

## Electron-Temperature Dependence of Electron-Ion Recombination in Argon\*

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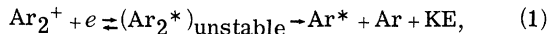
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(Received 22 May 1968)

A 3-mode microwave apparatus is used to study the dependence of the dissociative recombination coefficient  $\alpha(\text{Ar}_2^+)$  on electron temperature  $T_e$  over the range  $300^\circ\text{K} \leq T_e \leq 10\,000^\circ\text{K}$  while the ion and gas temperatures remain at  $300^\circ\text{K}$ . A high- $Q$  cavity mode is used to ionize the gas periodically, a second high- $Q$  mode is used to determine the decay of electron density during the afterglow from the change of resonant frequency of the cavity, and a nonresonant waveguide mode is used to apply a constant microwave heating field to the electrons. At  $T_e = 300^\circ\text{K}$ , a value  $\alpha(\text{Ar}_2^+) = (8.5 \pm 0.8) \times 10^{-7} \text{ cm}^3/\text{sec}$  is obtained from analysis of recombination-controlled electron-density decays using a computer solution of the electron continuity equation which includes recombination and ambipolar diffusion terms. Over the range  $300^\circ\text{K} \leq T_e \leq 10\,000^\circ\text{K}$ , the coefficient  $\alpha(\text{Ar}_2^+)$  is found to follow a simple  $T_e^{-0.67}$  variation. This result is reconciled with Fox and Hobson's  $T^{-1.3}$  variation, obtained under conditions where  $T_e = T_i = T$ , on the basis of their changing  $\text{Ar}_2^+$  vibrational-state populations with changing temperature. Finally, it is noted that our  $T_e^{-0.67}$  variation may be evidence for appreciable electron capture via the *indirect* as well as the direct dissociative process.

### I. INTRODUCTION

It has been established<sup>1</sup> that the very efficient capture of electrons by argon ions is the result of dissociative recombination, i. e.,



where the superscripts \* and + indicate excited and ionized states, respectively. Highly simplified theories<sup>2</sup> of the direct dissociative process indicate that, for a favorable potential curve crossing between the molecular ion and the unstable excited molecule, the two-body recombination coefficient  $\alpha$  varies with electron temperature  $T_e$  as  $T_e^{-1/2}$ , if the initial capture step [left-hand portion of the reaction (1)] is rate limiting, while  $\alpha$  varies as  $T_e^{-3/2}$  if stabilization by dissociation [right-hand portion of the reaction (1)] is rate limiting.

In our earlier studies<sup>3</sup> of dissociative recombination between electrons and  $\text{Ne}_2^+$  ions over the range  $300^\circ\text{K} \leq T_e \leq 11\,000^\circ\text{K}$ , a variation of  $\alpha$  as  $T_e^{-0.43}$  was observed, suggesting that the initial capture step is rate limiting. The present study is an extension of this earlier work to the case of argon in order to provide further insight concerning the electron temperature dependence of the dissociative recombination process inasmuch as, at present, *ab initio* theoretical calculations are not available.<sup>4</sup>

### II. MEASUREMENT TECHNIQUES

The recombination coefficients are determined by measuring the rates of decay of average electron density from an initially ionized gas. The microwave afterglow techniques used in these measurements have been described in detail previously<sup>3</sup>; consequently we shall only outline the method. The three-mode microwave system is shown schematically in Fig. 1. The gas sample<sup>5</sup>

to be ionized is introduced by means of an ultra-high-vacuum gas-handling system into the quartz bottle within the cylindrical microwave structure. Pulses of microwave energy (repeated 10 times/sec) excite either the  $\text{TM}_{010}$  or  $\text{TE}_{111}$  resonant-cavity mode to ionize the gas. The average electron-density values during the afterglow are determined from measurements of the change of resonant frequency of the  $\text{TM}_{010}$  cavity mode by means of a very low energy probing signal. The electrons are heated above the ambient gas temperature by means of constant microwave heating fields propagated in a nonresonant  $\text{TE}_{11}$  circular-waveguide mode.

