution function, the mobility, and the average energy of slow electrons in a weakly ionized molecular plasma (electrons + homonuclear molecules), where in the summation in (1.2a) over different inelastic channels we restrict ourselves to taking rotational transitions into account. In that case (see^[3,4]) we can use for the transition probability in (1.2a) the Born approximation and consider in the multipole expansion of the interaction potential $V(R, \theta)$ the terms

$$\sum_{\lambda=0} V_{\lambda}(R) P_{\lambda}(\cos \theta) = -\frac{\alpha}{2R^4} - \left(\frac{\alpha'}{2R^4} + \frac{Q}{R^3} \right) P_2(\cos \theta),$$

$$\alpha = 1/3(\alpha_{\parallel} + 2\alpha_{\perp}), \quad \alpha' = 2/3(\alpha_{\parallel} - \alpha_{\perp}); \quad (2.1)$$

here α_{\parallel} and α_{\perp} are the principal values of the polarizability tensor.

As the Fourier transform of an isotropic polarization potential $-\alpha/2R^4$ diverges one must in one way or another introduce a cut-off of the polarization potential at small distances. Rotational transitions are described by anisotropic terms in the expansion (2.1) and we choose therefore for the short-range isotropic forces a rather rough approximation

$$V_0(R) = -\alpha/2(R^2 + R_0^2)^2,$$

where the cut-off radius R_0 will be determined below (the scattering length $L = -\pi\alpha/4a_0R_0$; a_0 is the Born radius).

We show in the Appendix that one can use for the rotational correlator of homonuclear molecules the approximate expression (B is the rotational constant)

$$\langle e^{i\hat{H}V(\mathbf{q})} e^{-it\hat{H}V^*(\mathbf{q})} \rangle_T = |V_0(\mathbf{q})|^2 + |V_2(\mathbf{q})|^2 \exp\{-2^4/7B(it + t^2T)\},$$

$$|V_0(\mathbf{q})|^2 = \frac{\pi\alpha^2}{32R_0^2} e^{-2qR_0}, \quad |V_2(\mathbf{q})|^2 = \frac{7Q^2}{90\pi} \left(1 + \frac{3\alpha'q}{32Q}\right)^2. \quad (2.2)$$

Expanding the collision integral in terms of harmonics,

$$f(\mathbf{p}) = \sum_{l=0} f_l(p) P_l(\cos \theta),$$

$$\hat{I}_{12}f(\mathbf{p}) = \sum_{l=0} S_l(p) (l + 1/2) P_l(\cos \theta) \quad (2.3)$$

and changing in Eqs. (2.4)–(2.10) to dimensionless variables $t \rightarrow t/T$, $p^2 \rightarrow 2mTp^2$, we find

$$S_l(p) = 4\pi n_0 m \sqrt{2mT} \int_0^{\infty} dp' p'^2 \int_{-1}^{+1} dx \int_{-\infty}^{\infty} dt$$

$$\times \exp\left\{-q^2 \frac{m}{M} \left(it + t^2 \frac{T_1}{T}\right)\right\} \left[|V_0(q)|^2 + |V_2(q)|^2 \right]$$

$$\times \exp\left\{-\frac{2A}{7} \frac{B}{T} (it + t^2)\right\} \left[e^{it(\nu^2 - p'^2)} f_l(p') P_l(x) - e^{it(p^2 - p'^2)} f_l(p) \right]. \quad (2.4)$$

We write down the first two equations of the set of kinetic equations for the $f_l(p)$, neglecting terms containing f_2, f_3 , and so on, and terms of second and higher order in the small parameters m/M and B/T . We have (the spatial variables are in units $\sqrt{2/mT}$):

$$f_0 + \frac{1}{3} \sqrt{\epsilon} \frac{\partial f_1}{\partial z} + \frac{2}{3} \frac{E_0}{\sqrt{\epsilon}} \frac{\partial}{\partial \epsilon} (\epsilon f_1) = 4\pi^2 \gamma \frac{2}{\sqrt{\epsilon}} \frac{\partial}{\partial \epsilon} \left\{ \epsilon \left[\frac{12}{7} \frac{B}{T} \right. \right.$$

$$\left. + \frac{m}{M} (1 + \delta) \epsilon \right\} \left[f_0 + \frac{\partial f_0}{\partial \epsilon} \right], \quad (2.4a)$$

$$f_1 + \sqrt{\epsilon} \frac{\partial f_0}{\partial z} + 2E_0 \sqrt{\epsilon} \frac{\partial f_0}{\partial \epsilon} = -4\pi^2 \gamma \sqrt{\epsilon} f_1 (1 + \delta)$$

$$- \frac{12}{7} \frac{B}{T} \frac{2\epsilon + 1}{\epsilon^2} + O\left(\frac{m}{M}\right). \quad (2.4b)$$

