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Diffusion cooling of electrons in a finite gas

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Diffusion cooling and heating of electrons in a neutral gas is shown to be related to steep-gradient, nonlinear diffusive effects imposed by the presence of boundaries. A variational method of solution of Boltzmann's equation is outlined and the effective electron diffusion coefficient is obtained as the minimum of a certain integral. Gas mixtures and inelastic collisions are considered using model cross sections.

I. INTRODUCTION

Diffusion of electrons to the walls of the vessel containing a weakly ionized gas prevents the electrons from ever coming into thermal equilibrium with the neutral molecules of the gas. "Diffusion cooling" of electrons was first observed by Biondi[1] in measurements on the afterglow of low-pressure neon and argon discharges. In general, the space-charge field and ambipolar diffusion will make an important contribution, but for the experiments we wish to analyze[2-4] only the effects of free (no field) diffusion need be considered.

Some understanding of the phenomenon can be gained from mean-free-path arguments.[4] If $q_m(v)$ is the diffusion (or momentum transfer) cross section for collisions between electrons of speed v and neutral molecules whose number density is N, then such electrons diffuse at a rate controlled by the coefficient

$$D(v) = \tfrac{1}{3} v\lambda_m(v) ,$$

where $\lambda_m = (Nq_m)^{-1}$ is the mean free path for momentum transfer in electron-neutral collisions. If $q_m(v)$ varies less rapidly than linearly with v, then the diffusion rate is clearly greater for faster electrons and hence more of these are lost to the walls; the average energy of the remaining electrons is lowered, as is their mean speed, i.e., T_e (electron temperature) $< T$ (neutral gas temperature), $\overline{v} < \overline{v}_0$ (mean speed at thermal equilibrium). The macroscopically observed quantity is

$$D = \tfrac{1}{3}\overline{v\lambda_m(v)} \simeq \tfrac{1}{3}\overline{v}\lambda_m(\overline{v}) , \tag{1.1}$$

and clearly this too is less than the thermal-equilibrium diffusion coefficient D_0. On the other hand, if $q_m(v)$ increases more rapidly than v, then the diffusion rate to the walls is greatest for the slower electrons and consequently the average energy of the remaining electrons is *increased* above the thermal-equilibrium value, i.e., $T_e > T$, $\overline{v} > \overline{v}_0$ ("diffusion heating"). However, even in this case, it can be seen that

$$D < D_0 . \tag{1.2}$$

Only for the special model $q_m \propto v$ is the diffusion rate the same for all electrons, with the result that thermal equilibrium is attained ($T_e = T$, $\overline{v} = \overline{v}_0$, $D = D_0$).

The theory above is, of course, greatly simplified, and serves mainly to establish the connection between diffusion cooling (or heating) and the reduction in D. (It is D which is determined in experiment, not T_e.) To find the dependence of D upon the geometry of the containing vessel, we take a macroscopic theory which allows for boundary effects and nonlinear diffusion. This aspect of the problem is emphasized because of the recent interest shown in finding the limits of validity of Fick's law of diffusion for electrons[5,6] and ions[7,8] in gases. There is an intimate connection between diffusion cooling and nonlinear diffusion arising from boundary effects; this is discussed in detail in Sec. II.

To obtain quantitative results, however, one must solve Boltzmann's equation for the electron-energy distribution function under the appropriate boundary conditions. A variational method is outlined in Sec. III and results are given in Sec. IV for simple cases (model cross sections and single-parameter variational trial functions). This approach contrasts with the previous work of Parker[9] (perturbation theory) and Leemon and Kumar[10] (polynomial expansion method; see also Ref. 11) and is perhaps more suitable for dealing with inelastic collisions. Thus we obtain good agreement with the recent experiment of Rhymes and Crompton,[3] in which small traces of hydrogen are added to argon to improve the "thermal contact"[1] between electrons and gas, thus substantially inhibiting diffusion cooling (see Fig. 1).

