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SPECTRUM OF THE INELASTIC-COLLISION INTEGRAL IN MOLECULAR MIXTURES

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The linearized collision integral for a many-temperature molecular mixture is expressed in terms of correlation functions describing the internal degrees of freedom of the colliding particles. The influence of inelastic collisions on the form of spectrum of the Boltzmann operator is discussed in the impulse approximation, with collisions of structureless particles with diatomic molecules as an example. The dependence of the spectrum on the particle mass ratio and on the form of the collision pseudopotential is investigated. In the case of a large mass difference between the colliding particles, the transition from the integral Boltzmann operator to a differential operator of finite order is considered. An equation of the Fokker-Planck type for the eigenvalues of the Boltzmann operator (the s-spectrum), with allowance for the rotational transitions, is solved by the WKB method for electrons in a weakly-ionized plasma of homonuclear molecules.

1. INTRODUCTION

In the analysis of the spectrum of the linearized Boltzmann operator (and of the dispersion equation for a spatially inhomogeneous system) one usually confines oneself to a consideration of classical elastic collisions in different model approximations (see, e.g.,[1,2]). The transition to the quantum theory may change not only the eigenvalues, but also the very form of the spectrum; furthermore, a consistent allowance for the contribution of inelastic collisions is possible only on the basis of the quantum collision integral. The error due to failure to take into account the inelastic collisions of the molecules becomes quite appreciable at high temperatures $kT \gg \hbar\omega$ (ω is the vibrational frequency), when the excited states become populated and the exchange of energy between the translational and internal degrees of freedom increases sharply. At the same time, in the high-temperature region one can use the impulse approximation, according to which the inelastic scattering in molecular systems proceeds in a manner "similar" (accurate to the square of the modulus of the Fourier component of the pseudopotential) to the scattering of thermal neutrons by nuclei of atoms that are chemically bound in polyatomic molecules. This makes it possible to use the method of correlation functions, developed for the description of thermalization and transport of neutrons in a thermostat whose internal degrees of freedom can be excited, for the study of the influence of inelastic collisions on the spectrum of the Boltzmann operator.

As is well known (see[1]), if the arrival terms of the collision integral is compact, it follows from the Weyl-von Neumann theorem that the form of the limiting spectrum of the Boltzmann operator

$$\hat{I}f(\mathbf{p}) = \int d\mathbf{p}'[W(\mathbf{p}',\mathbf{p})f(\mathbf{p}') - W(\mathbf{p},\mathbf{p}')f(\mathbf{p})] = -\lambda f(\mathbf{p}) \qquad (1.1)$$

is determined by the behavior of the collision frequency $\nu(p)$. In the general case the set of eigenfunctions describing the discrete spectrum is not complete. In the region of variation of the function $\nu(p)$ there is located a continuous spectrum λ (and perhaps also individual eigenvalues). To determine the position of the band $\nu_{\min} < \lambda < \nu_{\max}$, we can regard the relation

$$Z(\eta) = \int d\mathbf{p}\nu(p)f_0(p), \quad f_0(p) = (\eta/\pi)^{3/2}e^{-\eta p^2} \qquad (1.2)$$

as the Fourier transform of the function $2\pi\nu$ and express the number of collisions $Z(\eta)$ in terms of a correlator of the collision operator $\hat{\tau}$ (henceforth $\hbar = k = e = 1$):

$$Z(\eta) = n_2 \int_{-\infty}^{\infty} dt \langle \hat{\tau}(t)\hat{\tau}^*(0)\rangle. \qquad (1.3)$$

We shall consider a two-component spatially-homogeneous system containing a non-equilibrium small admixture of relaxing particles (mass M_1) in a local-equilibrium thermostat of particles (mass M_2, concentration n_2) with translational temperature T. The symbol $\langle \ldots \rangle$ in (1.3) denotes quantum-mechanical averaging over the internal and external variables of the colliding particles and statistical averaging over the thermostats with internal temperature T_1 and T_2, the translational temperature T, and the "temperature" $(1/2)M_1\eta$. From the inversion theorem we get

$$\nu(p) = \frac{n_2}{4i\sqrt{\pi}}\frac{1}{p}\int_{c-i\infty}^{c+i\infty}\frac{d\eta}{\eta^{3/2}}e^{\eta p^2}\int_{-\infty}^{\infty} dt\langle\hat{\tau}(t)\hat{\tau}^*(0)\rangle. \qquad (1.4)$$

Even if it is impossible to invert the Laplace transform in explicit form, the behavior of the function $\nu(p)$ as $p \to \infty$ and $p \to 0$ can be determined with the aid of the corresponding limit theorems. In the Born approximation $\hat{\tau} = \hat{V}$, and changing over to the Fourier transform of the collision potential, the Boltzmann operator I and the frequency $\nu(p)$ can be expressed in terms of the correlation functions of the colliding particles. For example, for the collision frequency we have (see [3]; $\hat{H}$ is the internal-energy operator)

$$\nu(p) = n_2 \int d\mathbf{p}' \int_{-\infty}^{\infty} dt \langle \exp(it\hat{H}) V(q) \exp(-it\hat{H}) V^*(q) \rangle \exp\left[it\frac{p^2 - p'^2}{2M_1} - \frac{q^2}{2M_2}(it + t^2T) \right], \quad \mathbf{q} = \mathbf{p}' - \mathbf{p}. \qquad (1.5)$$

The differential scattering cross section averaged over the thermostat (and consequently also the collision integral) can be expressed in terms of the correlation functions of the colliding particles also in the case of resonance scattering, and also in different variants of the impulse approximation (see[4-7]). In[7] are discussed in detail the limits of applicability of the impulse approximation for the rate constants of vibrational transitions in collisions of polyatomic molecules with atoms. For atoms with small vibrational quanta (the halogens Br_2, I_2, centrally-symmetrical molecules of the type XCl_4, etc.), the main condition for the applicability of the impulse approximation $kT \gg \hbar\omega$ begins to be satisfied at temperatures $T \sim 1500$–$2000°K$, when the dissociation can still be neglected (see, e.g.,[8]). The rotational transitions can be considered in the impulse approximation already at room temperatures practically for all molecules with the exception of the lightest ones (H_2).