The "microwave-averaged" electron density  $\bar{n}_{\mu w}(t)$  defined by

$$\bar{n}_{\mu w}(t) = \Delta f_0(t)/C \equiv \frac{\int_{\text{cav.}} n_e(\vec{r}, t) E^2(\vec{r}) dv}{\int_{\text{cav.}} E^2(\vec{r}) dv}, \quad (2)$$

is determined from the measured frequency shifts  $\Delta f_0(t)$ . The quantity  $C$  represents a group of measurable quantities and physical constants,

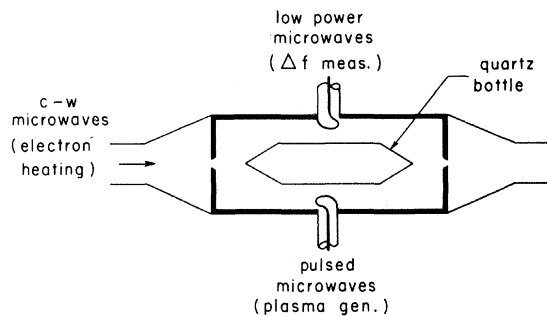


FIG. 1. Highly simplified diagram of microwave afterglow apparatus employing microwave electron heating.

$n_e(\vec{r}, t)$  is the electron density,  $\vec{E}(\vec{r})$  is the amplitude of the microwave-probing field, and the integrations are carried out over the cavity volume. The electron temperatures are calculated from the measured values of the microwave-heating field using the method discussed previously,<sup>3</sup> which is based on Margenau's distribution-function calculations.<sup>6</sup>

In the present afterglow studies in argon, experimental conditions are arranged so that  $\text{Ar}_2^+$  should be the dominant positive ion present and no negative ions are expected; thus the quasineutrality of a plasma permits us to set  $n_+ \approx n_e$ , and the electron-continuity equation reduces to

$$\partial n_e / \partial t \approx -\alpha n_e^2 + D_a \nabla^2 n_e, \quad (3)$$

where, in the absence of afterglow ionization processes, the loss processes of two-body recombination and ambipolar diffusion (coefficient  $D_a$ ) account for the rates of change of electron concentration.

It has been shown<sup>7</sup> that, when recombination loss greatly outweighs ambipolar diffusion, the solution of Eq. (3) indicates that  $1/\bar{n}_{\mu w}$  increases approximately linearly with time; therefore we display our measurements as graphs of  $1/\bar{n}_{\mu w}$  versus  $t$ . In order to obtain accurate values of the recombination coefficient,  $\alpha$ , Eq. (3) has been solved numerically<sup>8</sup> to obtain values of  $n_e(\vec{r}, t)$  using the known value of  $T_e$  and a value  $D_a p = 76.6 \text{ cm}^2/\text{sec Torr}$  at  $300^\circ\text{K}$  and treating  $\alpha$  as a parameter. It is interesting to note that the best-fit computer solution of Eq. (3) also permits a good selection of the appropriate  $D_a$  value, since this value is in good agreement with the one obtained from mobility measurements of  $\text{Ar}_2^+$  in Ar.<sup>9</sup> The computed values of  $n_e(\vec{r}, t)$  are used to generate curves of  $1/\bar{n}_{\mu w}(t)$  versus afterglow time for various values of  $\alpha$  and of the initial density  $1/\bar{n}_{\mu w}(0)$ . These curves are compared with the measured values of  $1/\bar{n}_{\mu w}(t)$  in order to determine the value of  $\alpha$  at each electron temperature.

