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Diffusion Cooling of Electrons in Ionized Gases

MANFRED A. BIONDI
Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania

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The term "diffusion cooling" is used to describe the situation in which the average energy of an electron swarm is reduced by the diffusion of the faster electrons to the container walls. In the present experiment, measurements of the ambipolar diffusion loss of electrons during the afterglow reveal the presence of diffusion cooling by the reduction in the ambipolar diffusion coefficient. In low-pressure neon and argon afterglows the "thermal contact" between electrons and gas atoms is poor; consequently the diffusion loss of the fast electrons causes a large reduction in electron "temperature" with respect to the gas temperature. When small amounts of helium are added, the thermal contact is greatly improved, and therefore the electrons are restored to thermal equilibrium with the gas. These experimental observations confirm the predictions of a qualitative theory given for the process.

THE term "diffusion cooling of electrons" describes the situation in which the average kinetic energy of electrons in an ionized gas is reduced by the diffusion of electrons to the walls of the containing vessel. There are two distinct processes which lead to diffusion cooling of a swarm of electrons. The first results from the fact that in a freely diffusing swarm the fast electrons diffuse more rapidly than the slow electrons.[1] Thus there is a transport of energy to the walls which tends to decrease the average energy of the remaining electrons. If this loss is not compensated by some energy supplying mechanism such as the acceleration of the electrons in an electric field, the electron energy will decrease as the diffusion process continues. The second process responsible for diffusion cooling occurs in an ionized gas (plasma) and is most effective under conditions of ambipolar diffusion. As will be shown in Sec. II, a space-charge field is set up by the excess of positive ions in the plasma which retards the diffusion of the electrons to the walls. This retarding field produces a cooling effect since only the faster electrons in the swarm have sufficient energy to overcome the space charge potential barrier and reach the walls. In the present experiment, we study the cooling which results from the diffusion of electrons against the ambipolar space charge field.

I. EXPERIMENTAL METHOD

The diffusion cooling of electrons is determined from studies of the ambipolar diffusion loss of electrons during the afterglow of a pulsed microwave discharge. Detailed descriptions of the type of experimental apparatus used in these measurements have been published previously.[2] The gas to be studied is contained in a quartz bottle enclosed by a microwave cavity. Application of a pulse of microwave power to the cavity lasting ~100 μsec ionizes the gas. The free electrons in the gas cause a change in resonant frequency which is proportional to the electron concentration. When the microwave maintaining field is removed from the cavity, the electron density decreases as a result of the ambipolar diffusion of the electrons and ions to the walls of the containing vessel. The electron density during the afterglow is determined from measurements of the resonant frequency of the cavity as a function of time by means of a low-energy probing signal.

The gas samples to be studied are introduced to the quartz bottle by means of an ultrahigh vacuum gas handling system.[3] Airco reagent grade gases are used in these measurements.

II. THEORY

In order to relate our ambipolar diffusion measurements to the diffusion cooling of electrons, let us outline briefly a theory for these processes.[4] In the absence of externally applied fields the drift motions of electrons and ions in an ionized gas depend on their concentration gradients and upon the space-charge field which they set up, according to the relations:

$$\mathbf{\Gamma}_e = -D_e \nabla n_e - \mu_e n_e \mathbf{E}, \qquad (1)$$

$$\mathbf{\Gamma}_+ = -D_+ \nabla n_+ + \mu_+ n_+ \mathbf{E}, \qquad (2)$$

where $\mathbf{\Gamma}$ is the particle current density, D the diffusion coefficient, n the density, and μ the mobility of the electrons and ions, denoted by the subscripts e and $+$, respectively. $\mathbf{E}$ is the space-charge field. Under ambipolar diffusion conditions $\mathbf{\Gamma}_e = \mathbf{\Gamma}_+$, $n_e \simeq n_+$, and $\nabla n_e \simeq \nabla n_+$. In addition, $D_e \gg D_+$ and $\mu_e \gg \mu_+$. Consequently, Eqs. (1) and (2) give for the ambipolar space charge field

$$\mathbf{E} \simeq -(D_e/\mu_e)\nabla(\ln n), \qquad (3)$$

where n represents the concentration of either particle. This space charge field acts to retard the diffusing electrons.

If we eliminate $\mathbf{E}$ from Eqs. (1) and (2), we find that the current of either particle may be characterized by a

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[1] This statement applies when the diffusion cross section of the electrons varies less rapidly than linearly with electron velocity.