2. INELASTIC-COLLISION INTEGRAL

In the impulse approximation, the scattering of the ν-th atom of the molecule of the first kind ($1 \leq \nu \leq N_1$, aggregate of internal temperatures T_1) by the n-th atom of the molecule of the second kind ($1 \leq n \leq N_2$; T_2) will be described by the pseudopotential $V_{\nu n}$. Analogously[3] we obtain for the integral of the inelastic collisions

$$\hat{I}f(\mathbf{p}) = n_2 \int_{-\infty}^{\infty} dt \int d\mathbf{p}' \left[f(\mathbf{p}') \exp\left(it\frac{p'^2 - p^2}{2M_1}\right) - f(\mathbf{p}) \exp\left(it\frac{p^2 - p'^2}{2M_1}\right)\right] \exp\left(-\frac{a^2}{2M_2}(it + t^2T)\right) \Phi(q, t), \tag{2.1}$$

$$\Phi(q, t) = \sum_{\nu,\nu'=1}^{N_1} \sum_{n,n'=1}^{N_2} V_{\nu n} V^{*}_{\nu' n'} \langle \exp\{iq\mathbf{r}_\nu(t)\} \exp\{-iq\mathbf{r}_{\nu'}\}\rangle_{T_{1_{1v}}} \times \langle \exp\{iq\mathbf{r}_n(t)\} \exp\{-iq\mathbf{r}_{n'}\}\rangle_{T_2}.$$

Neglecting the intermolecular interactions, the correlation between the oscillations, and the rotation and anharmonicity of the oscillations, and using the mass-tensor formalism (see, e.g.,[9]), we can write for the correlators in (2.1)

$$\Phi(q, t) = \sum_{\nu,\nu'=1}^{N_1} \sum_{n,n'=1}^{N_2} V_{\nu n} V^{*}_{\nu' n'} \langle\langle \exp\{iq\mathbf{x}_\nu(t)\} \exp\{-iq\mathbf{x}_{\nu'}\}\rangle_{T_{1_v}} \times \langle \exp\{iq\mathbf{x}_n(t)\} \exp\{-iq\mathbf{x}_{n'}\}\rangle_{T_{2v}} \exp[iq(\mathbf{R}_{\nu\nu'} + \mathbf{R}_{nn'}) - {}^1\!/_2(it + t^2T_{1r})q\rho_\nu q - {}^1\!/_2(it + t^2T_{2r})q\rho_n q]\rangle_\Omega; \tag{2.2}$$

here ρ_ν is the mass tensor; $R_{\nu\nu'}$ is the equilibrium distance between the atoms ν and ν', and x_ν is the displacement of the ν-the atom (mass m_ν); T_{1r} is the rotational temperature and T_{1v} is the set of vibrational temperatures (generally speaking, they are different for different vibrational modes) in molecules of the first kind. In the harmonic approximation we have

$$\mathbf{x}_\nu(t) = \sum_j \frac{\mathbf{c}_j^{(\nu)}}{\sqrt{2N_1 m_\nu \omega_j}} \{\hat{a}_j \exp(-i\omega_j t) + \hat{a}_j^+ \exp(i\omega_j t)\}, \tag{2.3}$$

ω_j and $c_j^{(\nu)}$ are the frequency and the amplitude vector of the ν-th atom for the j-th mode; $\hat{a}_j^+$ and $\hat{a}_j$ are the quantum creation and annihilation operators in the j-th mode.

Using (2.3), we can average in (2.2) over the vibrations and over the orientations. The averaging over the angles by introducing an effective mass after Krieger-Nelkin[9] gives fair results for highly-symmetrical polyatomic molecules (such as methane), but not for linear molecules[10]. We confine ourselves below to the simplest case of an admixture of simple particles in a thermostat of homonuclear molecules.

Averaging in (2.2) with the aid of (2.3), we can find a more general expression than is customarily employed (see, e.g.,[9]) for the oscillator correlation function

$$\langle\langle \exp\{iq\mathbf{r}(t)\} \exp\{-iq\mathbf{r}\}\rangle_T\rangle_{T_r} = \frac{1}{Z_{rot}} \int d\Omega\, d\Omega' |G(\Omega, \Omega')|^2 \exp\{iqR(z - z')\}\Phi_v, \tag{2.4}$$

$$\Phi_v = \exp\left\{-\frac{q^2}{2M_2\omega}\left[(z^2 + z'^2 - 2zz'\cos\omega t)\,\mathrm{cth}\frac{\omega}{2T_v} + 2izz'\sin\omega t\right]\right\},$$

$$z = \cos\theta;$$

the rotational Green's function G in the quasiclassical approximation was obtained in[3]:

When (2.4) is taken into account, the collision integral has a very complicated form, and we shall therefore use below the classical expression for G. Neglecting the interference term in (2.2) ($qR \gg 1$) we obtain ultimately ($p \rightarrow p\sqrt{2M_1T}$, $t \rightarrow t/T$)

$$\Phi(q, t) = 2|V|^2 \int_0^1 dz\, F, \quad F = \exp[-\gamma q^2(1 - z^2)(it + t^2T_r/T) - \gamma q^2 z^2 \Gamma],$$

$$\Gamma = \frac{2T}{\omega}\,\mathrm{cth}\frac{\omega}{2T_v}\left(1 - \cos\frac{\omega}{T}t\right) + i\frac{2T}{\omega}\sin\frac{\omega}{T}t, \quad \gamma = \frac{M_1}{M_2}. \tag{2.5}$$

From (2.1)--(2.5) we obtain for the symmetrized kernel

$$K(\mathbf{p}, \mathbf{p}') = \exp\{(p'^2 - p^2)/2\} W(\mathbf{p}, \mathbf{p}')$$

of the Boltzmann operator the expression

$$K(\mathbf{p}, \mathbf{p}') = 4n_2M_1\sqrt{2M_1T}|V|^2 \int_0^1 dz \int_{-\infty}^{\infty} dt \exp[(it - {}^1\!/_2)(p^2 - p'^2) - \gamma q^2(it + t^2)]F. \tag{2.6}$$

In the approximation where $|V|^2 = V_0^2$ and $F = 1$, the kernel (2.6) describes elastic collisions of structureless hard spheres

$$K_e(\mathbf{p}, \mathbf{p}') = K_0\sqrt{\frac{\pi}{\gamma}}\frac{1}{q}\exp\left[-\frac{1}{4}\gamma q^2 - \frac{(p^2 - p'^2)^2}{4\gamma q^2}\right], \tag{2.7}$$

$$K_0 = \frac{\sigma_0 v_0 n_2}{4\pi^2}, \quad v_0 = \sqrt{\frac{2T}{M_1}};$$

the cross section of the "hard" molecule is

$$\sigma_0 = 16\pi^2 M_1^2 V_0^2.$$

The kernel (2.7) with $\gamma = 1$ was investigated in detail by Carleman[11]. In[1] (see also[12]) it is shown that the third iteration of K_e is quadratically integrable, so that the corresponding operator is compact (fully continuous), i.e., it has a discrete spectrum and a complete set of quadratically integrable eigenfunctions. Let us prove the compactness of the operator with inelastic kernel (2.6) for pseudopotentials that admit of the representation

$$|V|^2 = V_0^2 \int dx\, v(x) e^{-xq^2}, \quad \int dx\, v(x) < \infty, \tag{2.8}$$

and let us consider first the particular case (2.7) (the hard-sphere approximation corresponds to $v(x) = \delta(x)$).