### III. RESULTS

The computed curves which best fit the experimental data at several electron temperatures are shown in Fig. 2. The gas temperature is  $300^\circ\text{K}$  and the argon pressure is 20 Torr. As predicted, at the lower electron temperatures, the experimental values of  $1/\bar{n}_{\mu w}$  at first increase linearly with time and then, as a result of the increasing importance of diffusion, increase more rapidly. At the higher electron temperatures the linear region is diminished, but in all cases, the computer solutions of Eq. (3) provide a satisfactory fit to the data. The deviations at late times for the  $T_e = 3000^\circ\text{K}$  curve can be explained in terms of the effect on the value of  $D_a$  of the  $\pm 10\%$  uncertainty in  $T_e$ .

The values of  $\alpha(\text{Ar}_2^+)$  deduced from the pure-argon data of the type shown in Fig. 2 are shown as a function of  $T_e$  by the solid circles in Fig. 3, which is plotted on a log-log scale. Representative estimates of the errors in the determinations of the values of  $T_e$  and of  $\alpha$  are shown by crosses on two of the data points. In order to provide an additional check on the calculated

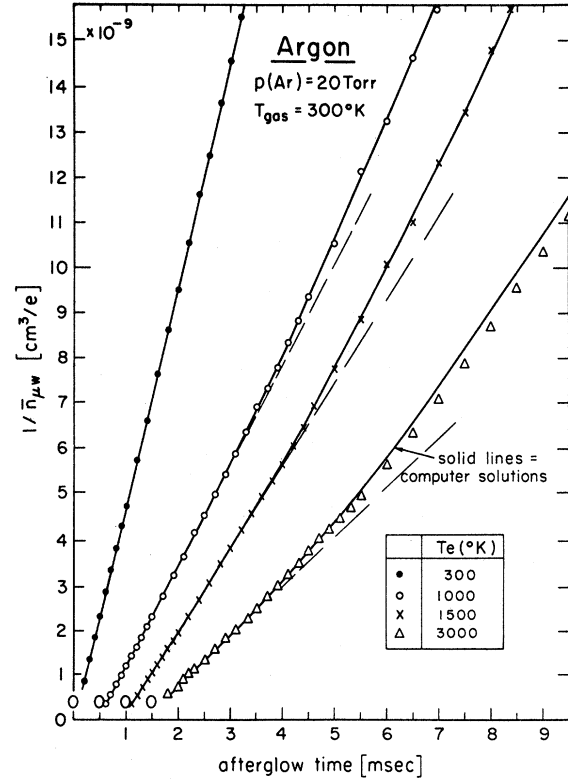


FIG. 2. Variation of  $1/\bar{n}_{\mu w}$  with afterglow time ("recombination plot") for several electron temperatures. The points represent the experimental data, the solid lines the "best-fit" computer solutions of the recombination-diffusion equation.

electron temperature scale, various argon-neon mixtures have also been used, as indicated by the open triangles, open circles, and crosses. In all cases, a sufficient argon pressure ( $\geq 5$  Torr) has

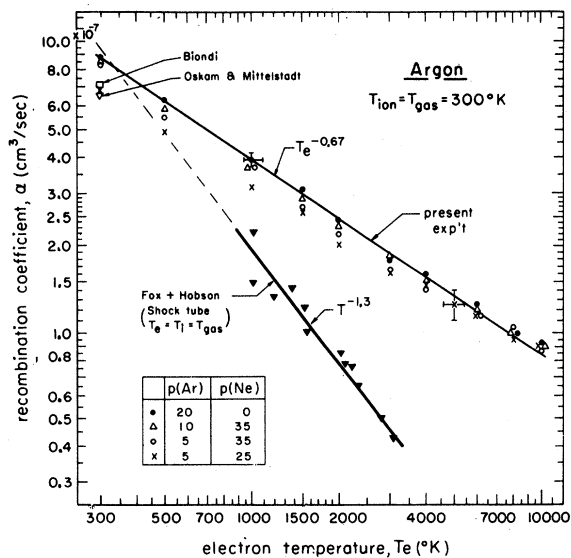


FIG. 3. Comparison of the various measurements of the recombination coefficient  $\alpha(\text{Ar}_2^+)$  and its dependence on electron temperature.