[2] See, for example, M. A. Biondi, Rev. Sci. Instr. **22**, 500 (1951); M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).

[3] D. Alpert, J. Appl. Phys. **24**, 860 (1953).

[4] The concept of the cooling of electrons as a result of ambipolar diffusion was originally developed by T. Holstein, Westinghouse Research Report R-94411-9-A (unpublished), pp. 206–219.

diffusion term alone, i.e.,

$$\mathbf{\Gamma}=-D_a\nabla n, \tag{4}$$

where the common diffusion coefficient D_a is the ambipolar diffusion coefficient, given by

$$D_a=(D_+\mu_e+D_e\mu_+)/(\mu_++\mu_e). \tag{5}$$

From kinetic theory[5] we have the relation

$$(D/\mu)_{+,e}=(ku)_{+,e}/q, \tag{6}$$

where q is the electronic charge and the subscripts $+$ and e refer to the ions and electrons, respectively, and u is the average kinetic energy of the particles. The quantity k is a number, of order unity, which depends on the form of the velocity distribution of the particles.[6] Equation (5) may now be written in terms of the average energy of the particles:

$$D_a\simeq D_+[1+x(u_e/u_+)], \tag{7}$$

where $x=k_e/k_+$ and is of the order of unity. Equation (7) shows that diffusion cooling may be determined from experimental measurements of the ambipolar diffusion loss of electrons.

During the afterglow the electric field which ionized the gas is no longer present. The electrons therefore do not gain sufficient energy to make inelastic exciting and ionizing collisions with the gas atoms. However, they continue to exchange energy with the gas atoms by elastic recoil collisions. Using the one-electron picture to describe qualitatively the energy balance for the electrons during the afterglow, we have

$$\partial u_e/\partial t\simeq(2m/M)\nu_c(u_{\text{gas}}-u_e)-\nu_d(Nu_e), \tag{8}$$

where m and M are the masses of the electron and gas atom, respectively; ν_c and ν_d are the average elastic collision frequency and diffusion frequency[7] of the electrons, and u_{gas} is the average energy of the gas atoms. The first term on the right of Eq. (8) represents the rate of exchange of energy as a result of elastic collisions between electrons and gas atoms. The second term represents the rate of transport of energy to the walls by those electrons which diffuse over the space charge barrier. Only the faster electrons in the distribution can reach the boundary; therefore each electron which diffuses to the walls carries away more than the average energy of the distribution. The factor (Nu_e) represents the excess energy carried to the walls and hence the diffusive energy loss in the one-electron description.

These processes are illustrated schematically in Fig. 1, which shows the diffusion of the electron swarm during the afterglow. The space-charge potential well for the electrons $V_{\text{s.c.}}$ reaches a maximum value V_w at the walls of the tube. The energy distribution of the electrons is indicated by the shaded area. If we fix our attention on a particular energy interval in the distribution, electrons (indicated by the dots) are being fed into and out of this interval as a result of elastic recoil collisions with gas atoms. The rate of such feeding depends on the "thermal contact" between the electrons and gas atoms, expressed by the factor $(2m/M)\nu_c$ in Eq. (8); the direction of the net flow of electrons in energy space depends on which is greater, u_{gas} or u_e.

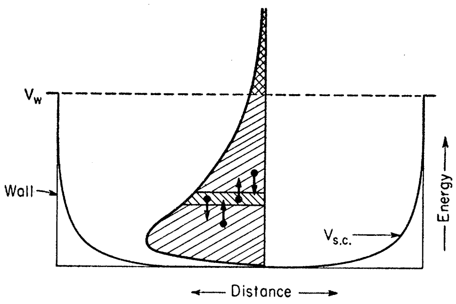

FIG. 1. Diffusion of electrons in the ambipolar space charge well. The electron energy distribution is indicated by the shaded area.

It is clear from the diagram that only those electrons with energy greater than V_w can reach the walls. As a result diffusion to the walls depletes the tail of the electron distribution, the ultimate effect on the shape of the distribution depending on how fast these higher energy electrons are resupplied by means of elastic recoil collisions. In any case the diffusion leads to a reduction in the average energy of the remaining electrons, which may be calculated by use of Eq. (8).