According to[11], the divergence of the integral with iteration K_e^2 is due to the insufficiently rapid decrease, as $p \to \infty$, of the function

$$P(p) = \int dp' K_e^2(p, p'). \qquad (2.9)$$

Carleman's direct estimate of the integral in (2.9) yielded

$$pP(p) \to \text{const}, \quad p \to \infty. \qquad (2.9')$$

In order to determine the rate of decrease of the integrals of the type (2.9) as $p \to \infty$, we shall employ the procedure used in the calculation of the frequency $\nu(p)$ in (1.2)–(1.4). We introduce a cutoff factor

$$\Pi(\eta) = \int dp e^{-\eta p^2} P(p) \qquad (2.9'')$$

and regard (2.9″) as the Laplace transform of the function $2\pi pP$. With the aid of a double integral representation (see (2.6)) of the square of the kernel $K_e^2(p, p')$, integrating with respect to p and p′, we obtain for $\Pi(\eta)$

$$\pi^3 K_0^2 \iint\limits_{-\infty} dt_1\, dt_2 [(t_1 + t_2 + i)^2 + i\eta(t_1 + t_2 + i) \qquad (2.10)$$

$$+ \eta\gamma(t_1^2 + t_2^2 + it_1 + it_2)]^{-3/2} = 2\sqrt{2}\,\pi^4 K_0^2/\eta\sqrt{\gamma(2\gamma + \eta + \eta\gamma^2)}.$$

Inverting the Laplace transform in (2.9″)–(2.10), we can explicitly calculate P(p) (see[13], 5.3.23). For our purposes, however, it suffices to know the behavior of $\Pi(\eta)$ as $\eta \to 0$ and to use the corresponding limit theorem for the Laplace transformation. Namely, since according to (2.10)

$$\lim_{\eta \to 0} \eta \Pi(\eta) = C_e, \quad C_e = 2\pi^4 \frac{1}{\gamma} K_0^2, \qquad (2.10')$$

we obtain (2.9′).

We proceed to consider the inelastic kernel (2.5) and (2.6), and for simplicity we shall assume throughout that the thermostat is in full equilibrium ($T_r = T_v = T$). In analogy with (2.10), we obtain

$$\Pi(\eta) = \pi^3 K_0^2 \iint\limits_0^1 dz_1\, dz_2 \iint dx_1\, dx_2 v(x_1) v(x_2) \Psi, \qquad (2.11)$$

$$\Psi = \iint\limits_{-\infty}^{\infty} dt_1\, dt_2 \{(t_1 + t_2 + i)^2 + i\eta(t_1 + t_2 + i) + \eta(x_1 + x_2)$$

$$+ \eta\gamma[A_1(t_1^2 + it_1) + A_2(t_2^2 + it_2) + z_1^2\Gamma(t_1) + z_2^2\Gamma(t_2)]\}^{-3/2}, \; A = 2 - z^2.$$

Using the integral representation for the denominator in (2.11) and expanding the kernel (2.6) in Bessel functions:

$$e^{-x\Gamma(t)} = e^{-x \operatorname{cth} \varphi/\varphi} \sum_{n=-\infty}^{\infty} e^{2i\varphi nt - \varphi n} I_n(x/\varphi \operatorname{sh} \varphi), \quad \varphi = \omega/2T, \qquad (2.12)$$

we can calculate the internal integrals with respect to t_1 and t_2 in (2.11). In the limit as $\eta \to 0$ we have

$$\Psi \to \frac{4\sqrt{\pi}}{\eta\gamma\sqrt{A_1 + A_2}} \sum_{n_1=-\infty}^{\infty} \sum_{n_2=-\infty}^{\infty} \int\limits_0^{\infty} du \exp\Big[-u^2 \Big(\frac{A_1 + A_2}{4} + \frac{x_1 + x_2}{\gamma} \Big) \qquad (2.13)$$

$$- u^2 \frac{\operatorname{cth} \varphi}{\varphi}(z_1^2 + z_2^2) - \frac{\varphi^2 (n_1 - n_2)^2}{u^2(A_1 + A_2)} \Big] I_{n_1}\Big(\frac{z_1^2 u^2}{\varphi \operatorname{sh} \varphi}\Big) I_{n_2}\Big(\frac{z_2^2 u^2}{\varphi \operatorname{sh} \varphi}\Big).$$

From (2.11)–(2.13) there follows the relation of the type (2.10′). Neglecting the factor

$$\exp\Big[-\frac{\varphi^2 (n_1 - n_2)^2}{u^2(A_1 + A_2)} \Big] \leqslant 1,$$

we obtain for the constant in (2.10′) the estimate ($\sum\limits_{n=-\infty}^{\infty} I_n(x) = e^x$)

$$C < 4\pi^4 \frac{1}{\gamma} K_0^2 \iint\limits_0^1 \frac{dz_1\, dz_2}{A_1 + A_2} \iint dx_1\, dx_2 v(x_1) v(x_2) \Big[1 \qquad (2.14)$$

$$+ \Big[4(x_1 + x_2) + 8\frac{\gamma}{\varphi}(z_1^2 + z_2^2) \operatorname{th} \frac{\varphi}{2} \Big] \Big/ \gamma(A_1 + A_2) \Big]^{-1/2}.$$

In particular, in the hard-molecule approximation we have $C < C_e = 2\pi^4 K_0^2/\gamma$. Thus, allowance for the vibrational transitions in collisions does not violate (2.9′).

Let us prove the boundedness of P(p) for any p, i.e., let us prove that the kernel K(p, p′) is a Carleman kernel. Using in (2.6) the expansion (2.12) and integrating with respect to t, we get

$$K(\mathbf{p}, \mathbf{p}') = 4n_2 M_1 \sqrt{2\pi M_2 T} \frac{1}{q} |V|^2 \int\limits_0^1 \frac{dz}{\sqrt{A}} \exp\Big[-\frac{1}{4}\gamma q^2 \Big(A + \frac{4}{\varphi} z^2 \operatorname{cth} \varphi \Big)$$

$$- \frac{(q^2 + 2\mathbf{pq})^2}{4\gamma A q^2} \Big] \Big[I_0\Big(\frac{\gamma q^2 z^2}{\varphi \operatorname{sh} \varphi}\Big) + 2\sum_{\Delta=1}^{\infty} I_\Delta\Big(\frac{\gamma q^2 z^2}{\varphi \operatorname{sh} \varphi}\Big) \qquad (2.15)$$

$$\times \exp\Big(-\frac{\varphi^2 \Delta^2}{\gamma A q^2} \Big) \operatorname{ch} \frac{\varphi(q^2 + 2\mathbf{pq})\Delta}{\gamma A q^2} \Big].$$

Here the term with $\Delta = 0$ describes elastic scattering by the ground and excited states of the oscillator, and the terms with $\Delta \neq 0$ take into account the contribution of the multiquantum transitions with change of the vibrational quantum number by Δ.