been used to assure that  $\text{Ar}_2^+$  should be the dominant positive ion. The energy-distribution calculations<sup>6</sup> of the  $T_e$  values involve consideration of the relative collision rates of electrons with neon and with argon atoms, while the  $D_a$  values used in the computer solutions of Eq. (3) involve use of Blanc's law<sup>10</sup> to determine the diffusion of  $\text{Ar}_2^+$  ions in neon-argon mixtures.<sup>11</sup>

Good agreement among the  $\alpha(\text{Ar}_2^+)$  values over the range  $300^\circ\text{K} \leq T_e \leq 10\,000^\circ\text{K}$  is obtained for the pure-argon data and for the argon-neon mixtures involving 35 Torr of neon. However, the data obtained using the 5-Torr argon - 25-Torr neon mixture are approximately 25% lower than the other data at  $300^\circ\text{K}$ , the difference becoming progressively smaller and falling within the estimated experimental error above  $\sim 1500^\circ\text{K}$ . We have no explanation for this discrepancy at low electron temperatures.

It will be seen that a simple power-law temperature dependence,  $\alpha \sim T_e^{-0.67}$ , fits the pure-argon data rather well (and the data for mixtures containing 35-Torr neon satisfactorily), starting at a value of  $8.8 \times 10^{-7}$  cm<sup>3</sup>/sec at  $T_e = 300^\circ\text{K}$  and decreasing to a value of  $8.5 \times 10^{-8}$  cm<sup>3</sup>/sec at  $T_e = 10\,000^\circ\text{K}$ . Also shown in Fig. 3 are afterglow data obtained by other investigators at  $300^\circ\text{K}$  and some recent shock-tube measurements obtained under conditions such that  $T_e = T_{\text{ion}} = T_{\text{gas}}$  over the range  $1000\text{--}3000^\circ\text{K}$ . A discussion of the various results is given in the next section.

#### IV. DISCUSSION AND CONCLUSIONS

The present experiment yields a value  $\alpha(\text{Ar}_2^+) = (8.5 \pm 0.8) \times 10^{-7}$  cm<sup>3</sup>/sec at  $300^\circ\text{K}$ , which is in reasonable agreement with the results of measurements by Biondi<sup>12</sup> ( $\sim 7 \times 10^{-7}$  cm<sup>3</sup>/sec) and by Oskam and Mittelstadt<sup>13</sup> ( $6.7 \pm 0.5 \times 10^{-7}$  cm<sup>3</sup>/sec). Early studies of argon,<sup>14</sup> using gas samples of lower purity, gave substantially smaller recombination coefficients ( $\sim 3 \times 10^{-7}$  cm<sup>3</sup>/sec) which may have applied to  $\text{N}_2^+$  ions,<sup>7</sup> since nitrogen was believed to be the principal impurity in these samples.

The major source of error in the present experiment (approximately  $\pm 5\%$ ) arises from the range of  $\alpha$  values in the computer solution of Eq. (3) which provide reasonable fits to the experimental data. Other sources of error, in such experimental determinations as frequency shift and afterglow time, are smaller, so that we assign an over-all error of  $\pm 10\%$  to our results. The earlier experiments<sup>12-13</sup> have assigned comparable error limits; therefore all the results are in agreement, within their probable error limits.

Very recently Fox and Hobson<sup>15</sup> have studied recombination in argon over a wide temperature range, using shock-tube and electrostatic double-probe techniques. In these studies, it is assumed that the kinetic temperatures of the electrons, ions, and gas atoms are all equal. It will be seen from Fig. 3 that their results disagree with the present experiment both as to the magnitude of the recombination coefficient and its dependence on temperature, although a rather extensive (and

therefore uncertain) extrapolation of their measurements to  $300^\circ\text{K}$  yields a value of  $\alpha$  which is in good agreement with the present room-temperature value.