II. EFFECTIVE DIFFUSION COEFFICIENT

The mean free path for energy transfer (averaged over all electron speeds) in elastic electron-neutral collision is

$$\bar{\lambda}_\epsilon = \bar{\lambda}_m (M/2m)^{1/2},$$

where m and M denote the masses of an electron and neutral molecule, respectively. Boundary effects[5] become important within a layer[12] of thickness $\bar{\lambda}_\epsilon$ and, in particular, Fick's law of diffusion and hence the well known diffusion equation[4,5-7] are not valid there. In many cases of interest, $\bar{\lambda}_\epsilon$ may be of the same order of magnitude as the dimensions L of the enclosing vessel (typically L is approximately a few cm), and the classical diffusion equation cannot be applied anywhere in such cases. Fortunately, the problem is not as serious as it might seem at first, as it turns out to be simply a matter of replacing the usual diffusion coefficient with an effective diffusion coefficient dependent upon the size and shape of the enclosure.

Let $\Lambda \sim n/|\nabla n|$ be the scale length for variations in the electron number density $n(\vec{r}, t)$. (Since n varies from a maximum somewhere within the enclosure to zero at the walls,[4,13] $\Lambda \lesssim L$. Later, we identify Λ as the diffusion length.) Then if the density gradient is at most moderately steep, that is, if[14]

$$\bar{\lambda}_\epsilon / \Lambda \lesssim 1, \qquad (2.1)$$

and if for simplicity we take plane-parallel geometry with L being the distance between walls, the electron number density is determined from the following transport equation[5]:

$$\frac{\partial n}{\partial t} = D_0 \frac{\partial^2 n}{\partial x^2} + (\bar{\lambda}_\epsilon)^2 \delta \frac{\partial^4 n}{\partial x^4} + \cdots, \qquad (2.2)$$

where D_0 is the familiar (thermal-equilibrium) diffusion coefficient and the correction terms on the right-hand side arise from nonlinear diffusion[5-7] owing to the steepness in ∇n imposed by the presence of boundaries.

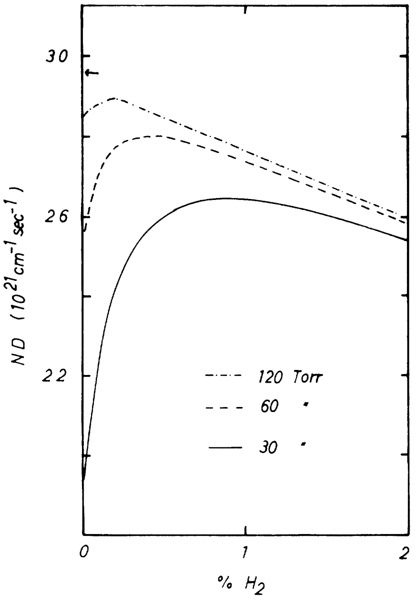

FIG. 1. Composition and pressure dependence of the effective electron diffusion coefficient in an Ar-H_2 mixture at room temperature, based upon the model cross sections given in Sec. IV B. The arrow on the ordinate indicates the thermal equilibrium value of ND for pure Ar attained in the limit of high gas pressures.

There are two points which we mention in passing concerning Eq. (2.2). Firstly, the spatial dependence of the diffusion coefficient (through n) is neglected on the basis that the degree of ionization is very low ($n \ll N$), so that mutual electron interactions can be neglected.[13] This assumption is consistent with the Boltzmann theory given in Sec. III, where it is clear from the formulas that $\partial D/\partial n = 0$. Secondly, it is emphasized that modification of Fick's law through higher-order derivatives is not in general a valid procedure, with some upper limit on density gradient as in (2.1) being required to avoid divergences.[5,7] For strong gradients, this approach is not valid, and one must appeal to the more rigorous theory of Sec. III for an adequate description of the transport process.