Immediately following a discharge, $u_e\gg u_{\text{gas}}$; thus both terms in Eq. (8) contribute to the energy decay.[8] At a later time in the afterglow, energy equilibrium is reached, i.e., $\partial u_e/\partial t=0$. Equation (8) then gives for the ratio of electron energy to gas energy

$$\frac{u_e}{u_{\text{gas}}}\simeq 1\bigg/\left[1+N\left(\frac{\nu_d}{\nu_c}\right)\frac{M}{2m}\right]. \tag{9}$$

This equation is at best qualitative since we have only order-of-magnitude knowledge of N and have neglected the dependence of ν_c and ν_d on the average electron energy; however, it does demonstrate that the electron energy drops appreciably below the gas energy when the "thermal contact" between the electrons and the gas atoms is poor and/or the rate of diffusive transport of energy to the walls is large.

A gas such as helium is said to offer good thermal contact with the electrons since, excepting hydrogen, it has the largest value of $2m/M$ of any gas and, in

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[5] E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), p. 466.

[6] For example, in the case of the positive ions, which have a Maxwellian velocity distribution $k=\frac{2}{3}$.

[7] See Eq. (11) of Sec. III.

[8] When the energy decay rate due to elastic recoil is small, e.g., in low-pressure mercury afterglows, the diffusion cooling term is primarily responsible for the energy decay immediately following the discharge. G. Mierdel [Z. Physik **121**, 574 (1943)] has observed rapid electron energy decays in mercury afterglows which probably result from diffusion cooling but has incorrectly attributed them to the effects of excitation collisions between fast electrons and mercury atoms.

addition, exhibits a normal elastic collision cross section to electrons. Conversely, gases such as neon and argon, which exhibit very small elastic collision cross sections to slow electrons[9] and have smaller $2m/M$ factors, are said to give poor thermal contact with the electrons. For this reason diffusion cooling effects are more pronounced in neon and argon.

In the present experiment there are two limiting cases of interest. When the thermal contact between the electrons and the gas is sufficiently good, the electrons are brought into thermal equilibrium with the gas, i.e., $u_e = u_{\mathrm{gas}}$. In this case Eq. (7) predicts that $D_a = 2D_+$.[10] In the hypothetical limit in which there is *no* thermal contact between electrons and gas atoms (achieved only at zero gas pressure), the electron energy diminishes to zero. In this case Eq. (7) predicts $D_a = D_+$. In the next section we shall compare our measured values of D_a with these limiting values.

III. MEASUREMENTS OF DIFFUSION COOLING

After energy equilibrium is reached in the afterglow the electrons and ions diffuse to the walls with a constant diffusion frequency, ν_d, leading to a decrease in electron (and ion) density given by

$$n_e = (n_e)_0 \exp(-\nu_d t). \qquad (10)$$

ν_d is related to the ambipolar diffusion coefficient by

$$\nu_d = D_a/\Lambda^2, \qquad (11)$$

where Λ is the characteristic diffusion length of the container[11] and is equal to 0.735 cm in the present experiment. Measurements are made sufficiently late in the afterglow so that energy equilibrium is reached and Eq. (10) is obeyed.

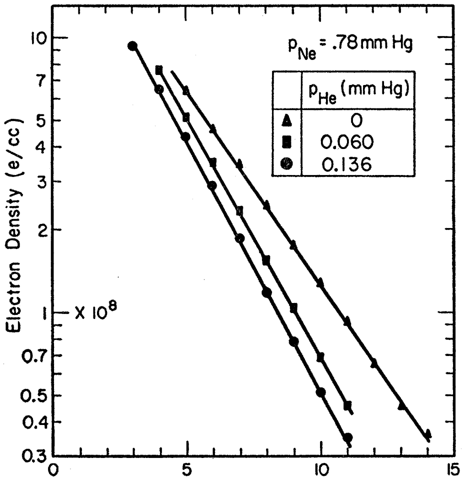

FIG. 2. The effect of the addition of small amounts of helium on the ambipolar diffusion loss of electrons in neon. The gas temperature is 300°K.

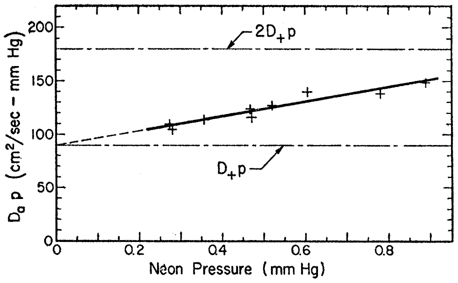

FIG. 3. Diffusion cooling of electrons in neon. The gas temperature is 300°K.