We change over in (2.9) from the variable p′ to q. Taking into account the inequalities

$$q^2 - 2pq \leqslant q^2 + 2\mathbf{pq} \leqslant q^2 + 2pq, \quad I_\Delta(x) < I_0(x), \qquad (2.15')$$

we obtain

$$P(p) < 128\pi^2 n_2 T M_2 M_1^2 \int\limits_0^{\infty} dq e^{-\gamma q^2} B^2(q), \qquad (2.16)$$

where

$$B(q) = |V|^2 \int\limits_0^1 \frac{dz}{\sqrt{A}} I_0\Big(\frac{\gamma q^2 z^2}{\varphi \operatorname{sh} \varphi}\Big) \exp\Big[\frac{1}{4}\gamma q^2 z^2 - \frac{\gamma}{\varphi} q^2 z^2 \operatorname{cth} \varphi \qquad (2.16')$$

$$- \frac{(q - 2p)^2}{4\gamma A} \Big] \Big[1 + 2\sum_{\Delta=1}^{\infty} \exp\Big(-\frac{\varphi^2 \Delta^2}{\gamma A q^2} \Big) \operatorname{ch} \frac{\varphi(q + 2p)\Delta}{\gamma A q} \Big].$$

For finite q we have $B(q) < \infty$. Let us prove the convergence of the integral in (2.16) as $q \to \infty$. Replacing in (2.16′) the summation over Δ by integration ($q \geq q_0 \gg \varphi/\sqrt{\gamma}$) we obtain for the integral with respect to q ($|V|^2 < \infty$ as $q \to \infty$)

$$\int\limits_{q_0}^{\infty} dq q^2 I_0\Big(\frac{\gamma q^2 z_1^2}{\varphi \operatorname{sh} \varphi}\Big) I_0\Big(\frac{\gamma q^2 z_2^2}{\varphi \operatorname{sh} \varphi}\Big) e^{-\beta_1 q^2 + \beta_2 q} |V|^4 < \infty, \qquad (2.17)$$

$$\beta_1 = \frac{\gamma}{4}(A_1 + A_2) + \frac{\gamma}{\varphi} \operatorname{cth} \varphi (z_1^2 + z_2^2), \quad \beta_2 = \frac{p}{\gamma}\Big(\frac{1}{A_1} + \frac{1}{A_2} \Big).$$

Since $P(p) < \infty$, we conclude from (2.9′) that

$$P(p) < C'/(1 + p). \qquad (2.18)$$

Further, following Dorfman exactly[12], we obtain for the square of the third integration of the kernel the estimate

$$\int dp' K_3^2(\mathbf{p}, \mathbf{p}') < C''/(1+p)^5, \tag{2.18'}$$

from which follows compactness of the operator with the kernel $K(\mathbf{p}, \mathbf{p}')$.

3. COLLISION FREQUENCY

In the general case of inelastic collisions with excitation of rotational, vibrational, and electronic degrees of freedom, the correlator in (1.5)—(2.1) is a complicated function of q and t. We shall therefore first consider the case of elastic collisions. The collision frequency can be expressed in terms of the probability $W_0(p, p')$ of the change of the absolute magnitude of the momentum

$$\nu(p) = \int d\mathbf{p}' W(\mathbf{p}, \mathbf{p}') = \frac{1}{p}\int_0^\infty dp' p' W_0(p, p'), \tag{3.1}$$

$$W_0(p, p') = pp' \int d\Omega W(\mathbf{p}, \mathbf{p}').$$

For the one-dimensional probability of the elastic collisions W_0 we can easily obtain from (1.5) ($\hat{H} = 0$) and (3.1) (Φ is the probability integral)

$$W_0(p, p') = \frac{\pi^2}{\sqrt{\gamma}} K_0 \int \frac{dx\, v(x)}{\sqrt{\gamma + 4x}} \exp\left[\frac{p^2 - p'^2}{2\gamma}(\gamma - 1)\right] \cdot \tag{3.2}$$

$$\times \left\{\exp\left[\frac{p^2 - p'^2}{\sqrt{\gamma}} c_1\right] [\Phi(c_1 p + c_2 p') + \Phi(c_2 p' - c_1 p)\Theta(p, p')] - (c_1 \rightleftarrows -c_2)\right\},$$

$$c_{1,2} = \frac{\sqrt{\gamma^2 + 4x\gamma} \pm 1}{2\sqrt{\gamma}}, \qquad \Theta(p, p') = \begin{cases} +1, & p' < p \\ -1, & p' > p \end{cases}.$$

For the collision frequency we obtain from (3.1) and (3.2) (the same result follows directly from (1.2), see the formulas for the inversion of the Laplace integral[13], 5.3.22)

$$\omega(p) = \frac{\nu_e(p)}{\pi^2 K_0} = \frac{1}{p}\int \frac{dx}{x} v(x) [\Phi(u) - a\Phi(au) e^{-u^2(1-a^2)}], \tag{3.3}$$

$$u = \frac{p}{\sqrt{\gamma}}, \qquad a = \frac{\alpha}{\sqrt{x + \alpha^2}}, \qquad \alpha^2 = \frac{(\gamma + 1)^2}{4\gamma}.$$

In the particular case of hard-sphere collisions $v(x) = \delta(x)$, and (3.2) and (3.3) go over into the well known result (see, e.g.[14]). Let us consider in greater detail the case of the Born approximation for a Gaussian potential, when $V(r) \sim \exp(-r^2/2r_0^2)$, $v(x) = \delta(x - x_0)$, and

$$\omega(p) = \frac{1}{px_0}[\Phi(u) - a_0\Phi(ua_0) e^{-u^2(1-a_0^2)}],$$

$$a_0 = \frac{\alpha}{\sqrt{x_0 + \alpha^2}}, \qquad x_0 = 2M_1 T r_0^2, \tag{3.4}$$

whence

$$\omega(0) = \frac{2}{(x_0 + \alpha^2)\sqrt{\pi\gamma}}, \quad \omega^{\mathrm{I}}(0) = 0, \quad \omega^{\mathrm{II}}(0) = \frac{4(\alpha^2 - x_0)}{3(x_0 + \alpha^2)^2\sqrt{\pi\gamma}}. \tag{3.5}$$

When $x_0 = \alpha^2$ we have $\omega^{\mathrm{II}}(0) = \omega^{\mathrm{III}}(0) = 0$, $\omega^{\mathrm{IV}}(0) = -4/5 x_0 \sqrt{\pi\gamma} < 0$.

Since asymptotically $\omega(p) \sim 1/p$ for all $x_0 \neq 0$, it is necessary to discuss two different cases: $x_0 \geq \alpha^2$ and $x_0 < \alpha^2$.

I. If $x_0 \geq \alpha^2$ ($a_0 \leq 1/\sqrt{2}$), $\omega(p)$ decreases monotonically with increasing p and the spectrum lies in the region $\lambda' > \omega_{\max} = \omega(0)$ ($\lambda = \lambda'\pi^2 K_0$). A Gaussian potential with sufficiently large radius of action can be regarded as "semi-hard" and the limiting case of very large x_0 corresponds to a soft long-range potential ($r_0 \to \infty$).