The question of extensions to Fick's law has also been discussed by de Schepper *et al.*[15] in connection with self-diffusion; they find long time divergences in these higher-order corrections.

With the boundary conditions $n = 0$ at $x = 0, L$, the solution of (2.2) is

$$n(x,t) = \sum_{k=1}^{\infty} A_k e^{-t/\tau_k} \sin\left(\frac{x}{\Lambda_k}\right), \qquad (2.3)$$

where $\Lambda_k = L/k\pi$ is the diffusion length for the kth mode,

$$(\tau_k)^{-1} = D_0 \Lambda_k^{-2} \left[1 - \frac{\delta}{D_0}\left(\frac{\bar{\lambda}_\epsilon}{\Lambda_k}\right)^2 + \cdots\right] \qquad (2.4)$$

gives the corresponding decay constant τ_k, and the A_k are constants fixed by initial conditions.

In experiment,[2-4] the total number of electrons within the enclosure is measured at various time intervals. At long times ($t > \tau_1 > \tau_2 > \cdots$), it can be seen that the $k = 1$ mode dominates the sum (2.3) and hence

$$n(x,t) \sim \sin(x/\Lambda) e^{-t/\tau}, \qquad (2.5)$$

where we have written Λ for Λ_1 and

$$\tau^{-1} = (\tau_1)^{-1} = D_0 \Lambda^{-2} \left[1 - \frac{\delta}{D_0}\left(\frac{\bar{\lambda}_\epsilon}{\Lambda}\right)^2 + \cdots\right] \equiv D\Lambda^{-2}. \qquad (2.6)$$

Equation (2.6) defines an effective diffusion coefficient D. This is measured in experiment by fitting to the data an exponential decay in time and using Eq. (2.5).

When $\bar{\lambda}_\epsilon$ is small compared with the dimensions of the enclosure ($\bar{\lambda}_\epsilon \ll \Lambda$), gradients in n are weak, giving small nonlinear diffusion effects; in addition, the electrons become effectively thermalized with the gas molecules, resulting in little diffusion cooling. The ratio $\bar{\lambda}_\epsilon/\Lambda$ can be made small in a number of ways, by reducing $\bar{\lambda}_\epsilon$ by increasing gas pressure (i.e., increase N), reducing $\bar{\lambda}_\epsilon$ by using a light gas or by using a gas in which inelastic collisions are significant (see Secs. III and IV), or increasing the size of the enclosure.

It is clear from (2.6) that $D \to D_0$ as $\bar{\lambda}_\epsilon/\Lambda \to 0$. The effect of the speed-dependence of the cross section is carried by the quantity δ. For example, when $q_m(v) \propto v$, it can be shown directly from Skullerud's work[5] that δ and all higher-order correction terms vanish. In this case, $D = D_0$ and there is thermal equilibrium even if $\bar{\lambda}_\epsilon/\Lambda$ is not small.

In other cases, the indications are[5,7] that δ is positive, and hence $D < D_0$. This is in accord with the simplified argument of Sec. I, and is confirmed by the theory given below.

Although we have specifically taken plane-parallel geometry as a mathematical simplification, the *form* of most of the above equations remains the same, whatever the geometry, and only the value of Λ and the spatial dependence of n change. For example, for a cylindrical cavity[4,13] of height h and radius a, we have for the lowest-order mode

$$\Lambda^{-2} = (\xi_0/a)^2 + (\pi/h)^2 \tag{2.7}$$

and

$$n(r, z, t) = J_0(\xi_0 r/a)\sin(\pi z/h)e^{-t/\tau}, \tag{2.8}$$

where ξ_0 is the first zero of the Bessel function J_0 and r and z are cylindrical coordinates.

Finally, we note from (2.2), (2.5), and (2.6) that the electron number density satisfies a diffusionlike equation; in general, we have

$$\frac{\partial n}{\partial t} = D\nabla^2 n, \tag{2.9}$$

regardless of geometry and independently of whether or not $\bar{\lambda}_\epsilon/L$ is small. This will be verified in Sec. III.