Here

$$\gamma = \frac{7Q^2 n_0 m}{45\pi} \sqrt{\frac{2m}{T}}, \quad E_0 = \frac{E}{T\sqrt{2mT}},$$

$$\delta(\epsilon) = 4\delta_0 \int_0^1 du u^3 e^{-8uR_0\sqrt{\epsilon}},$$

$$\delta_0 = \frac{5}{7} \left(\frac{3\pi\alpha\sqrt{mT}}{4\sqrt{2}QR_0} \right)^2. \quad (2.5)$$

When changing from (2.3) to (2.4) we put $T = T_1$ as under the usual conditions the exchange of energy between translational and rotational degrees of freedom takes place fast and we may assume that the subsystem of the molecules is completely in equilibrium. We neglected the contribution of the polarization forces in $V_2(q)$ as $3\alpha'\sqrt{2mT}/32Q \ll 1$.

For a non-equilibrium stationary uniform system (a molecular plasma in a constant electrical field) we get by substituting (2.4b) to (2.4a) the equation

$$(\epsilon + X + A)f_0 + (\epsilon + A)f_0' = 0, \quad A(\epsilon) = \frac{12BM}{7mT(1 + \delta)},$$

$$X(\epsilon) = \frac{2M}{3mb^2(1 + \delta)^2}, \quad b = 4\pi^2 \frac{\gamma}{E_0} = \frac{56\pi Q^2 m^2 n_0 T}{45E}. \quad (2.6)$$

In the limiting cases $X \rightarrow 0$, $A \rightarrow 0$, and $X \rightarrow \infty$ we find from (2.6) the Maxwell, Davydov, and Druyvesteyn distributions, respectively. When $A \neq 0$ Eq. (2.6) describes the spherically symmetric part of the non-equilibrium electron distribution function in a molecular plasma, taking inelastic collisions into account. We can find the cut-off factor R_0 by comparing the kinetic coefficients calculated from (2.4) to (2.6) with experiment.

Thus, for the mobility

$$v_d = \int_0^{\infty} dv v^3 f_1(v) \left/ 3 \int_0^{\infty} dv v^2 f_0(v) \right.$$

assuming that the dependence $\delta = \delta(\epsilon)$ in (2.5) is weak and that we can put

$$\delta(\epsilon) \approx \delta_0 [1 - 32/5 R_0 \sqrt{\epsilon}],$$

we find

$$v_d = \frac{4\sqrt{2T/m}}{3\sqrt{\pi} b (1 + \delta_0) \sqrt{1 + \kappa}} \left\{ 1 + \frac{24\sqrt{\pi} R_0 \delta_0}{5(1 + \delta_0) \sqrt{1 + \kappa}} \right.$$

$$\left. \times \left[1 + \kappa \left(\frac{5}{2} - \frac{16}{3\pi} \right) \right] \right\},$$

$$\kappa = X(0) / A(0) (1 + \delta_0). \quad (2.7)$$

For the electron average energy we have

$$\frac{\bar{\epsilon}}{T} = \frac{3}{2} (1 + \kappa) + \frac{128\delta_0 R_0}{5\sqrt{\pi} (1 + \delta_0)} \kappa \sqrt{1 + \kappa}. \quad (2.8)$$

In the case of H_2 molecules ($Q = 0.464$ at. un., $\alpha = 0.79 \times 10^{-24}$ cm³, $B = 7.6 \times 10^{-3}$ eV) if we put $R_0 = 0.5 \text{ \AA}$, the disagreement* of Eq. (2.7) with experiment

*This disagreement can be explained by the fact that in the case considered the quasi-classical calculation of the rotational correlator (see Appendix) is a too rough approximation, as the condition $B/T \gg 1$ is not satisfied.