II. For $x_0 < \alpha^2$ the function $\omega(p)$ has a minimum at the point $p = 0$, and consequently is not monotonic, so that possibly $\omega(0) < \lambda < \omega_{\max}$. Thus, for hard forces with small radius of action the continuous spectrum occupies a broader region than for "semi-hard." In the limit as $x_0 \to 0$, the width of the band of the continuous spectrum becomes infinite, and a discrete spectrum appears at $x_0 = 0$ in the region $\lambda' < 2/\alpha^2\sqrt{\pi\gamma}$ (see (3.4)). The width of the band of the discrete spectrum depends on the ratio $\gamma = M_1/M_2$. It is maximal at $\gamma = 1/3$ and tends to zero as $\gamma \to 0$ and $\gamma \to \infty$ (the former case corresponds, e.g., to scattering of neutrons or light atoms in the hard-sphere approximation by a heavy gas, and to scattering of electrons by molecules).

Of considerable interest is the special case $x_0 = \alpha\sqrt{\alpha^2 - 1}$. As follows from (3.2), in this case the symmetrized kernel $\overline{W}_0(p, p') = W_0(p, p') e^{(p'^2 - p^2)/2}$ factors out (if $\gamma^2 + 4x_0\gamma = 1$, then $c_2 = 0$):

$$\overline{W}_0(u, u') = \begin{cases} 2\Phi(u')\exp\left(\dfrac{u'^2 - u^2}{2}\right), & u' < u \\ 2\Phi(u)\exp\left(\dfrac{u^2 - u'^2}{2}\right), & u < u' \end{cases}, \tag{3.6}$$

and coincides with the Green's function of the operator

$$\hat{L} = \frac{d}{du}\left[k(u)\frac{d}{du}\right] + k(u)[k(u)e^{-u^2} - u^2], \qquad \frac{1}{k(u)} = e^{-u^2} + u\sqrt{\pi}\,\Phi(u), \tag{3.7}$$

The corresponding differential equation in the particular case of scattering of neutrons ($x_0 = 0$) by hydrogen ($\gamma = 1$) was considered in[9].

A curious feature of the Gaussian potential (or pseudopotential in the impulse approximation) $|V|^2 = V_0^2\exp(-x_0 q^2)$ is the possibility of nonmonotonic behavior of the function $\nu_e(p)$ (in the classical analysis[1] the frequency $\nu_e(p)$ increases monotonically for hard potentials $V(r) \sim r^{-s}$, $s > 4$, or decreases monotonically for soft potentials with $s < 4$). Notice should also be taken of the unstable character of the spectrum: at the pole $\lambda < \nu_e(0)$, at an arbitrarily small $x_0 \neq 0$, the discrete spectrum goes over into a continuous one.

In the general case of an arbitrary $|V(q)|^2$ dependence the collision frequency $\omega(p)$ from (3.3) can be expressed in terms of the frequency $\omega(p, x_0) = \overline{\omega}$ for a Gaussian potential (pseudo-potential):

$$\omega(p) = \int dx\, v(x)\, \overline{\omega}(p, x). \tag{3.8}$$

From (3.3)—(3.8) we obtain

$$\nu_e(p) = 4\pi n_2 M_1 \sqrt{2\pi M_1 T}\,\frac{1}{p}\int_0^\infty dq q |V(q)|^2 + O\left(\frac{1}{p}\right), \tag{3.9}$$

$$\nu_e(0) = 8\pi n_2 M_1 \sqrt{2\pi M_2 T}\int_0^\infty dq q |V(q)|^2 e^{-\alpha^2 q^2}, \qquad \nu_e'(0) = 0,$$

and the non-monotonicity condition $\nu_e''(0) > 0$ is satisfied when

$$\int_0^\infty dqq|V(q)|^2 e^{-\alpha^2q^2} < 2\alpha^2 \int_0^\infty dqq^3|V(q)|^2 e^{-\alpha^2q^2}. \qquad (3.10)$$

It is possible to generalize the foregoing results to include the case of averaging over the orientations (the vibrations are "turned off," i.e., $\Gamma = 0$, see (2.5) and (2.6)) by replacing in (3.2) and in the succeeding formulas γ by $\gamma(2 - z^2)$ with further integration with respect to z. For example,

$$W_0(p, p', \gamma) \to W_0 = \int_0^1 dz W_0[p, p', \gamma(2 - z^2)]. \qquad (3.11)$$

Averaging over the orientations does not change the asymptotic properties of $\nu(p)$, but shifts the point $\nu(0)$, i.e., changes the band width of the spectrum. Thus, in the hard-molecule approximation we obtain from (3.5)

$$\omega(0) = \begin{cases} 2\sqrt{\gamma/\pi}(2+\pi), & \gamma \ll 1 \\ 4/\gamma\sqrt{\pi\gamma}, & \gamma \gg 1 \end{cases} \qquad (3.12)$$

in place of $8\sqrt{\gamma/\pi}$ and $8/\gamma\sqrt{\pi\gamma}$ respectively.

In the general case of collisions with molecules, with allowance for the vibrational transitions, we have for the frequency of the inelastic collisions

$$\nu(p) = \pi^{3/2} K_0 \int dx\, v(x) \int_0 dz \int_{-\infty} \frac{dt}{(it + \Gamma')^{3/2}} \exp\left(-\frac{p^2t^2}{it + \Gamma'}\right) \qquad (3.13)$$

where

$$\Gamma' = x + \gamma z^2 \Gamma + \gamma(2 - z^2)(it + t^2). \qquad (3.13')$$

Since the main contribution to the integral (3.13) when $p \to \infty$ is made by the region $t \to 0$ and

$$\Gamma'(t) \to \gamma(2 + z^2)(it + t^2) + x, \quad t \to 0, \qquad (3.13'')$$

we obtain

$$\nu(p) \to \int_0^1 dz \nu_e[p, \gamma(2 + z^2)], \quad p \to \infty, \qquad (3.14)$$

where the frequency of the elastic collisions is

$$\nu_e(p, \gamma) = \pi^{3/2} K_0 \int dx\, v(x) \int_{-\infty}^{\infty} dt [it + \gamma(it + t^2) + x]^{-3/2}.$$

$$\times \exp\left[-\frac{p^2t^2}{it + \gamma(it + t^2) + x}\right]. \qquad (3.14')$$

It is easy to verify (see[9], p. 34) that the integral in (3.14′) coincides with (3.3), so that the asymptotic properties of $\nu(p)$ and $\nu_e(p)$ are the same.