III. VARIATIONAL SOLUTION OF BOLTZMANN'S EQUATION

Parker[9] and Leemon and Kumar[10] solve the Boltzmann equation for electrons diffusing freely in a neutral gas of one component and making only elastic collisions with the neutrals. We take a gas of two components, temperature T, molecular masses M_1 and M_2, in which collisions with species 1 are elastic and described by the momentum transfer cross section $(q_m)_1$, but collisions with species 2 may be either elastic [cross section $(q_m)_2$] or inelastic. If x_1 and x_2 are the relative concentrations of the two neutral species and if $Q_j(\epsilon)$ represents the cross section for an inelastic collision between an electron of energy $\epsilon = \frac{1}{2}mv^2$ and a neutral molecule in the jth excited state in which the electron loses energy ϵ_j, then the Boltzmann equation for the electron-energy distribution function $f(\epsilon, \vec{r}, t)$ is[4,16]

$$\left(\frac{m\epsilon}{2}\right)^{1/2}\frac{\partial f}{\partial t} = \frac{\epsilon}{3NQ_m}\nabla^2 f + \frac{2m}{M}\frac{\partial}{\partial\epsilon}\left[N\epsilon^2\bar{Q}_m\left(f + kT\frac{\partial f}{\partial\epsilon}\right)\right] + x_2 N I(f). \tag{3.1}$$

The inelastic collision term is defined by[4,16]

$$I(f) = \sum_j \{(\epsilon+\epsilon_j)Q_j(\epsilon+\epsilon_j)[f(\epsilon+\epsilon_j) - e^{-\epsilon_j/kT}f(\epsilon)] - \epsilon Q_j(\epsilon)[f(\epsilon) - e^{-\epsilon_j/kT}f(\epsilon-\epsilon_j)]\}, \tag{3.2}$$

and other symbols are defined as follows:

$$\bar{Q}_m \equiv M[(x_1/M_1)(q_m)_1 + (x_2/M_2)(q_m)_2], \tag{3.3a}$$

$$Q_m \equiv x_1(q_m)_1 + x_2(q_m)_2, \tag{3.3b}$$

$$M^{-1} \equiv x_1(M_1)^{-1} + x_2(M_2)^{-1}. \tag{3.3c}$$

In writing (3.2) we have made use of the Klein-Rosseland relation[4] to account for collisions involving deexcitation of the jth state, in which an electron gains energy ϵ_j.

Equation (3.1) is solved by making a separation of variables,

$$f(\epsilon, \vec{r}, t) = F(\epsilon)R(\vec{r})\mathcal{T}(t), \tag{3.4}$$

and hence

$$\nabla^2 R = -\Lambda^{-2}R, \tag{3.5a}$$

$$\frac{d\mathcal{T}}{dt} = -\Lambda^{-2}D\mathcal{T}, \tag{3.5b}$$

$$\frac{2m}{M}\frac{d}{d\epsilon}\left[N\epsilon^2\bar{Q}_m\left(F + kT\frac{dF}{d\epsilon}\right)\right] + x_2 N I(F) + \Lambda^{-2}\left[\left(\frac{m\epsilon}{2}\right)^{1/2}D - \frac{\epsilon}{3NQ_m}\right]F = 0, \tag{3.5c}$$

where Λ and D are separation constants. Λ is determined by solving the eigenvalue equation (3.5a) with the boundary condition $R = 0$. Only the lowest mode is important at long times, and for cylindrical geometry Λ is given by (2.7).

Similarly, (3.5c) is an eigenvalue equation in which D appears as an eigenvalue; again only the lowest eigenvalue is important at long times.