(for instance, ^[5]) when E/n_0 changes by three orders of magnitude ($10^{-20} \text{ V cm}^2 \leq E/n_0 \leq 10^{-17} \text{ V cm}^2$) does not exceed $\sim 20\%$. When $E/n_0 > 10^{-17} \text{ V cm}^2$, $\kappa > 1$ and the second term in (2.7) is large so that it is impossible to use the expansion for $\delta(\epsilon)$. Moreover, when the fields are large the approximation that the molecules are rigid rotators is no longer applicable as $\bar{\epsilon}$ is close to the rotational threshold ($\bar{\epsilon} \leq \omega$). We can use Eq. (2.8) only for sufficiently small values of E/n_0 (already for $E/n_0 = 5 \times 10^{-18} \text{ V cm}^2$ the second term in (2.8) is equal to ~ 1) for which the experimental data on $\bar{\epsilon}$ are very unreliable.

In the approximation $\delta(\epsilon) \approx \delta_0$ the spherically symmetric distribution function is equal to $f_0(\epsilon) = C e^{-\epsilon/(1+\kappa)}$, i.e., the molecular plasma is a two-temperature medium with an effective electron temperature $T_e \approx T(1+\kappa)$. This qualitative conclusion is the same as the result reached in ^[6] by a numerical integration of the kinetic equation taking into account rotational transitions for electrons in a nitrogen plasma. A numerical integration of the kinetic equation with the inelastic collision integral in the usual form (1.2a) was also carried out in a series of papers by Phelps et al. (see the review ^[7]). In contrast to numerical methods ^[6,7] the integration of the kinetic equation using rotational correlators gives us the distribution function (in principle to any order in B/T and m/M) in explicit form, which enables us after appropriate normalization (choice of the cut-off factor R_0) to obtain the different kinetic coefficients without limiting ourselves to the first approximation in the corresponding gradients. The polyatomic molecules of different kinds (linear molecules, symmetric tops, spherical tops) differ then only in the form of the collisional potential and the rotational correlator (see the Appendix) so that the results of calculations can easily be transferred to the case of a multicomponent molecular plasma.

Using the expansion (2.3) of the collision integral and Eqs. (2.4) and (2.5) we can easily obtain the heat conductivity, viscosity, and other kinetic coefficients. It follows from (2.4b) that in the first approximation in the gradients (under conditions of weak non-isothermality) we can neglect the contribution of rotational transitions to the transfer processes as $B/T(1+\delta_0) \ll 1$. We find, for instance, for the heat conductivity in the approximation $\delta(\epsilon) \approx \delta_0$

$$\frac{n_e}{3\pi^{1/2}m\gamma} \int_0^\infty \frac{dx x^2 (x - 5/2) e^{-x}}{1 + \delta - 1/2(B/T)(2x+1)/2x^2} \approx \kappa_0 \left(1 - \frac{5}{2} a_1\right),$$

$$a_1 = \frac{6B}{7T(1+\delta_0)},$$

$$\kappa_0 = \frac{15n_e}{7\pi n_0(1+\delta_0)m^2Q^2} \sqrt{\frac{T}{2\pi m}}. \quad (2.9)$$

Similarly, for the electrical conductivity in a weak field (the Euler constant $C = 0.577$)

$$\frac{n_e}{3\pi^{1/2}m\gamma T} \int_0^\infty \frac{dx x e^{-x}}{1 + \delta - 1/2(B/T)(2x+1)/2x^2} \approx \frac{\kappa_0}{T} [1 - a_1(C + \ln a_1)]. \quad (2.10)$$

The correction term to the generalized Wiedemann-Franz law which takes into account rotational transitions is thus equal to $a_1(5/2 - C - \ln a_1) \ll 1$. As the molecular thermal conductivity $\sim \sigma^{-1} \sqrt{T/m}$ it follows

from (2.9) that the contribution from collisions with electrons to the thermal conductivity dominates at a degree of ionization

$$\frac{n_e}{n_0} \gtrsim \frac{1 + \delta_0}{\sigma} \left(\frac{Q}{ea_0}\right)^2 \sqrt{\frac{m}{M}}.$$

3. EVALUATION OF THE AVERAGE ELECTRON ENERGY LOSSES

We evaluate the average speed with which energy is transferred between the translational degrees of freedom of the electrons (energy operator \hat{K} , temperature T_e) and the translational (\hat{K}_1 , T_1) and internal (\hat{H} , T) degrees of freedom of the heavy particles. We have

$$-\frac{1}{n_0} \frac{d\bar{K}}{dt} = \int_{-\infty}^{\infty} dt \langle [\hat{K}, \hat{V}(t)] \hat{V}^*(0) \rangle,$$

$$\hat{V}(t) = e^{i(\hat{K}_1 + \hat{H})t} \hat{V} e^{-i(\hat{K}_1 + \hat{H})t}. \quad (3.1)$$