In order to study the behavior of $\nu(p)$ as $p \to 0$, we expand (3.13) in powers of p^2:

$$\nu(p) = \sum_{n=0} C_n p^{2n}, \quad C_n = \frac{\pi^2 K_0 \varphi \operatorname{sh}\varphi}{\gamma\Gamma(n + 3/2)} \int_0^1 \frac{dz}{z^2} \frac{d^n}{d\mu^n}\Big|_{\mu=\gamma(2-z^2)} S(\mu),$$

$$S(\mu) = \frac{1}{\sqrt{\mu}} \int dx\, v(x) \int_0^\infty du e^{-u(1+b)} \Big[I_0(u)$$

$$+ 2\sum_{\Delta=1}^\infty I_\Delta(u) e^{-d\Delta^2/u} \operatorname{ch}\left(\varphi\Delta \frac{\nu - \mu + 1}{\mu}\right)\Big], \qquad (3.15)$$

$$b = \operatorname{ch}\varphi - 1 + \frac{\varphi \operatorname{sh}\varphi}{\gamma z^2}\left[x + \frac{(\gamma + 1)^2}{4\mu}\right], \quad d = \frac{\varphi\gamma z^2}{\mu \operatorname{sh}\varphi}.$$

The internal integral in (3.15) can be calculated with the aid of the Macdonald formula (see, e.g.[13], 4.17.4). We obtain

$$S(\mu, x) = \frac{1}{\sqrt{\mu b(b+2)}} - \frac{4}{\sqrt{\mu}} \frac{d}{db} \sum_{\Delta=1}^\infty K_\Delta(X_+\Delta) I_\Delta(X_-\Delta) \operatorname{ch}\left(\varphi\Delta \frac{\gamma - \mu + 1}{\mu}\right).$$

$$S(\mu) = \int dx\, v(x) S(\mu, x), \quad X_\pm = \sqrt{bd + 2d} \pm \sqrt{bd}. \qquad (3.15')$$

The summation over the multiquantum transitions in (3.15′) can be carried out by using asymptotic (with respect to the index) formulas for the Bessel functions (see[13], 7.13.2). We have[1)]

$$S(\mu, x) = \frac{1}{\sqrt{\mu b(b+2)}} - \frac{2}{\sqrt{\mu}} \sum_{\Delta=1}^\infty \frac{1}{\Delta} \operatorname{ch}\left(\varphi\Delta \frac{\gamma - \mu + 1}{\mu}\right) \frac{d}{db}\left(\frac{e^{-2D\Delta}}{\sqrt{Q}}\right)$$

$$2D = Y + \operatorname{arsh}(Y/2d), \quad Y^2 = (Q - 1)^2 - 4d^2,$$

$$Q = \sqrt{4bd + (2d + 1)^2}. \qquad (3.16)$$

Summing in (3.16), we obtain ultimately

$$\nu(p) = \frac{\sigma_0 v_0 n_2}{4\gamma} \varphi \operatorname{sh}\varphi \int_0^1 \frac{dz}{z^2} \int dx\, v(x) \sum_{n=0}^\infty \frac{p^{2n}}{\Gamma(n + 3/2)} \frac{d^n}{d\mu^n} \Big\{ \frac{1}{\sqrt{\mu b(b+2)}}$$

$$+ \frac{1}{\sqrt{\mu} Q} \frac{dQ}{db} \Big[\frac{4}{U} \frac{dD}{dQ} \Big(1 - \operatorname{ch}\left(\varphi \frac{\gamma - \mu + 1}{\mu}\right) e^{-2D} \Big) - \frac{1}{2Q} \ln U \Big] \Big\},$$

$$U = 1 + e^{-4D} - 2e^{-2D} \operatorname{ch}\left(\varphi \frac{\gamma - \mu + 1}{\mu}\right). \qquad (3.17)$$

In particular, in the mass-tensor approximation for collisions of light atoms with hard molecules with small vibrational quanta, at sufficiently high temperatures when $\varphi \ll 1$ and $\gamma \ll 1$ but $\varphi/\gamma > 1$, we get from (3.17) for $\nu(0)$

$$\nu(0) = 2\sqrt{\gamma/\pi}\, \sigma_0 v_0 n_2 (1 + \sqrt{\varphi/\gamma}). \qquad (3.18)$$

The first term in (3.18) coincides with (3.5) (for $\gamma \ll 1$), the second describes the contribution of the inelastic collisions. For example, in the mixture He + I_2 ($\gamma = 0.016$, $\Theta = \hbar\omega/k = 306°K$) at $T = 2000°K$ the contribution of the vibrational transitions amounts to ~ 69%, and in the mixture He + Br_2 ($\gamma = 0.025$, $\Theta = 465°K$) we have respectively ~ 67%. Thus, if the internal degrees of freedom can be easily excited in collisions, the total frequency greatly differs from the frequency of the elastic collisions only.

From the foregoing analysis it also follows that the already-noted unstable behavior of the spectrum remains in force also when account is taken of inelastic collisions. If the pseudo-potential differs from the pseudo-potential in the hard-molecule approximation, the continuous spectrum starts with the point $\lambda = 0$. This means that the usual opinion that the relaxation time is equal to the reciprocal of the smallest eigenvalue λ_{min} of the Boltzmann operator is incorrect, and the distribution function can have a nonexponential asymptotic behavior as $t \to \infty$ (see also[15]).

4. RELAXATION OF PARTICLES WITH LARGE MASS DIFFERENCE

In the absence of external perturbations, for a spatially-homogeneous system, different harmonics in

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[1)] Owing to the partial cancellation of the correction terms, the asymptotic formulas for the products of Bessel functions ensure good accuracy even when $\Delta \gtrsim 1$ (at $\Delta = 1-5$ the error is less than ~5% in the region of values of X_+ and X_- of greatest interest).

the expansion of the non-equilibrium distribution function in a series (integral)

$$f(p,t)=\sum_{nlm}C_{nlm}Y_{lm}(\mathbf{n})\frac{1}{p}R_{nl}(p)\exp(-\lambda_{nl}t),\quad \mathbf{n}=\frac{\mathbf{p}}{p},\tag{4.1}$$

relax independently, and it is possible to obtain from the Boltzmann equation a system of integral equations for the radial eigenfunctions R_{nl} and eigenvalues λ_{nl}:

$$[\nu(p)-\lambda_{nl}]R_{nl}(p)=\int_0^\infty dp'\,W_l(p',p)R_{nl}(p'),\tag{4.2}$$

$$\nu(p)=\frac{1}{p}\int_0^\infty dp'p'W_0(p,p'),\quad W_l(p',p)=pp'\int d\Omega P_l(\cos\theta)W(p',p).$$

Because of the complicated structure of the kernels $W_l(p', p)$, Eqs. (4.2) have no analytic solutions even for model potentials of the hard-sphere type. An exception is a gas of Maxwellian molecules, and also the case of relaxation in a two-component mixture of particles with large mass difference. The existence of a small parameter $\gamma = M_1/M_2 \ll 1$ (Lorentz gas) or $1/\gamma \ll 1$ (Rayleigh gas) greatly simplifies the solution of the eigenvalue problem, since the expansion of the kernels in (4.2) in powers of γ or $(1/\gamma)$ makes it possible to change over from integral equations to differential ones.