Note that the electron number density is obtained by integrating $f(\epsilon, \vec{r}, t)$ over all energies; assuming that $F(\epsilon)$ is normalized,

$$n(\vec{r}, t) = \frac{4\pi}{m}\left(\frac{2}{m}\right)^{1/2} \int_0^\infty f(\epsilon, \vec{r}, t)\epsilon^{1/2} d\epsilon$$

$$= R(\vec{r})\mathcal{T}(t),$$

and from (3.5a) and (3.5b) it is clear that n satisfies a diffusion equation of the type (2.9).

It is convenient at this stage to make all variables dimensionless; cross sections are measured in units of $Q_0 = 10^{-16}$ cm^2, the new energy variable is $u = \epsilon/kT$, and the other dimensionless variables are defined as follows:

$$\kappa = \overline{\lambda}_\epsilon/(\sqrt{3}\Lambda), \tag{3.6a}$$

$$\theta = 3D/(\overline{v}_{\text{th}}\overline{\lambda}_m), \tag{3.6b}$$

where $\overline{v}_{\text{th}} \equiv (2kT/m)^{1/2}$ and $\overline{\lambda}_m$ and $\overline{\lambda}_\epsilon$ are representative mean free paths defined as in Secs. I and II but with the actual cross section $q_m(\epsilon)$ replaced by the constant Q_0. The time constant (2.6) for the lowest-order mode is thus given by

$$\tau^{-1} = [(2m/M)\overline{v}_{\text{th}}/\overline{\lambda}_m]\kappa^2\theta. \tag{3.6c}$$

From the discussion in Sec. II, we anticipate that boundary effects and diffusion cooling will be significant unless κ is very small.

These definitions, together with the substitution in (3.5c) of

$$F(u) = e^{-u}G(u), \tag{3.7}$$

yield the eigenvalue equation

$$\frac{d}{du}\left(u^2\overline{Q}_m e^{-u}\frac{dG}{du}\right) + x_2\frac{M}{2m}I(G) + \kappa^2\left(u^{1/2}\theta - \frac{u}{Q_m}\right)e^{-u}G = 0, \tag{3.8}$$

where the inelastic collision term is now given by

$$I(G) = \sum_j \Big((u+u_j)Q_j(u+u_j)e^{-(u+u_j)}[G(u+u_j) - G(u)]$$

$$- uQ_j(u)e^{-u}[G(u) - G(u-u_j)]\Big). \tag{3.9}$$

The lowest eigenvalue θ of Eq. (3.8) can be found from a variational principle which relies on the self-adjointness of the collision operators [the first two terms in (3.8)]. Thus, for example, if $\phi_1(u)$ and $\phi_2(u)$ are arbitrary functions, then

$$\int_0^\infty du\, \phi_1 I(\phi_2) = \int_0^\infty du\, \phi_2 I(\phi_1). \tag{3.10}$$

The proof relies upon establishing the following identity:

$$\int_0^\infty du\, \phi_1 I(\phi_2) = -\sum_j\left(\int_0^\infty du\,(u+u_j)Q_j(u+u_j)e^{-(u+u_j)}\,[\phi_1(u+u_j) - \phi_1(u)][\phi_2(u+u_j) - \phi_2(u)]\right). \tag{3.11}$$

If we define

$$\vartheta = \int_0^\infty du\left(u^2\overline{Q}_m e^{-u}(\phi')^2 + \kappa^2 e^{-u}\frac{u}{Q_m}\phi^2 - \frac{x_2 M}{2m}\phi I(\phi)\right)$$

$$\times\left(\kappa^2\int_0^\infty du\, u^{1/2}e^{-u}\phi^2\right)^{-1}, \tag{3.12}$$

then the function $\phi(u)$ which renders ϑ stationary (actually a minimum) with respect to all other functions is the eigenfunction $G(u)$ of (3.8) corresponding to the lowest eigenvalue θ; in that case $\theta = \vartheta$. The proof follows along lines similar to proofs given in elementary texts on the calculus of variations.[17]

Note that by virtue of (3.11), the last term in the integrand in the numerator of (3.12) can be written in the form

$$-\int_0^\infty du\, \phi I(\phi) = \sum_j \int_0^\infty du\,(u+u_j)Q_j(u+u_j)e^{-(u+u_j)}$$

$$\times[\phi(u+u_j) - \phi(u)]^2, \tag{3.13}$$

which is clearly non-negative.