Changing to the Fourier transform of the collisional potential and using (1.5) we find

$$-\frac{1}{n_0} \frac{d\bar{K}}{dt} = -i \int d^3q \int_{-\infty}^{\infty} \exp\left\{-\frac{q^2}{2M}(it + t^2 T_1)\right\} \times \langle e^{i\hat{H}t} V(\mathbf{q}) e^{-i\hat{H}t} V^*(\mathbf{q}) \rangle_T d \exp\left\{-\frac{q^2}{2m}(it + t^2 T_e)\right\}. \quad (3.2)$$

Similarly, we can consider the relaxation of subsystems in local equilibrium with different temperatures as an effective damping of a spatially uniform monochromatic beam of particles in a thermostat. Averaging in (3.1) over the distribution

$$\delta(\mathbf{p} - \mathbf{p}_0) = \lim_{T_e \rightarrow 0} (2\pi m T_e)^{-3/2} \exp\left[-\frac{(\mathbf{p} - \mathbf{p}_0)^2}{2m T_e}\right] \quad (3.3)$$

and for the sake of simplicity restricting ourselves to taking only elastic collisions into account ($\hat{H} = 0$) we get

$$-\frac{1}{n_0} \frac{d\bar{K}}{dt} = \left(\frac{2\pi\mu}{T}\right)^{3/2} \int_0^\infty dq q^2 |V(q)|^2 \left(q \frac{T_e - T_1}{mM} - \frac{2T_1 p_0}{mM}\right) \times \exp\left[-\frac{\mu(p_0/m + q/2\mu)^2}{2T}\right]$$

$$\mu = \frac{mM}{m+M} \quad \frac{\bar{T}}{\mu} = \frac{T_e}{m} + \frac{T_1}{M}. \quad (3.4)$$

The limit $T_e \rightarrow 0$ corresponds to the effective damping of the beam in (3.4); the case $p_0 = 0$ describes the elastic relaxation of two subsystems with temperatures T_e and T_1 . In particular, for a Coulomb relaxation we get from (3.4) the usual result

$$\frac{1}{\tau} = \frac{4n_0\mu \sqrt{2\pi\mu}}{3mMT^{3/2}} \ln \frac{1}{x_0}, \quad x_0 = \frac{\pi n_0}{2\mu^2 T} \left(\frac{1}{T_e} + \frac{1}{T_1}\right) \quad (3.5)$$

In order to take inelastic processes into account for the relaxation of electrons in a molecular plasma we must substitute into (3.1) the rotational correlator from (2.2). The total electron energy losses are equal to

$$-\frac{1}{n_0} \frac{d\bar{K}}{dt} = \frac{64\mu^2}{15m} \sqrt{\frac{2\pi\mu}{T}} BQ^2 (T_e - T) \left[1 + \frac{2\eta}{A(0)(1+\delta_0)} \times \frac{T_e - T_1}{T_e - T} + \frac{2\eta\delta_0}{A(0)(1+\delta_0)} \frac{T_e + T_1}{T_e - T} \int_0^\infty dx x \exp\{-x - 8R_0 \sqrt{\eta x}\}\right] \quad (3.6)$$

Here $\eta = \mu \bar{T}/mT \approx 1$ and $R_0 \sqrt{2/mT} = 0.5 \text{ \AA}$ (for H_2 molecules).

The three terms in (3.6) describe, respectively, the electron energy losses through the excitation of rota-

tions, the elastic losses due to the quadrupole interaction, and the elastic polarizational losses. For H_2 (at $T = 300^\circ K$) $\delta_0 = 64$, $A(0)(1 + \delta_0) = 1860$ so that the inelastic collisions make the main contribution ($\sim 97\%$) to the total energy losses of the electrons.