An example of the experimental data obtained in pure neon is shown by the triangular points of Fig. 2. The slope of the curve gives ν_d, from which we obtain the value of D_a. Since the ambipolar diffusion coefficient is inversely proportional to the gas concentration, we multiply the values of D_a by the pressure p to remove the dependence on gas density. The measured values of $D_a p$ *versus* p for pure neon are shown in Fig. 3.

As predicted in the previous section the measured values of D_a lie between the limits D_+ and $2D_+$[12] which correspond to the respective cases, $u_e = 0$ and $u_e = u_{\mathrm{gas}}$. The extrapolation of the experimental data to zero pressure (no thermal contact, infinite diffusion rate) gives the expected value $D_a = D_+$. According to Eq. (7), at the lowest pressure for which measurements were made, the average electron energy corresponds to a "temperature" of ~30°K although the gas temperature was 300°K, illustrating the extreme diffusion cooling which can occur in low pressure afterglow studies.[13]

IV. EFFECT OF HELIUM ON DIFFUSION COOLING

In order to demonstrate that the measured values of $D_a < 2D_+$ result from a reduction in the average electron energy rather than from some other effect, small amounts of helium were added to the neon gas. In low-pressure neon afterglows the dominant process is the ambipolar diffusion of electrons and Ne$^+$ ions.[14] The addition of small amounts of helium (~0.1-mm Hg) does not affect the type of ions formed since the ionization potential of helium is four volts higher than that of neon. Also, from Eq. (7) it is clear that the ionic diffusion coefficient, rather than that of the electrons, controls the ambipolar diffusion. Since

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[9] A. V. Phelps *et al.*, Phys. Rev. **84**, 559 (1951).

[10] In the present experiments, the positive ions remain in thermal equilibrium with the gas at all pressures, i.e., $u_+ = u_{\mathrm{gas}}$.

[11] A detailed discussion of the electron density decay equation and its solution is given in M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949).

[12] The values of D_+ were obtained from theory; T. Holstein, J. Phys. Chem. **56**, 832 (1952), and from positive ion mobility measurements, J. Hornbeck, Phys. Rev. **84**, 615 (1951); M. A. Biondi and L. M. Chanin, (to be published).

[13] Under these conditions the electron energy distribution will be strongly non-Maxwellian; therefore, the term "temperature" is very loosely used to emphasize the low average energy of the electrons.

[14] The present measurements were confined to pressures sufficiently low to avoid significant conversion of atomic ions to molecular ions during the measurements. Conversion would have seriously complicated the analysis of the experimental data.

experimental measurements[15] show that a helium atom presents only $\frac{1}{6}$ the momentum transfer cross section to a Ne$^+$ ion that a neon atom does, the added helium has only a slight effect on the ionic diffusion coefficient.[16]

The primary effect of the added helium is on the average electron energy. A helium atom is 29 times more effective in its "thermal contact" with electrons [the factor $(2m/M)\nu_c$ of Eq. (8)] than is a neon atom.[9] Thus, the addition of small amounts of helium to the neon should raise the average electron energy in accordance with Eq. (9) and, consequently, cause D_a to approach the value $2D_+$ as predicted by Eq. (7).

The effect of adding various amounts of helium to a constant pressure of neon is shown in Fig. 2. It will be seen that, as helium is added, the rate of diffusion loss of the electrons *increases*, in agreement with our previous discussion. This behavior is illustrated in greater detail in Fig. 4. Here we plot the ambipolar diffusion coefficient times the neon pressure *versus* the pressure of the added helium for three different neon pressures. The points on the axis are taken from the pure neon data shown in Fig. 3. As helium is added to the 0.78-mm Hg of neon filling (top curve) the value of D_ap increases from its initial value of 137. At approximately 0.09-mm Hg of helium, D_ap reaches the value 180, which is equal to the predicted limit $2D_+p$.[12] The addition of more helium has no further effect on the measured value of the ambipolar diffusion coefficient, since the electrons were brought into thermal equilibrium with the gas at 0.09-mm Hg of helium and remain in thermal equilibrium thereafter. At a lower neon pressure (0.47-mm Hg) the more rapid diffusion loss of electrons makes the cooling more severe; consequently more helium is required to bring the electrons into thermal equilibrium with the gas. At the lowest neon pressure (0.28-mm Hg) the addition of a nearly equal amount of helium is insufficient to compensate completely the cooling, although the electron "temperature" is raised from its initial estimated value of ~30°K to ~210°K by the addition of 0.25-mm Hg of helium.