There is a rather straightforward explanation of the apparent discrepancy between the two sets of measurements, which we can only present qualitatively, inasmuch as certain key pieces of information concerning the  $\text{Ar}_2^+$  ion and the unstable molecule state of the reaction (1) are not available. In the present experiment  $T_{\text{ion}}$  remains at  $300^\circ\text{K}$  as  $T_e$  varies, while in Fox and Hobson's work  $T_{\text{ion}}$  and  $T_e$  vary together. The attendant effects on the dissociative recombination process can be understood with the aid of the highly simplified potential diagram of Fig. 4, which shows a single stable potential curve of the  $\text{Ar}_2^+$  ion and a single repulsive branch of the unstable excited molecule, which is assumed to cross the ion curve at its minimum. (The curves shown are hypothetical; e.g., neither the binding energy nor the vibrational spacing of the ion is known.)

In the direct dissociative process the initial electron-capture step [left-hand member of Eq. (1)] depends on the overlap between the  $\text{Ar}_2^+$  ion state and the unstable molecule state. This overlap depends on the vibrational state of the  $\text{Ar}_2^+$  ion and for the case shown probably decreases<sup>16</sup> with increasing vibrational quantum number  $v$ . In addition, the fraction of unstable molecules which

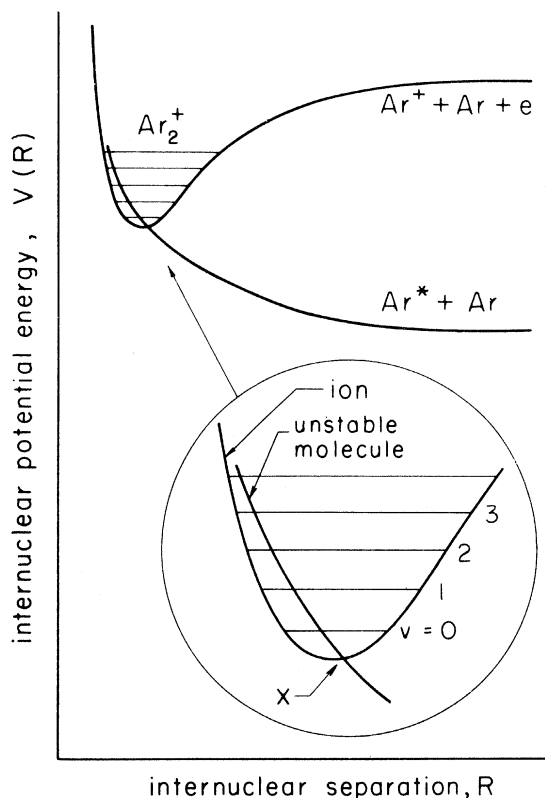


FIG. 4. Hypothetical potential-energy curves involved in the direct dissociative recombination process showing a single stable  $\text{Ar}_2^+$  ion curve and a single branch of the unstable excited  $\text{Ar}_2^*$  molecule. Inset: enlarged view of the curve-crossing region.

dissociate before autoionization occurs also decreases with increasing  $v$ , as a result of the increase in the time required<sup>17</sup> to reach the stabilization point  $X$  (see inset of Fig. 4). Thus, if as  $T_{\text{ion}}$  increases in the shock-tube experiments the vibrational temperature follows, the electron-capture rate decreases, even if  $T_e$  is held constant. From this, one can use our experimental results to make plausible both the stronger temperature dependence observed by Fox and Hobson and the reasonable agreement at 300°K between our experiment and the extrapolation of their results.