We find similarly to (3.6) for the average losses of molecular rotational energy

$$-\frac{1}{n_0} \frac{d\bar{H}}{dt} = \frac{64}{15} \mu \sqrt{\frac{2\pi\mu}{T}} BQ^2(T - \bar{T}). \quad (3.7)$$

We can calculate the higher moments of energy transfer by analogy to (3.2) to (3.7). For instance, we have for the ν -th order moment of transfer of internal energy

$$\sum_{n, n'} N_n (E_n - E_{n'})^\nu W_{nn'} = \left(-i \frac{d}{du} \right)^\nu \Big|_{u=0} \int_0^\infty dt \int d^3q \times \exp \left\{ -\frac{q^2}{2\mu} (it + t^2 \bar{T}) \right\} \cdot \langle e^{i(t+u)\hat{H}} V(\mathbf{q}) e^{-i(t+u)\hat{H}} V^*(\mathbf{q}) \rangle. \quad (3.8)$$

Equations such as (3.2) to (3.8) are much simpler than the expressions for the average energy losses in a two-temperature gas which are usually employed and which contain cumbersome multiple sums (for instance, [8]). If we put $\mu \approx m$ and assume $T_e \approx \bar{T}$ (as $T_e - \bar{T} = (\mu/M)(T_e - T_1) \approx 0$) Eq. (3.7) for the first moment of the transfer of rotational energy goes over into the well-known result [9] obtained by means of a direct approximate evaluation of the sum in (3.8) with $\nu = 1$.

In conclusion we estimate the contribution of the vibrational transitions to the inelastic losses when $T < \omega$ (i.e., when there is no resonance scattering so that we can neglect the mechanism of exciting vibrational levels through electron collisions, which is connected with the formation of an intermediate molecular complex). We can consider the quadrupole interaction as the first term in a multipole expansion of the interaction potential ($2\rho_0$ is the equilibrium distance between the nuclei; $2\lambda\rho_0$ the equilibrium distance between the centers of the same kind of charges in the molecule):

$$\frac{Q}{2(\lambda\rho_0)^2} \left[\frac{2}{R} - \frac{1}{|\mathbf{R} + \lambda\rho_0|} - \frac{1}{|\mathbf{R} - \lambda\rho_0|} \right] = -\frac{Q}{R^3} P_2(\cos\theta) + \dots \quad (3.9)$$

Taking the vibrational motion into account we get instead of (3.9)

$$V(R, \theta, x) \approx -\frac{Q}{R^3} P_2(\cos\theta) \left(1 + \frac{x}{\rho_0} \right). \quad (3.10)$$

The time correlator for the coordinate, x , of a harmonic oscillator,

$$\hat{x}(t) = \frac{1}{M\omega} (\hat{a}e^{-i\omega t} + \hat{a}^\dagger e^{i\omega t}),$$

is equal to

$$\langle \hat{x}(t) \hat{x}^*(0) \rangle = \frac{1}{M\omega} \frac{e^{i\omega T_0 - i\omega t} + e^{i\omega t}}{e^{i\omega T_0} - 1}; \quad (3.11)$$

here T_0 is the vibrational temperature.

Substituting (3.11) into the expression for the inelastic rotational-vibrational correlator ($\hat{H} = \hat{H}_{\text{rot}} + \hat{H}_{\text{vib}}$)

$$\langle e^{i\hat{H}t} V(\mathbf{q}) e^{-i\hat{H}t} V^*(\mathbf{q}) \rangle = \frac{7Q^2}{90\pi} \exp \left\{ -\frac{24}{7} B(it + t^2 T) \right\} \left(1 + \frac{1}{\rho_0^2} \langle \hat{x}(t) \hat{x}^*(0) \rangle \right) \quad (3.12)$$

and using, for instance, (3.8) with $\nu = 1$ we find for the rotational and vibrational losses

$$-\frac{1}{n_0} \frac{d\bar{H}}{dt} = \frac{64}{15} BQ^2 \mu \sqrt{\frac{2\pi\mu}{T}} (T - \bar{T}) + \frac{7}{8} \omega \bar{T} A_- F_1$$

$$+ B(T - \bar{T}) A_+ F_1 + B T A_- F_0,$$

$$F_{0,1} = \frac{32Q^2 \mu \sqrt{2\pi\mu} e^{\omega/2T} K_{0,1}(\omega/2T)}{15M\rho_0^2 T^{3/2} (e^{\omega/T_0} - 1)}, \quad A_\pm = 1 \pm \exp \left\{ \omega \left(\frac{1}{T_0} - \frac{1}{T} \right) \right\}, \quad (3.13)$$