In practice, we choose a physically reasonable form of trial function with one or more adjustable parameters $\alpha_1, \alpha_2, \ldots$, calculate $\vartheta(\alpha_1, \alpha_2, \ldots)$ and then minimize with respect to these parameters. The method is first illustrated in the case of a single-component gas with no inelastic collisions and the results are compared with model cross section calculations of previous work.[9, 10]

IV. RESULTS AND DISCUSSION FOR MODEL CROSS SECTIONS

A. Single-component neutral gas, elastic collisions

Since $x_2 = 0$ and $x_1 = 1$, we have

$$\overline{Q}_m = Q_m = u^{\gamma-1},$$

where γ is a constant. As we deal with models only, it is in the spirit of the calculation to consider only the simplest, single-parameter trial functions. Hence we choose

$$\phi(u) = e^{-\alpha u}, \tag{4.1}$$

where α is an adjustable parameter. Equation (3.12) then gives

$$\vartheta = \frac{2\pi^{-1/2}}{\kappa^2}\left(\frac{\alpha^2\Gamma(\gamma+2)}{(1+2\alpha)^{\gamma+1/2}} + \frac{\kappa^2\Gamma(3-\gamma)}{(1+2\alpha)^{3/2-\gamma}}\right). \qquad (4.2)$$

The values of α which minimize ϑ, together with $\theta = \vartheta_{\min}$, are shown below for various γ.

$\gamma = \frac{1}{2}$ *(constant collision frequency).*

$$\alpha = \tfrac{1}{2}[(1+4\kappa^2)^{1/2}-1], \quad \theta = \tfrac{3}{4}\kappa^{-2}[(1+4\kappa^2)^{1/2}-1].$$

In this case, (4.1) is the exact eigenfunction, as can be verified by direct substitution in (3.8).

$\gamma = 1$ *(constant cross section).*

$$\alpha = (1 - \tfrac{1}{2}\kappa^2 + \tfrac{1}{4}\kappa^4)^{1/2} - (1 - \tfrac{1}{2}\kappa^2).$$

If $\kappa < 1$,

$$\alpha \approx \tfrac{1}{4}\kappa^2, \quad \theta \approx 2\pi^{-1/2}(1 - \tfrac{1}{8}\kappa^2),$$

and hence from (3.6b),

$$D \approx D_0[1 - \tfrac{1}{24}(\bar{\lambda}_\epsilon/\Lambda)^2], \qquad (4.3)$$
$$D_0 = (\tfrac{2}{3}\pi^{-1/2})\,\bar{v}_{\mathrm{th}}\bar{\lambda}_m.$$

The correct value[9,10] of the coefficient of κ^2 in the expression for θ is (approximately) $\frac{1}{6}$, rather than $\frac{1}{8}$. This minor discrepancy is not unexpected in view of the simplified trial function (4.1). It can be seen that equation (2.6), based upon the nonlinear diffusion equation (2.2), gives an expression for D of the same form as the above.

$\gamma = \frac{3}{2}$ *(cross-section α speed).*

$$\alpha = 0, \quad \theta = 1, \quad D = D_0 = \tfrac{1}{3}\bar{v}_{\mathrm{th}}\bar{\lambda}_m.$$

There is no diffusion cooling in this case.[10] Again, (4.1) is an eigenfunction of (3.8), and the above results are exact.