Our measured variation of  $\alpha(\text{Ar}_2^+)$  with  $T_e$  probably applies to ions in the  $v=0$  state (since  $T_{\text{ion}} = 300^\circ\text{K}$ ). Our results are indicated by the medium-weight solid line in Fig. 5. If now all the  $\text{Ar}_2^+$  ions were in the  $v=1$  state, a similar variation with  $T_e$  would be expected, but with smaller  $\alpha$  values at each point. Thus, if one were to plot  $\alpha$  versus  $T_e$  for fixed values of  $T_{\text{ion}}$ , a series of curves such as shown by the dashed lines in Fig. 5 might be obtained. (As the ion temperature is increased, successively higher vibrational levels become substantially populated, and by our previous arguments, the  $\alpha$  values decrease.) The results obtained by Fox and Hobson are then represented by those points on the graph, where  $T_e = T_{\text{ion}}$  (circles). In addition, our data at  $T_e = 300^\circ\text{K}$  and the extrapolation of Fox and Hobson's results to 300°K would be expected to agree, since in this case our data also apply to the situation where  $T_e = T_{\text{ion}}$ .

From Fig. 3, it will be seen that our values of  $\alpha(\text{Ar}_2^+)$  vary as  $T_e^{-2/3}$ , which is somewhat more rapid than the  $T_e^{-1/2}$  variation predicted when the initial capture step is rate limiting in the direct dissociative recombination process (refer to the discussion in the Introduction). Fox and Hobson's result that  $\alpha$  varies as  $T^{-1.3}$  should not be taken as an indication that dissociation is the rate-limiting step in the reaction (1), since the theoretical predictions<sup>2</sup> consider only the effect of the *electron* energy on the reaction rate. Thus, in the two cases where  $T_e$  alone has been varied, the experimental results for  $\text{Ne}_2^+$  ( $\alpha \sim T_e^{-0.43}$ ) and for  $\text{Ar}_2^+$  ( $\alpha \sim T_e^{-0.67}$ ) indicate the inadequacies of the present simplified theories of the energy dependence of the recombination.<sup>2</sup>

Recently several theoretical calculations of dissociative recombination rates have appeared<sup>4, 17-18</sup> which represent interesting blends of *ab initio* calculation elements, use of spectroscopic information, and application of simplifying assumptions in order to obtain estimates of the recombination coefficients at 300°K. Of these, probably the most interesting for our purposes are the calculation of Bardsley,<sup>17</sup> who discusses quite clearly not only the direct dissociative process of the

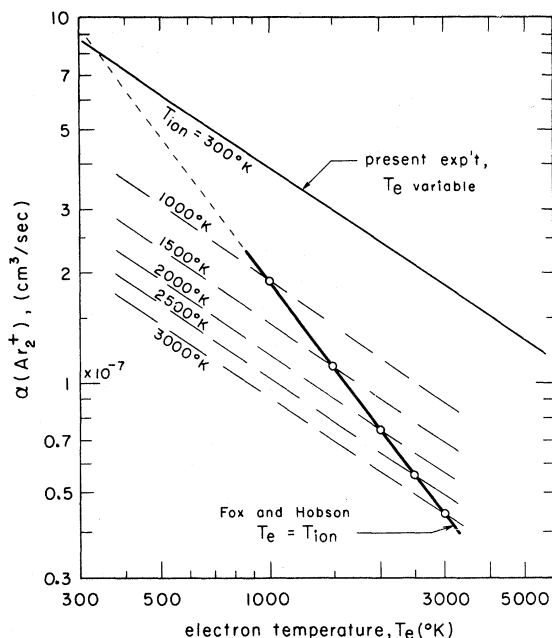


FIG. 5. Effect on  $\alpha(\text{Ar}_2^+)$  of varying  $T_e$  while holding  $T_{\text{ion}}$  constant (medium-weight solid line and long dashed lines) and of varying  $T_e$  and  $T_{\text{ion}}$  together (heavy solid line).

reaction (1) but also the possible effect of an indirect dissociative process.

Referring to Fig. 4, directly below the molecular-ion state there may be stable, Rydberg states of the excited molecule  $\text{Ar}_2^*$  (not shown). In the indirect process, the initial capture step involves a "resonant" capture of the electron into a vibrationally (or rotationally) excited state of  $\text{Ar}_2^*$ , which coincides in energy with the  $\text{Ar}_2^+ + e$  state. This state then quickly predissociates into the  $(\text{Ar}_2^*)$  unstable state shown in Fig. 4, and the remainder of the reaction proceeds as in the direct process.