$K_0(x)$ and $K_1(x)$ are MacDonald functions. The terms in (3.13) describe, respectively, purely rotational, purely vibrational, rotational-vibrational, and vibrational-rotational inelastic losses. When $T_0 \approx \bar{T} \ll \omega$ the relative contributions of the last three terms in the inelastic losses are exponentially small and, respectively, equal to $\sqrt{\omega/T_e} e^{-\omega/T_0}$, $\sqrt{mT}/M\omega e^{-\omega/T_0}$, and $\sqrt{m\omega/MT} e^{-\omega/T_0}$. Under the conditions considered one can neglect the contribution from two-quanta vibrational transitions to (3.10) to (3.13). Moreover, we assume (as in Secs. 1 and 2) that the collisional potential is independent of the degree of excitation of the internal degrees of freedom of the molecules.

The results given in this section can be generalized to the case of energy transfer in an external electromagnetic field. The correlators for electrons in uniform electrical and magnetic fields or in the field of a light wave can be obtained in closed form, and the appropriate change in (3.4) to (3.13) enables us to take into account the influence of external fields on the collision integral and the rate of elastic and inelastic energy losses.

APPENDIX

CALCULATION OF THE ROTATIONAL CORRELATION FUNCTIONS

In the case of a linear molecule, we can obtain in closed form an expression for rotational correlation functions such as $\Phi_T(\mathbf{q}, t)$ of (1.4) (in the following we write it for the sake of simplicity as $\Phi(t)$):

$$\Phi(t) = \langle e^{i\hat{H}t} e^{i\mathbf{q}\cdot\mathbf{r}} e^{-i\hat{H}t} e^{-i\mathbf{q}\cdot\mathbf{r}} \rangle = 1 - \frac{1}{3} q^2 r^2 + q^2 r^2 \langle e^{i\hat{H}t} P_1(\cos\theta) e^{-i\hat{H}t} P_1(\cos\theta) \rangle + \dots \quad (A.1)$$

Using the Eckart theorem (see, for instance, [10])

$$\frac{1}{(2l+1)(2l'+1)} \sum_{mm'} |(e^{i\mathbf{q}\cdot\mathbf{r}})_{lm, l'm'}|^2 = \sum_L (2L+1) \begin{pmatrix} L & l & l' \\ 0 & 0 & 0 \end{pmatrix}^2 j_L^2(qr),$$

$$\begin{pmatrix} L & l & l' \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{2} \int_{-1}^{+1} dx P_L(x) P_l(x) P_{l'}(x); \quad (A.2)$$

and the expansion [11]

$$\frac{\sin(2qr \sin^{1/2}\theta)}{2qr \sin^{1/2}\theta} = \sum_L (2L+1) P_L(\cos\theta) j_L^2(qr), \quad (A.3)$$

we find easily for the real correlation function $\Phi(t - i/2T)$

$$\Phi \left(t - \frac{i}{2T} \right) = \frac{1}{2Z} \int_{-1}^{+1} dx \frac{\sin(2qr \sqrt{(1-x)/2})}{2qr \sqrt{(1-x)/2}} |G(x, \beta)|^2,$$

$$G(x, \beta) = \sum_{l=0}^{\infty} (2l+1) P_l(x) e^{-\beta l(l+1)}, \quad \beta = B \left(\frac{1}{2T} - it \right). \quad (A.4)$$

Changing from a summation to an integration and applying in (A.4) the formula [11]

$$P_l(\cos\theta) \approx \sqrt{\frac{\theta}{\sin\theta}} J_0 \left[\theta \left(l + \frac{1}{2} \right) \right],$$

we get for the quasi-classical Green function of a rotator $G(x, \beta)$

$$|G(x, \beta)|^2 \approx \frac{\theta}{\sin \theta} \frac{1}{|\beta|^2} \exp \left[-\frac{\theta^2}{4} \left(\frac{1}{\beta} + \frac{1}{\beta^*} \right) \right], \quad x = \cos \theta. \quad (\text{A.5})$$

If, for instance, we limit ourselves to the dipole term in the expansion in powers of qr :

$$\frac{\sin(2qr \sin^2 \theta)}{2qr \sin^2 \theta} = 1 - \frac{1}{3} q^2 r^2 + \frac{1}{3} q^2 r^2 \cos \theta + \dots,$$

we find for the rotational correlator from (A.1), (A.4), and (A.5) in the dipole approximation ($Z = T/B$)

$$\langle e^{i\hat{H}P_1(\cos \theta)} e^{-it\hat{H}} P_1(\cos \theta) \rangle = \frac{1}{3} \int_0^\infty du e^{-u} \cos(2\sqrt{BT}ut(t+i/T)). \quad (\text{A.6})$$

In a similar way we can obtain the rotational correlator for a linear molecule in the quadrupole approximation, and so on.