$\gamma = \frac{3}{2} + \Delta$ *($\Delta \ll 1$).* If $\Delta = 0$, then $\alpha = 0$ also; hence, if Δ is small but nonzero, α must be $O(\Delta)$. Retaining only leading terms in small quantities in Eq. (4.2), we have

$$\vartheta \approx (2\pi^{-1/2}/\kappa^2)[\alpha^2\Gamma(\tfrac{7}{2}) + \kappa^2\Gamma(\tfrac{3}{2}-\Delta)(1+2\alpha\Delta)],$$

and setting $d\vartheta/d\alpha = 0$ gives

$$\alpha \approx -\tfrac{4}{15}\Delta\kappa^2, \qquad (4.4)$$

$$\theta \approx 2\pi^{-1/2}\Gamma(\tfrac{3}{2}-\Delta)[1 - \tfrac{4}{15}\Delta^2\kappa^2]. \qquad (4.5)$$

Assuming the eigenfunction of (3.8) to be of the form (4.1), it follows from (3.7) that the energy-distribution function for the electrons is

$$F(\epsilon) = \exp(-\epsilon/kT_e), \qquad (4.6)$$

where the electron temperature is given by

$$T_e = T/(1+\alpha). \qquad (4.7)$$

If the cross section varies less rapidly than linearly with electron speed (i.e., $\gamma < \frac{3}{2}$ in the model above) then α is positive and hence there is diffusion cooling, with $T_e < T$. On the other hand, if $\gamma > \frac{3}{2}$, α is negative [Eq. (4.4)] and $T_e > T$ (diffusion heating). Notice that in all cases $D < D_0$ regardless of the energy dependence of the cross section, confirming the earlier results in Secs. I and II.

B. Two-component gas, inelastic collisions

The model parameters are listed below:

$$T = 293\ {}^\circ\mathrm{K}, \quad M_1 = 40 \text{ amu} \quad M_2 = 2 \text{ amu}$$

$$(q_m)_1 = 10^{-10}(ukT)^{-1/2}, \quad (q_m)_2 = 8.0.$$

Molecules of type 2 have excitable rotational states, quantum number J, and selection rule $|\Delta J| = 2$ (Gerjuoy and Stein[18]):

$$Q_{J,J+2}(u) = (Z_J e^{-U_J}/Z)\sigma_{J,J+2}(u) \quad (J = 0, 1, 2, \ldots),$$

$$Z_J = (2t+1)(t+a)(2J+1),$$

$$t = \tfrac{1}{2}, \quad a = \begin{cases} 0 \text{ if } J \text{ even}, \\ 1 \text{ if } J \text{ odd}, \end{cases}$$

$$Z = \sum_J Z_J e^{-U_J},$$

$$U_J = J(J+1)B_0/kT, \quad B_0 = 0.007\,54 \text{ eV},$$

$$\sigma_{J,J+2}(u) = \frac{(J+2)(J+1)}{(2J+3)(2J+1)}\sigma_0\left(1 - \frac{u_J}{u}\right)^{1/2},$$

$$u_J = (4J+6)B_0/kT, \quad \sigma_0 = 8\pi Q^2 a_0^2/15,$$

$a_0 =$ Bohr radius,

$Q = 0.62$ (quadrupole moment in units of ea_0^2).

The above model approximately duplicates conditions for electrons in an argon-hydrogen mixture at room temperature (argon = 1, hydrogen = 2).

The formulas for the cross sections for excitation of rotational levels of H_2 are based on the assumption that the interaction is dominated by long-range quadrupole force,[18] and they have been used by Phelps and co-workers[16] in calculation of transport coefficients. Inelastic collisions of electrons with H_2 molecules are possible if $\epsilon > 0.045$ eV and are therefore significant at room temperature. (Inelastic collisions involving excitation of vibrational states can be safely neglected, since the threshold energy is about 0.5 eV.)

