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Abstract

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PHYSICS

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MOTION OF IONS IN THEIR OWN GAS IN A CONSTANT ELECTRIC FIELD

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1. In the case of ion mobility in its own gas, the mechanism of ion braking is determined by resonant charge exchange of the ion on the atom ⁽¹⁾. If elastic scattering plays no role here—which is obviously valid at thermal and higher collision energies of the ion and atom—then the kinetic equation for the ion velocity distribution function has a relatively simple structure. This makes it possible to solve the kinetic equation for ions in the limit of large and small electric-field strengths ^(2–5) and to determine the ion mobility in these limiting cases. At intermediate field strengths the kinetic equation was solved ^(4, 5) under the condition that elastic scattering of ions by atoms is unimportant and that the cross section for resonant charge exchange is independent of velocity. In the present work a variational method is proposed for finding the mobility under these conditions. The result obtained is extended to the general case, in which the dependence of the resonant charge-exchange cross section on velocity is taken into account and elastic scattering of the ion by atoms is included.

2. In writing the kinetic equation for the ion velocity distribution function, we shall first assume that the cross section for resonant charge exchange is independent of velocity. Then the kinetic equation for the ion velocity distribution function has the form ⁽²⁾

$$\beta \frac{\partial f}{\partial u_x} = \varphi(u) \int f(\mathbf{u}') |\mathbf{u} - \mathbf{u}'| d\mathbf{u}' - f(\mathbf{u}) \int \varphi(u') |\mathbf{u} - \mathbf{u}'| d\mathbf{u}', \quad (1)$$

where $\beta = eF/2TN\sigma_0$; $\mathbf{u}, \mathbf{u}' = \frac{\mathbf{v}, \mathbf{v}'}{\sqrt{2T/M}}$, so that F is the electric-field strength; T, N are the temperature and density of the gas atoms; M is the mass of an atom or ion; σ_0 is the cross section for resonant charge exchange of an ion on an atom; $\mathbf{v}, \mathbf{v}'$ are the velocities of an atom or ion; $\varphi(u) = \pi^{-3/2} \exp(-u^2)$ is the Maxwellian ion velocity distribution function ($\int \varphi(u) d\mathbf{u} = 1$).

Multiplying kinetic equation (1) by u_x and u_x^2 and integrating over ion velocities, we obtain the relations

$$\beta = \int (u_x - u'_x) |\mathbf{u} - \mathbf{u}'| f(\mathbf{u}) \varphi(\mathbf{u}') d\mathbf{u} d\mathbf{u}', \quad (2)$$

$$2w\beta = \int (u_x^2 - u_{x'}^2) |\mathbf{u} - \mathbf{u}'| f(\mathbf{u}) \varphi(\mathbf{u}') d\mathbf{u} d\mathbf{u}'. \quad (3)$$

Here $w = \int u_x f(\mathbf{u}) d\mathbf{u}$ is the reduced drift velocity of the ion; the distribution function $f(\mathbf{u})$ is normalized to unity, $\int f(\mathbf{u}) d\mathbf{u} = 1$. Relation (2) was obtained and studied earlier by Kihara ⁽⁶⁾ in a more general case than the one considered here.

3. Relations (2) and (3) are exact. We shall use these relations for an approximate determination of the drift velocity. For this purpose we prescribe a trial distribution function with variable parameters, and determine these parameters from relations (2), (3). We prescribe ...

distribution function with one variable parameter, since this will also provide us with a higher accuracy in determining the drift velocity than that with which the resonant charge-transfer cross section is known. The use of the two indicated relations gives two methods for determining the drift velocity, and comparison of the results of these methods makes it possible to determine the accuracy with which the drift velocity has been found.

Let us require that at small electric-field strengths $\beta \ll 1$ the trial distribution function go over into the Maxwellian one $\varphi(u) = \pi^{-3/2} \exp(-u^2)$, and that at large electric-field strengths $\beta \gg 1$ it coincide with its asymptotic expression ^(2, 5) $f(u) = C \exp(-u_x^2/2\beta) \eta(u_x) \delta(u_\rho^2)$. In addition, let us require that at small electric-field strengths the trial distribution function provide the correct form of the expansion of the drift velocity w in the small parameter β : $w/\beta = c_1 + c_2\beta^2$. These requirements, in the case of a single variable parameter, uniquely determine the form of the trial distribution function

$$f(\mathbf{u}) = \frac{C}{\pi^{3/2}} \exp[-u^2(1 - \alpha \cos \vartheta)], \quad (4)$$

where α is the variable parameter, and ϑ is the angle between the vectors $\mathbf{u}$ and $\mathbf{F}$. In this case the normalization constant is equal to