It was shown in Secs. 2 and 3 that for the evaluation of the kinetic coefficients and the distribution function of the electrons in a molecular plasma we need know the rotational correlation functions of different kinds of polyatomic molecules, of both dipole (CO, NH₃, and so on) and quadrupole (N₂, CO₂, and so on) molecules. We consider therefore the general case of symmetric top type molecules for which

$$\begin{aligned} & \langle e^{i\hat{H}V(\mathbf{q})} e^{-it\hat{H}} V^*(\mathbf{q}) \rangle \\ &= \frac{1}{Z} \sum_{J'K'} \exp \left\{ -\frac{E_{JK}}{T} + it(E_{JK} - E_{J'K'}) \right\} \sum_{MM'} |V_{JK'M'}^{J'K'M'}|^2. \end{aligned} \quad (\text{A.7})$$

The collisional potential has the form

$$V(R, \theta) = -\frac{d}{R^2} P_2(\cos \theta) - \frac{Q}{R^3} P_2(\cos \theta) - \frac{a}{2(R^2 + R_0^2)^2} + \dots \quad (\text{A.8})$$

Writing the Fourier transform of (A.8) as

$$V(\mathbf{q}) = \sum_{\lambda, \nu} \frac{4\pi}{2\lambda + 1} V_{\lambda}(\mathbf{q}) Y_{\lambda\nu} \left(\frac{\mathbf{q}}{q} \right) Y_{\lambda\nu}^* \left(\frac{\mathbf{q}}{q} \right),$$

substituting this expansion into (A.7) and using the Eckart theorem we get in the dipole approximation

$$\begin{aligned} \Phi_1(t) &= \frac{2d^2}{3\pi Z q^2} \sum_{JK} (2J+1)(2J'+1) \left| \begin{pmatrix} J & J' & 1 \\ K & -K & 0 \end{pmatrix} \right|^2 \\ & \times \exp \left\{ -\frac{E_{JK}}{T} + it(E_{JK} - E_{J'K'}) \right\}, \\ & K = K', \quad \Delta = |J' - J| = 0, 1. \end{aligned} \quad (\text{A.9})$$

By analogy with (A.9) the quadrupole part of the rotational correlation function is equal to

$$\begin{aligned} \Phi_2(t) &= \frac{2Q^2}{45\pi Z} \sum_{JK} (2J+1)(2J'+1) \left| \begin{pmatrix} J & J' & 2 \\ K & -K & 0 \end{pmatrix} \right|^2 \\ & \times \exp \left\{ -\frac{E_{JK}}{T} + it(E_{JK} - E_{J'K'}) \right\}, \\ & K = K', \quad \Delta = |J' - J| = 0, 1, 2 \end{aligned} \quad (\text{A.10})$$

and so on.

We write

$$\begin{aligned} \frac{E_{JK}}{T} &= \frac{B}{T} J(J+1) + \frac{A-B}{T} K^2 = \varphi J(J+1) + \varphi g K^2, \\ \varphi &= B/T, \quad g = (A-B)/B. \end{aligned} \quad (\text{A.11})$$

In the high-temperature limit $\varphi \rightarrow 0$ we can consider the rotation of the molecules to be classical. Changing in (A.9) and (A.10) from a summation to an integration

and using for $J, J' \gg 1$ the asymptotic expression for the $3J$ -symbols from^[10]

$$\left(\begin{matrix} J & J' & \lambda \\ K & -K & 0 \end{matrix} \right)^2 = \frac{1}{2J+1} \frac{(\lambda - \Delta)!}{(\lambda + \Delta)!} |P_{\lambda, \Delta}(x)|^2, \quad x = \frac{K}{J}, \quad (\text{A.12})$$

we find

$$\begin{aligned} \Phi_1(t) &\approx \frac{2d^2 \sqrt{1+g}}{3\pi q^2} \int_0^1 \frac{dx}{(1+gx^2)^{3/2}} x^2 + (1-x^2) \left(1 + 2B \frac{d}{dB} \right) \\ & \times \exp \left(-\frac{BTt^2}{1+gx^2} \right). \end{aligned} \quad (\text{A.13})$$