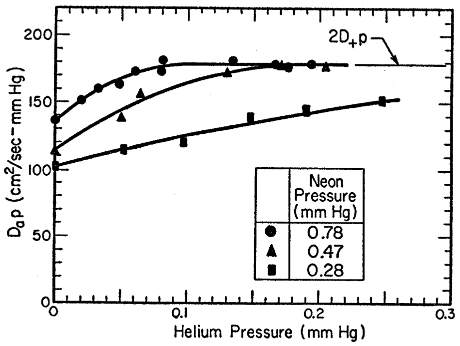

FIG. 4. The effect of helium on the measured ambipolar diffusion of electrons in neon.

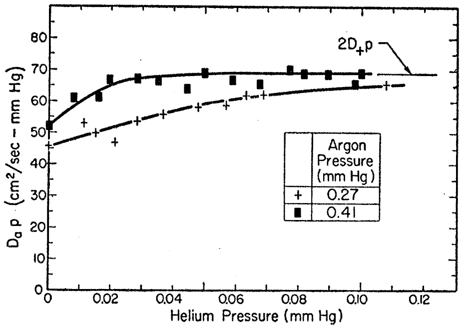

FIG. 5. The effect of helium on the measured ambipolar diffusion of electrons in argon.

Since argon gas also exhibits a small elastic cross section for slow electrons and has a larger mass than neon, we should also expect diffusion cooling of electrons to take place in low-pressure argon afterglows. The measurements obtained with argon are analogous to the neon results; they are summarized in Fig. 5. In pure argon we again find values of $D_a<2D_+$. At 0.41-mm Hg of argon it requires approximately 0.05-mm Hg of helium to bring the electrons into thermal equilibrium with the gas, as indicated by the value $D_a=2D_+$, with the addition of more helium producing no further effect.

V. SUMMARY AND DISCUSSION

The present paper has demonstrated that under special circumstances the average kinetic energy of electrons in an ionized gas may decrease below that of the gas. This effect is attributed to diffusion cooling, a process in which the energy loss by diffusion of the fast electrons to the walls is imperfectly compensated through elastic collisions of the electrons with gas atoms. An elementary theory of the process is developed whose predictions are borne out by experiment. The term "thermal contact" is introduced to describe the rate at which energy is transferred between electrons and gas atoms in elastic recoil collisions. It is shown that helium exhibits good thermal contact, while neon and argon exhibit poor thermal contact with slow electrons. Diffusion cooling effects are experimentally demonstrated in low-pressure neon and argon afterglows. These effects are removed by the addition of small amounts of helium to the neon and argon, which brings the electrons into thermal equilibrium with the gas atoms.

The demonstration of the existence of diffusion cooling effects in afterglow studies serves a twofold purpose. First of all, when care is taken to avoid such effects, the neon and argon ionic diffusion coefficients determined from microwave studies are found to be in good agree-

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[15] See reference 12 and R. J. Munson and A. M. Tyndall, Proc. Roy. Soc. (London) **A172**, 33 (1939).

[16] It may be shown that the resultant diffusion decay time in the mixture, $T_D=1/\nu_d$ [see Eq. (10)], is simply $T_D=T_{\mathrm{Ne}}+T_{\mathrm{He}}$, where T_{Ne} is the diffusion decay time of Ne$^+$ in pure neon at its partial pressure and T_{He} is the value for Ne$^+$ in pure helium at its partial pressure.

ment with the results obtained from mobility studies.[12] Second, the very low electron energies ($u_e \sim 0.004$ ev) attained in these experiments permit studies of the behavior of very slow electrons in gases. For example, the microwave determinations of elastic collision cross sections[9] may be extended to subthermal electron energies. Finally, these studies of diffusion cooling provide information concerning diffusive energy transport which supplements that obtained from measurements of positive column characteristics.[17]

The author wishes to thank W. A. Rogers, who assisted in data-taking, and the various members of the Atomic Physics group, especially T. Holstein, for helpful discussions concerning this work.