Using the expansion of the Neumann type

$$\exp(2\mathbf{pp}'\Gamma')=\sqrt{\pi/4pp'\Gamma'}\sum_{l=0}^\infty(2l+1)P_l(\cos\theta)I_{l+1/2}(2pp'\Gamma'),\tag{4.3}$$

we obtain from (4.2)

$$W_l(p',p)=2\pi^{3/2}K_0\sqrt{pp'}\int_0^1dz\int dx\,v(x)\int_{-\infty}^\infty\frac{dt}{\sqrt{\Gamma'}}$$
$$\times\exp\left[it(p'^2-p^2)-\Gamma'(p'^2+p^2)\right]I_{l+1/2}(2pp'\Gamma').\tag{4.4}$$

Going over in (4.2) to the variable $\epsilon = p^2$ and expanding the eigenfunction in a Taylor series in $\epsilon' - \epsilon$, we obtain

$$[\nu(\varepsilon)-\lambda_{nl}]\,r_{nl}(\varepsilon)=\frac{1}{2\sqrt{\varepsilon}}\sum_{k=0}^\infty B_{kl}(\varepsilon)\frac{d^k}{d\varepsilon^k}r_{nl}(\varepsilon),$$

$$B_{kl}(\varepsilon)=\frac{1}{k!}\frac{d^k}{ds^k}\Big|_{s=0}A_l(s,\varepsilon),\quad R_{nl}(\varepsilon)=\sqrt{\varepsilon}\,r_{nl}(\varepsilon);\tag{4.5}$$

here $A_l(s, \epsilon)$ is the generating functions for the moments of the energy transfer:

$$A_l(s,\varepsilon)=\int_0^\infty d\varepsilon'\,e^{(\varepsilon'-\varepsilon)s}\,W_l(\varepsilon',\varepsilon).\tag{4.6}$$

The Taylor expansion (4.5) for the s-branch in the approximation of structureless hard sphere was considered in[17] (the case of a Rayleigh gas is discussed in detail).

We use the mass-tensor approximation for the molecules—hard spheres—for the integration in (4.4)--(4.6). Then $\Gamma' = \gamma(it + t^2 + \Gamma)$ and

$$A_l(s,\varepsilon)=2\pi\sqrt{\pi/\gamma}\,K_0\int_{-\infty}^\infty\frac{dt}{\sqrt{it+t^2+\Gamma}}\int_0^\infty d\varepsilon'(\varepsilon\varepsilon')^{1/4}I_{l+1/2}\left[2\gamma\sqrt{\varepsilon\varepsilon'}(it+t^2+\Gamma)\right]$$
$$\times\exp\left[(\varepsilon'-\varepsilon)(s+it)-\gamma(\varepsilon+\varepsilon')(it+t^2+\Gamma)\right].\tag{4.7}$$

The integrals in (4.7) for $\Gamma = 0$ (the vibrations are turned off) and in the harmonic approximation, when

$$\Gamma=\frac{2T}{\omega}\operatorname{cth}\frac{\omega}{2T_v}-\frac{\exp\{\omega/T_v-i\omega t/T\}+\exp\{i\omega t/T\}}{\omega(\exp\{\omega/T_v\}-1)/2T},\tag{4.7$'$}$$

can be calculated. It suffices for us, however, to consider the behavior of (4.7) as $\gamma \to 0$ and $\gamma \to \infty$. We confine ourselves below to the case of a Lorentz gas, which is of greater practical interest than the case $\gamma \gg 1$. In the limit as $\gamma \to 0$ we have

$$A_l(s,\varepsilon)=\frac{2\pi^{3/2}}{\Gamma(l+3/2)}K_0\gamma^l\int_{-\infty}^\infty dt\,(it+t^2+\Gamma)^l\int_0^\infty d\varepsilon'(\varepsilon\varepsilon')^{(l+1)/2}e^{(\varepsilon'-\varepsilon)(s+it)}[1$$
$$-\gamma(\varepsilon+\varepsilon')(it+t^2+\Gamma)+O(\gamma)].\tag{4.8}$$

From (4.8) it follows that in the approximation $\gamma^l \neq 0$ but $\gamma^{l+1} = 0$, the quantity $A_l(s, \epsilon)$ has the form of a polynomial in s, of degree $2l (l \geq 1)$, so that the expansion in (4.5) contains derivatives of the eigenfunctions $r_{nl}(\epsilon)$ of order $k \leq 2l$. In the i-th approximation ($\gamma^{i+1} = 0$) we have $A_l(s, \epsilon) \equiv 0$ if $l > i$. Thus, in the i-th approximation ($i \geq 1$) the integral equations for the eigenfunctions $r_{nl}(\epsilon)$ go over into differential equations of order 2i (or for $\Gamma \neq 0$ into differential-difference equations that take into account multiquantum transitions with change of the vibrational quantum number by $\Delta \leq i$, see (4.7′)).

In molecular mixtures the inequality $M_1 \ll M_2$ is usually not well satisfied, and the expansion in powers of γ converges slowly, while the solution of the complicated differential-difference equations describing the transitions between the states of the discrete oscillator spectrum entails considerable difficulties. In a molecular plasma for collisions of electrons with molecules $\gamma = m/M \lesssim 10^{-4}$, and in the expansion in powers of γ it is therefore sufficient to confine oneself to consideration of the s-spectrum. Let us discuss the concrete case of relaxation of electrons in a weakly-ionized plasma consisting of homonuclear molecules of one kind.

As shown in[3], an appreciable contribution to the relaxation of the energy of the electrons is made by inelastic collisions with excitation of rotational degrees of freedom. With the aid of approximate rotational correlation functions obtained in[3] by averaging over the smeared rotational spectrum, we can rewrite the system (4.2) in the form

$$\lambda_{nl}r_{nl}(\varepsilon)={}^7/_{45}Q^2n_2m\sqrt{2\pi mT}\int_0^\infty d\varepsilon'\sqrt{\varepsilon'}\int_{-\infty}^\infty dt\exp[-\gamma(\varepsilon+\varepsilon')(it+t^2)]$$
$$\times\left\{\delta_0+\exp\left[-\frac{24B}{7T}\left(it+t^2\frac{T_r}{T}\right)\right]\right\}\sum_{k=0}^\infty\frac{[\gamma\sqrt{\varepsilon\varepsilon'}(it+t^2)]^{2k}}{k!\,\Gamma(k+3/2)}\left\{e^{it(\varepsilon-\varepsilon')}r_{nl}(\varepsilon)\right.\tag{4.9}$$
$$\left.-\frac{[\gamma\sqrt{\varepsilon\varepsilon'}(it+t^2)]^l\,\Gamma(k+3/2)}{\Gamma(k+l+3/2)}e^{it(\varepsilon'-\varepsilon)}r_{nl}(\varepsilon')\right\},\quad\delta_0=\frac{5}{7}\left(\frac{3\pi\alpha\sqrt{mT}}{4\sqrt{2}\,QR_0}\right)^2$$

In (4.9), B, α, and Q are respectively the rotational constant, the polarizability, and the quadrupole moment of the molecules, and R_0 is the cutoff radius of the polarization potential (see[3]).