The interesting features of the indirect process are that it may contribute significantly to the total dissociative capture rate and that it may exhibit quite a different electron temperature dependence from that of the direct process; for example, Bardsley estimates that variations up to  $T_e^{-1.5}$  are possible. Thus our observed variation of  $\alpha(\text{Ar}_2^+)$  as  $T_e^{-0.67}$  may indicate the importance of both the direct and indirect processes in determining the over-all recombination rate.

#### V. ACKNOWLEDGMENT

The authors wish to thank L. Frommhold for his many contributions to the development of the microwave apparatus used in these studies.

\*This research was supported, in part, by the Defense Atomic Support Agency and the U. S. Army Research Office (Durham), under Contract No. DA-ARO-D-124-

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<sup>3</sup>L. Frommhold, M. A. Biondi, and F. J. Mehr, *Phys. Rev.* **165**, 44 (1968).

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<sup>5</sup>The gas samples used in these studies are Airco reagent grade, contained in 1-liter glass flasks. The only significant impurities in the argon are nitrogen (< 3 ppm) and helium (< 5 ppm), while in the neon they are nitrogen (< 5 ppm) and helium (< 25 ppm). These impurities should not contribute to the afterglow ion composition (presumed to be  $Ar_2^+$ ), since Penning ionization by argon metastables is not energetically possible, and charge transfer is too slow.

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<sup>11</sup>In order to use Blanc's Law to estimate  $D_{\alpha}p$  in the neon-argon mixtures it was necessary to know the mobility of  $Ar_2^+$  ions in neon. This value was estimated from Fig. 6 of L. M. Chanin and M. A. Biondi, *Phys. Rev.* **107**, 1219 (1957).

<sup>12</sup>M. A. Biondi, *Phys. Rev.* **129**, 1181 (1963).

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<sup>14</sup>M. A. Biondi and S. C. Brown, *Phys. Rev.* **76**, 1697 (1949).

<sup>15</sup>J. N. Fox and R. M. Hobson, *Phys. Rev. Letters* **17**, 161 (1966), and in Contributed Papers of the Eighth International Conference on Phenomena in Ionized Gases, Vienna (International Atomic Energy Commission, Vienna, 1968), p. 5 *ff.*

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## Radial Distribution Function for a Quantum Plasma

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(Received 30 July 1968)

The radial distribution function for a plasma is calculated for small interparticle separations. Quantum effects are taken into account by using either a modification of the path-integral technique or the equivalent sum-over-states expression under the assumption that the charged particles interact via a shielded Coulomb potential.

### 1. INTRODUCTION

The problem of finding the radial distribution function (r.d.f.) for a plasma is beset with many difficulties. For example, a purely classical calculation results in essential singularities for small interparticle separations, the long-ranged interactions are shielded by many-body effects, and at low enough temperatures, the radial distribution function of two electrons is affected drastically if one of the electrons is in a bound state with a proton. The latter situation obviously involves the solution of at least a three-body problem, and we will not consider that problem here. However, we will make some progress towards the solution of the first two difficulties mentioned. We consider a gaseous hydrogen plasma at temperatures high enough for the hydrogen molecules to be dissociat-

ed, say above  $10^4$  °K, and study the radial distribution function of only those sets of two particles which are not bound to other particles in the plasma. We are not, however, excluding the possibility that they may be bound to each other.

Quantum effects for fully ionized plasma have been studied previously by several authors,<sup>1-3</sup> mainly with a view to obtaining corrections which would be valid in the high temperature region. Recently Matsuda<sup>4</sup> has also obtained approximations to the sum-over-states expressions which are valid over a wider temperature range. In this paper we take account of the classical many-body effects by making the assumption that the interaction between two charged particles in a plasma can be described by a screened Coulomb potential,

$$V(r) = \pm e^2 \exp(-r/\lambda_D)/r.$$