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[17] M. J. Druyvesteyn and F. M. Penning, Revs. Modern Phys. 12, 87 (1940); see Fig. 73.

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Variational Formulas in Evaporation Theory*

John Greenstadt
International Business Machines Corporation, New York, New York

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The Laplace transformation is first applied to the linearized one-dimensional Boltzmann equation to enable some remarks on the spectrum of the problem to be made. The original (linearized) equation is then brought into the form of a Fredholm equation, following K. Schwarzschild. A Schwinger variational function is then established for the distribution of molecules returning after being "sprayed" into a gas. Using these results, an integral equation is derived for the probability distribution of molecules at a liquid-vapor interface during slow (steady or time-dependent) evaporation. Finally, this theory is compared with elementary evaporation theory.

1. SCATTERING PROBLEM

In Fig. 1 is shown a volume of gas with a "molecule spray" imbedded in it. This spray injects molecules into the right-hand volume of gas with a variable but slow rate. Given the probability distribution of the molecules injected, the problem is to find the distribution of the molecules returning from the right as a consequence of collision.

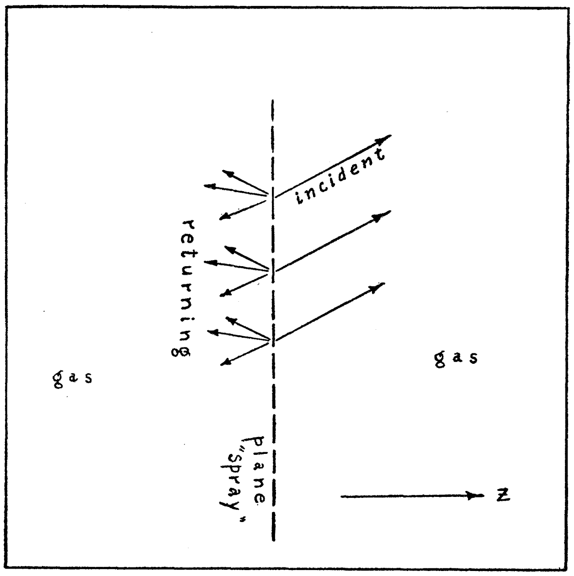

FIG. 1. Diagram of fictitious "spray" with incident and backscattered particles.

2. BOLTZMANN'S EQUATION

The equation for gas transport is Boltzmann's equation:[1]

$$\partial f_1/\partial t + v_{1z}\partial f_1/\partial z = \int \{f_1' f_2' - f_1 f_2\} g_{12} b\,db\,d\epsilon\,d^3\mathbf{v}_2, \quad (2.1)$$

where f is the distribution function (d.f.) for the gas and depends on t, z, v_x, v_y, and v_z. The subscripts refer to the arguments $\mathbf{v}_1$ and $\mathbf{v}_2$ of which f is a function.

We make the following substitutions:

$$\begin{aligned} &z = \Lambda u, \quad t = V_0 \Lambda \tau, \quad \mathbf{v} = V_0 \mathbf{C}, \\ &b = \sigma\beta, \quad g_{12} = V_0 \gamma_{12}, \quad f(z,\mathbf{v},t) = n_0 V_0^{-3} \varphi(u,\mathbf{C},\tau), \end{aligned} \quad (2.2)$$

where

$$\Lambda \equiv (n_0\sigma^2)^{-1}, \quad \mathbf{C} \equiv (\xi,\eta,\zeta), \quad V_0 \equiv (2kT_0/m)^{\frac{1}{2}},$$

and m is the mass of the gas molecules, T_0 the mean temperature, $\pi\sigma^2$ an "effective" collision cross section, n_0 the mean number density, V_0 the rms speed of the molecules, and Λ their mean free path. All the quantities in the resulting equation are then dimensionless:

$$\partial\varphi_1/\partial\tau + \zeta_1 \partial\varphi_1/\partial u = \int \{\varphi_1'\varphi_2' - \varphi_1\varphi_2\} \gamma_{12} \beta\,d\beta\,d\epsilon\,d^3\mathbf{C}_2. \quad (2.3)$$

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* Part of a dissertation presented to the faculty of Yale University in candidacy for the degree of Doctor of Philosophy.

[1] See S. Chapman and T. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, 1939), p. 66.