$$C = \alpha \sqrt{1 - \alpha^2} / [\sqrt{1 + \alpha} - \sqrt{1 - \alpha}], \quad (5)$$

and the drift velocity $w = \int u_x f(\mathbf{u}) d\mathbf{u}$ is expressed in the following way in terms of the quantity α :

$$w = \frac{1}{\sqrt{\pi}} (\sqrt{1 + \alpha} - \sqrt{1 - \alpha})^{-1} \left[\frac{2}{\sqrt{1 - \alpha^2}} - \frac{\sqrt{1 - \alpha^2}}{\alpha} \ln \frac{1 + \alpha}{1 - \alpha} \right]. \quad (6)$$

4. Substitution of the distribution function (4) into relation (2) gives

$$\beta = \beta^{(0)} - \beta^{(1)},$$

where

$$\beta^{(0)} = \frac{8C}{\pi} \int_0^\infty \exp(-u^2) u^2 du s(\alpha u^2) \int_0^\infty \exp(-u'^2) u'^2 du' \left(u^2 + \frac{2}{3} u'^2 - \frac{u'^4}{15u^2} \right),$$

$$\begin{aligned} \beta^{(1)} = & \frac{8C}{\pi} \int_0^\infty \exp(-u^2) u^2 du s(\alpha u^2) \int_u^\infty \exp(-u'^2) u'^2 du' \times \\ & \times \left(u^2 + \frac{2}{3} u'^2 - \frac{u'^4}{15u^2} - \frac{4}{3} uu' - \frac{4u^3}{15u'} \right), \end{aligned}$$

$$s(t) = 2(\operatorname{ch} t/t - \operatorname{sh} t/t^2).$$

For small α , $\beta^{(0)} = 5/3\alpha$, $\beta^{(1)} = (8/3\pi - 5/6)\alpha = 0.0154\alpha$, i.e., the contribution to β from the second term ($< 1\%$) is considerably less than the accuracy to which we aspire. As α increases, this contribution decreases even more, since with increasing α the main contribution to β is made by ever larger values of u , while the asymptotic value as $u \rightarrow \infty$ of the integral over du' entering into the integral $\beta^{(1)}$ has the form $\exp(-u^2)/4u^5$, i.e., the integral $\beta^{(1)}$ is determined by small values of u . Therefore the quantity $\beta^{(1)}$ may be neglected with accuracy satisfactory for us, so that

$$\begin{aligned} \beta = \beta^{(0)} = & \frac{\sqrt{1-\alpha^2}}{\sqrt{1+\alpha} - \sqrt{1-\alpha}} \left[\frac{1}{2(1-\alpha)^{3/2}} + \frac{1}{2(1+\alpha)^{3/2}} - \frac{4}{3\alpha}(\sqrt{1+\alpha} - \sqrt{1-\alpha}) + \right. \\ & \left. + \frac{1}{6}(\sqrt{1+\alpha} + \sqrt{1-\alpha}) \right], \end{aligned} \quad (7)$$

$$\beta = 1.65\alpha + 1.20\alpha^3, \quad \alpha \rightarrow 0.$$

5. As is evident, a substantial simplification in the calculation of integral (2) is connected with the fact that the main contribution to this integral is made by velocities $u > 1$, $u' \sim 1$.

Fig. 1. Mobility of ions in their own gas. 1 —formulas (6), (7); 2 —formulas (6), (8)

Figure 1: Fig. 1. Mobility of ions in their own gas. 1 —formulas (6), (7); 2 —formulas (6), (8)

Using this circumstance in calculating integral (3) with the trial function (4), we obtain

$$\beta = \frac{\alpha\sqrt{1-\alpha^2}}{\left(\frac{2}{\sqrt{1-\alpha^2}} - \frac{\sqrt{1-\alpha^2}}{\alpha} \ln \frac{1+\alpha}{1-\alpha}\right)} \left[\frac{1}{12} + \frac{2}{(1-\alpha^2)^2} - \frac{1+\alpha^2}{\alpha^2(1-\alpha^2)} + \frac{1}{2\alpha^3} \ln \frac{1+\alpha}{1-\alpha} - \frac{5}{24\alpha} \ln \frac{1+\alpha}{1-\alpha} \right], \quad (8)$$

$$\beta = 1.55\alpha + 2.84\alpha^3, \quad \alpha \rightarrow 0.$$

6. The relations obtained, (6)–(8), should be used to find the drift velocity as a function of the parameter $\beta = eF/2TN\sigma$. For this purpose, by eliminating the parameter α from equations (6) and (7), or (6) and (8), we determine the drift velocity as a function of β . In the case of small electric-field strengths $\beta \ll 1$, the first method, based on the use of relations (6) and (7), gives $w = 0.455\beta$. The second method for finding $w(\beta)$, based on the use of relations (6) and (8), gives the relation $w = 0.486\beta$. The latter relation is especially close to the exact value $w = 0.483\beta$, obtained as a result of the exact solution of the kinetic equation ^(4, 5).