In the case of a discrete spectrum of the Boltzmann operator, the relaxation time τ of the distribution function is determined by the first non-zero eigenvalue. We shall consider below only the s-spectrum ($l = 0$). Retaining in (4.9) terms of order not higher than the first in γ and B/T, we obtain an equation of the Fokker-Planck type ($x = p$):

$$\psi''+\left[2+\frac{1}{4x^2}+4gx-x^2+\beta\left(4x^2-x^4-\frac{3}{4}\right)-\frac{\beta}{(1+\beta x^2)^{3/2}}\right]\frac{\psi}{1+\beta x^2}$$

$$+\frac{T_r-T}{T}\frac{\beta}{x^2(1+\beta x^2)}\left[x^4\left(\frac{e^{-x^2/2}\psi}{\sqrt{x(1+\beta x^2)}}\right)'\right]'=0;$$

$$R_{n0}(x)=\frac{e^{-x^2/2}\sqrt{x}}{\sqrt{1+\beta x^2}}\psi_n(x), \quad \beta=\frac{7\gamma T}{12B}(1+\delta_0), \qquad (4.10)$$

$$\lambda_{n0}=\frac{32}{15}\pi n_2 BQ^2 m\sqrt{\frac{2m}{T}}g_n.$$

We shall assume the molecular thermostat to be completely in equilibrium (rotational temperature $T_r = T$). Equation (4.10) has the form of the Schrödinger equation $-\frac{1}{2}\psi'' + V(x, g)\psi = E(g)\psi$, with the possible values of the parameter g being determined by the condition $E_n(g) = 0$.

At $T \sim 300°K$ we have $\beta \lesssim 10^{-2}$, so that the thermal motion of the heavy particles can be regarded as a perturbation:

$$V=\frac{1}{2}x^2-2gx-\frac{1}{8x^2}-1+\beta(2gx^3-x^2+1)+O(\beta). \qquad (4.11)$$

We can apply the WKB method to (4.10) and (4.11), if the singularities of the potential are limited by changing over from the semiaxis $0 \leq x < \infty$ to the entire axis with the aid of the transformation $x = e^{\varphi}$, $\psi = e^{\varphi/2}z(\varphi)$, so that

$$d^2z/d\varphi^2+K^2z(\varphi)=0,$$
$$\int_{\varphi_1}^{\varphi_2} d\varphi e^{\varphi}[2(1-\beta)+4ge^{\varphi}(1-\beta e^{2\varphi})-e^{2\varphi}(1-2\beta)]^{1/2}=\pi(n+{}^1/_2). \qquad (4.12)$$

In the approximation $\beta = 0$ we find $\varphi_1 = -\infty$, $\varphi_2 = \ln(2g + \sqrt{2 + 4g_2})$, and since

$$\int_{-\infty}^{\varphi_2} d\varphi K(\varphi)=(1+2g^2)\left[\operatorname{arctg}(g\sqrt{2})-\arcsin\frac{2g-e^{\varphi_2}}{\sqrt{2+4g^2}}\right], \qquad (4.13)$$

we obtain the "quantization" condition:

$$\operatorname{arctg}(g\sqrt{2})=\pi\frac{n-g^2}{1+2g^2}. \qquad (4.14)$$

Equation (4.14) has as the first two exact roots $g_0 = 0$ and $g_1 = 1/\sqrt{2}$, and an asymptotic solution $g_n \approx \sqrt{n/2}$, which is applicable with accuracy ~2% already to g_2 and g_3. When $\beta \neq 0$, representing $g = g^{(0)} + \beta g^{(1)}$, and neglecting the shift of the turning point in (4.13) as an effect of order $\beta^{3/2}$, we obtain for the correction $g^{(1)}$

$$\int_0^{\sqrt{2n}+\sqrt{2n+2}} dx\frac{2-4g^{(1)}x-2x^2+4g^{(0)}x^3}{\sqrt{2+4g^{(0)}x-x^2}}=0. \qquad (4.15)$$

We do not present the rather cumbersome exact value of $g^{(1)}$ in accord with (4.15). When $n = 0$ we have $g^{(1)} = 0$ and when $n = 1$ we have $g^{(1)} = 9.7$. Thus, for $l = 0$ the Boltzmann operator has a discrete spectrum (with increasing g the potential well in (4.10) becomes deeper and deeper and the energy levels move through the point $E = 0$ in a downward direction).

The quasiclassical eigenfunctions can be easily obtained from (4.10)–(4.14). Namely (c_n is the normalization constant, $\beta = 0$),

$$R_{n0}(p)=\frac{c_n e^{-p^2/2}\sqrt{p}}{|y^2-2(n+1)|^{1/4}}\cos\left[\frac{y}{2}\sqrt{2(n+1)-y^2}+(n+1)\arcsin\frac{y}{\sqrt{2(n+1)}}-\frac{\pi}{2}\left(n+\frac{1}{2}\right)\right] \qquad (4.16)$$
$$y=p-\sqrt{2}n<\sqrt{2(n+1)};$$

$$R_{n0}(p)=\frac{c_n e^{-p^2/2}\sqrt{p}}{2[y^2-2(n+1)]^{1/4}}\left[\frac{y+\sqrt{y^2-2(n+1)}}{\sqrt{2(n+1)}}\right]^{n+1}\times\exp\left\{-\frac{y}{2}\sqrt{y^2-2(n+1)}\right\}, \qquad (4.16')$$
$$y>\sqrt{2(n+1)}.$$

Greatest interest attaches to the first eigenvalues, which generally speaking cannot be calculated in the WKB approximation. However, in analogy with the results[9] (article by N. Korngold) we can hope the exact eigenvalues to be close everywhere to the WKB spectrum.

For the relaxation time of the distribution function we obtain

$$\frac{1}{\tau}=\lambda_{10}=\frac{32\pi}{15\sqrt{2}}BQ^2n_2m\sqrt{\frac{2m}{T}}(1+13{,}7\beta). \qquad (4.17)$$

As expected, the relaxation time of the distribution function differs little ($\lesssim$15%) from the relaxation time of the electron energy

$$\frac{1}{\tau_1}=\frac{2}{3}\frac{1}{\Delta T}\overline{\frac{dK}{dt}}$$

(see[3], formula (3.6)[2)] with $\mu = m$, $T_e = T_1 = T$).

[2)] There is a misprint in this formula: the T_1 in the third term should be preceded by a minus sign.

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