To calculate D, we again minimize the integral (3.12) using the single-parameter trial function (4.1). Equation (3.12) becomes in this case

$$\vartheta(\alpha) = \frac{2\pi^{-1/2}}{\kappa^2}(1+2\alpha)^{3/2} \times \int_0^\infty du\, e^{-(1+2\alpha)u}\left(\alpha^2 u^2 \overline{Q}_m + \frac{\kappa^2 u}{Q_m} + x_2\frac{M}{2m}\mathcal{g}_\alpha(u)\right), \qquad (4.8)$$

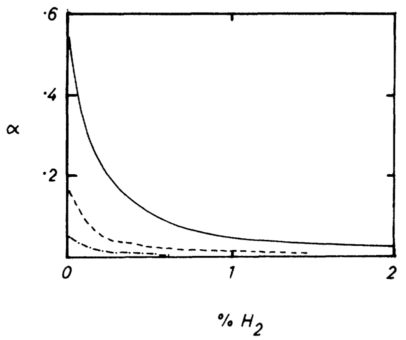

FIG. 2. Variational parameter corresponding to values of effective diffusion coefficient shown in Fig. 1. Electron temperature is given by Eq. (4.7).

where

$$\mathcal{G}_{\alpha}(u) \equiv \sum_{J} (u+u_J) Q_{J,\,J+2}(u+u_J) e^{-u_J}(1-e^{-\alpha u_J})^2 \, . \tag{4.9}$$

Figures 1 and 2 show ND and α, respectively, as functions of hydrogen concentration for several total gas pressures, assuming a cylindrical enclosure of the same dimensions used in experiment.[2,3] The variation with pressure is as expected; α decreases (towards zero) and ND increases with increasing pressure, i.e., thermal equilibrium conditions are approached. The pure argon equilibrium diffusion coefficient, whose theoretical value is given by $ND_0 = 29.6 \times 10^{21}$ cm^{-1} sec^{-1}, has not been measured in experiment because of difficulties associated with the high pressures required. Thus in contrast to other gases, like helium and neon, it has not been possible to determine the momentum transfer cross section for electrons in pure argon from thermal-equilibrium diffusion coefficient data.[2,10] (The special interest in the argon cross section derives from the deep Ramsauer-Townsend minimum.[4]) The addition of even a small amount of H_2 helps to bring about thermal equilibrium even at quite low total gas pressures. Electron-H_2 collisions, although comparatively rare, generally involve a far greater energy transfer than the (elastic) electron-Ar collisions and hence tend to thermalize the electrons, reducing diffusion cooling. The steep rise in ND (and the steep fall in α) indicate just how effectively the thermal contact is improved in this way. It is interesting to note that Biondi[1] employed a similar experimental procedure. He used traces of helium in argon and neon gases, and the increased efficiency of energy transfer there results from the lighter mass of the helium atom rather than from inelastic collisions. Biondi's experimental curves are not unlike those shown in Fig. 1 (see Ref. 1, Fig. 5).

It is evident from the diagrams that $\alpha \approx 0$ for even a few percent H_2 and that thermal equilibrium can be considered to be established not far beyond the maximum in ND. Under these conditions, we therefore have from (3.3b), (3.6b), and (4.8) that

$$\theta \approx \vartheta(0)$$

and

$$ND \approx ND_0 = \frac{1}{3}\left(\frac{8kT}{\pi m}\right)^{1/2} \int_0^{\infty} du\, e^{-u} u [x_1 (q_m)_1 + x_2 (q_m)_2]^{-1} \, . \tag{4.10}$$

The curves in Fig. 1 slope downward towards the value for pure hydrogen, $ND_0 = 4.43 \times 10^{21}$ cm^{-1} sec^{-1}.

The 30-Torr curve for ND is in qualitative agreement with experiment; better agreement would be expected with more realistic cross sections and a variational trial function with several adjustable parameters. Nevertheless, the present simplified calculation is useful because it serves to establish the existence of thermal equilibrium beyond the "bump" in the ND curve; in practice, we can therefore use Eq. (4.10) to derive the argon cross section $(q_m)_1$ from the experimental data. (The hydrogen cross section $(q_m)_2$ is well known,[4] so that $(q_m)_1$ can be found unambiguously.) The fitting of the experimental data will be discussed elsewhere.

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