The limiting transition to a linear molecule corresponds to $A/T \rightarrow \infty$ and must be taken directly in (A.9):

$$\Phi_1'(t) \approx \frac{2d^2}{3\pi q^2} \int_0^\infty du e^{-u} \cos(2Tt\sqrt{\varphi u}). \quad (\text{A.14})$$

In the quadrupole approximation we have instead of (A.10)

$$\begin{aligned} \Phi_2(t) &\approx \frac{2Q^2 \sqrt{1+g}}{45\pi} \int_0^1 \frac{dx}{(1+gx^2)^{3/2}} \left\{ \frac{1}{4} (1-3x^2)^2 \right. \\ & + 3 \left(1 + 2B \frac{d}{dB} \right) \left[x^2(1-x^2) \exp \left(-\frac{BTt^2}{1+gx^2} \right) \right. \\ & \left. \left. + \frac{1}{4} (1-x^2)^2 \exp \left(-\frac{4BTt^2}{1+gx^2} \right) \right] \right\} \end{aligned} \quad (\text{A.15})$$

and for linear molecules

$$\Phi_2'(t) \approx \frac{2Q^2}{45\pi} \int_0^\infty du e^{-u} \left[1 + \frac{3}{4} \cos(4Tt\sqrt{\varphi u}) \right]. \quad (\text{A.16})$$

In order to take terms of second and higher order in φ into account we must when changing from a summation to an integration introduce correction terms in accordance with the Euler-Maclaurin summation formula.^[12] We can obtain the correct analytical properties by the substitution^[13] $t \rightarrow \sqrt{t(t+i/T)}$ in (A.14) to (A.16). Such a substitution changes, for instance, (A.14) into (A.6) and guarantees the principle of detailed balancing.

Finally, we get for the quasi-classical rotational correlators of symmetric top kind molecules and linear molecules in the quadrupole approximation up to terms of first order in B/T

$$\Phi_2 = \frac{2Q^2}{45\pi} \exp[-6B(it + i^2T)], \quad (\text{A.15a})$$

$$\Phi_2' = \frac{7Q^2}{90\pi} \exp \left[-\frac{24}{7} B(it + i^2T) \right]. \quad (\text{A.16a})$$

In first approximation in B/T the correlators Φ_2 for a symmetrical top and a spherical top are thus the same, while the correlator Φ_2' for a linear molecule can be obtained from Φ_2 by the substitution $Q^2 \rightarrow \frac{7}{4} Q^2$, $B \rightarrow \frac{4}{7} B$. Under this substitution BQ^2 remains unchanged so that, for instant, the inelastic rotational energy losses of quadrupole origin (3.7) are the same for different kinds of molecules.

¹L. P. Kadanoff and G. Baym, Quantum Statistical Mechanics, Benjamin, New York, 1962.

²L. Van Hove, Phys. Rev. 95, 249 (1954).

³E. Gerjuoy and S. Stein, Phys. Rev. 97, 1671 (1955).

⁴A. Dalgarno and R. S. W. Henry, Proc. Phys. Soc. 85, 679 (1965).

⁵ E. W. MacDaniel, *Collision Processes in Ionized Gases*, Wiley, 1964.

⁶ M. S. Bell and M. D. Kostin, *Phys. Rev.* **169**, 150 (1968).

⁷ A. V. Phelps, *Rev. mod. Phys.* **40**, 399 (1968).

⁸ F. S. McCormack, *J. Chem. Phys.* **49**, 1442 (1968).

⁹ M. H. Mentzoni and R. V. Row, *Phys. Rev.* **130**, 2312 (1963).

¹⁰ *Deformatsiya atomnykh yader (Deformation of Atomic Nuclei)*, Ed. L. A. Sliv, IIL, 1958.

¹¹ A. Erdélyi et al., *Higher transcendental function*, McGraw-Hill, New York, Vol. 2, 1953.

¹² M. A. Avgrafov, *Asimptoticheskie otsenki i tselye funktsii (Asymptotic Estimates and Entire Functions)* Fizmatgiz, 1962.

¹³ P. Schofield, *Phys. Rev. Lett.* **4**, 239 (1960).

Translated by D. ter Haar

210