Fig. 1. Mobility of ions in their own gas.
1 —formulas (6), (7); 2 —formulas (6), (8)

At larger values of the electric-field strength $\beta \gg 1$, both methods give the value of the drift velocity $w = \sqrt{2\beta/\pi}$, coinciding with that obtained by an exact solution of the kinetic equation (2).

The values of the reduced mobility w/β , found on the basis of the first method (relations (6), (7)) and the second method (relations (6), (8)), are shown in Fig. 1. The calculated values of the mobility are compared with the values obtained on the basis of the approximation formulas:

$$w = 0.483\beta(1 + 0.13\beta^2)^{1/4}, \quad (9a)$$

$$w = 0.486\beta(1 + 0.22\beta^{3/2})^{1/3}. \quad (9)$$

Formula (9) better approximates the results of the present variational calculation and agrees with the results of previous calculations ^(4, 5). In this case the

degree of agreement of formula (9) with the results of the calculations is, in any event, better than 10%, i.e., higher than the accuracy with which the resonant charge-exchange cross section is known.

7. To include in expression (9) the dependence of the resonant charge-exchange cross section on velocity, we use the asymptotic expressions

of the drift velocity W in the limit of small and large field strengths, which, taking into account the logarithmic dependence of the cross section on the velocity, have the form⁵ ($W = \sqrt{2T/Mw}$)

$$W = 0.483 \sqrt{\frac{2T}{M}} \frac{eF}{2TN\sigma_{\text{res}}(\sqrt{9T/M})}, \quad \beta \rightarrow 0;$$

$$W = \sqrt{\frac{4eF}{\pi MN\sigma_{\text{res}}(1.3\sqrt{eF/MN\sigma})}}, \quad \beta \rightarrow \infty, \quad (10)$$

where the argument indicates at what velocity the charge-exchange cross section is to be taken. Considering the dependence of the resonant charge-exchange cross section on velocity to be weak, we can determine the reduced drift velocity from formula (9b), where the quantity β satisfies the relation

$$\beta = \frac{eF}{2TN\sigma_{\text{res}} \left[\sqrt{9T/M} (1 + 0.22\beta^{3/2})^{1/3} \right]}. \quad (11)$$

Relations (9b), (11) make it possible to determine the drift velocity of ions in their own gas in the absence of elastic scattering of the ion by the atom. They give the correct values of the drift velocity (10) in the limit of small and large field strengths. It is interesting that the result obtained is readily generalized to a more general case, taking into account scattering of the ion by the atom as a result of the polarization interaction. Indeed, let us write relations (9b), (11) in the form

$$W = 0.488 (1 + 0.22\beta^{3/2})^{1/3} \sqrt{2T/M}, \quad (12a)$$

$$\beta = eF/TN\sigma^* \left[\sqrt{9T/M} (1 + 0.22\beta^{3/2})^{1/3} \right], \quad (12b)$$

where σ^* is the diffusion cross section for scattering of the ion by the atom. In the limiting case when elastic scattering is insignificant, we have⁷ $\sigma^* = 2\sigma_{\text{res}}$, i.e., relations (12) coincide with relations (9b), (11). In the other limiting case of low temperatures, when charge exchange and scattering of the ion by the atom are caused mainly by polarization capture, the diffusion scattering cross section σ^* is inversely proportional to the relative collision velocity of the ion and atom g .

In this case the collision frequency of the ion with the atom $\nu = Ng\sigma^*(g)$ does not depend on velocity, and the ion drift velocity according to formulas (12) is equal to $W = 2.04eF/M\nu$ at any field strength. The exact value of the drift velocity turns out to be⁶ $W = 2eF/M\nu$. Moreover, at small field strengths and weak elastic scattering, the second terms of the expansion of the drift velocity in the small parameter $\alpha e^2/T\sigma_{\text{res}}^2 \ll 1$, obtained from formulas (12) and on the basis of the Chapman-Enskog approximation, differ by 10%.

Thus, relations (12) make it possible to determine the drift velocity of ions in their own gas at arbitrary field strengths and temperatures. The accuracy they provide is no worse than the accuracy with which the collision cross sections of the ion and atom are known.

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