Comments

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Comment on "Comparative calculations of electron-swarm properties in N_2 at moderate E/N values"

G. L. Braglia and L. Romanò
Istituto di Fisica, Gruppo Nazionale di Elettronica Quantistica e Plasmi, Consiglio Nazionale delle Ricerche, Università degli Studi di Parma, I-43100 Parma, Italy
M. Diligenti
Istituto di Matematica, Università degli Studi di Parma, I-43100 Parma, Italy
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The recent paper by Pitchford and Phelps raises a number of questions concerning the electron velocity distribution and transport and rate coefficients in (molecular) gases. In this paper we will present some of our related Monte Carlo simulation results as a contribution to the solution of the open problems.

The recent paper by Pitchford and Phelps[1] (hereafter referred to as I) on the applicability of the multiterm technique developed by Pitchford, ONeil, and Rumble[2] to the calculation of energy distribution and transport and excitation coefficients for electrons in N_2, raises a number of questions. On the basis of some of our results, part of which we obtained during some other researches before reading the manuscript of Paper I,[3–5] we believe we have data that provides the correct answers to most of these problems. Almost all our results reported below have been obtained using the Monte Carlo (MC) technique we described in a recent paper,[5] which not only permits very accurate calculations of transport and rate coefficients but also of the electron velocity distribution $F(\vec{v})$. This is due to the extremely large number of events (i.e., some 10^7) one can distribute which allow an accurate calculation of $F(\vec{v})$ and, as a consequence, of the (first) coefficients of its Legendre expansion $\sum_l f_l(\epsilon)P_l(\cos\theta)$. However, in some cases, where a significant discrepancy was observed between our results and those of Paper I, we also had recourse to a completely different Monte Carlo technique,[4] for the sake of comparison. This happened, in particular, for the diffusion coefficient D_L parallel to the electric field.[5]

The first question concerns the behavior of the electron energy distribution $f(\epsilon)=f_0(\epsilon)$ in the limit as the electron energy $\epsilon=\frac{1}{2}mv^2$ tends to zero. A substantial discrepancy has been observed in Paper I between the behavior of $f(\epsilon)$ in N_2 as obtained by the multiterm solution of the Boltzmann equation[2] and by the MC technique. This discrepancy not only has been observed[1] in N_2 but also[2] in CH_4 and in a so-called "ramp model," which was suggested and used by Reid to determine the conditions under which the two-term approximation leads to significant errors in the calculation of transport coefficients.[6] The model gas has an atomic mass 4, elastic cross section $Q_e=6$ Å^2, and an inelastic cross section $Q_x=10(\epsilon-0.2)$ for $\epsilon\geq 0.2$ eV ($Q_x=0$ for $\epsilon<0.2$), with an associated energy loss of 0.2 eV. It is now known[7] that, in this case at least, and by inference in the other cases as well, the discrepancy is due to an error in the MC code used in Paper I which was developed and used by Reid. However, in Paper I it is observed that a depletion of the $f(\epsilon)$'s at the origin, with respect to the corresponding energy distributions obtained by solving Boltzmann's equation, seems to be present in almost all the MC distributions available in the literature. As these simulations have all been done in different gases with quite different codes, it is important to indicate the exact limits of the agreement between MC and theory in a number of different cases. It is for this reason we have decided to include here the results of our comparisons between energy distributions obtained with our MC codes and corresponding distributions calculated by the multiterm technique.[1,2] The results are reported in Figs. 1–4. They have been generally obtained using the equation

$$f_l\left(\epsilon+\frac{\Delta}{2}\right)=\frac{2l+1}{2}\frac{1}{\Delta\sqrt{\epsilon+\Delta/2}}\int_{\epsilon}^{\epsilon+\Delta}\epsilon^{1/2}\,d\epsilon\int_0^{\pi}P_l(\cos\theta)f(\epsilon,\theta)\sin\theta\,d\theta\ ,$$

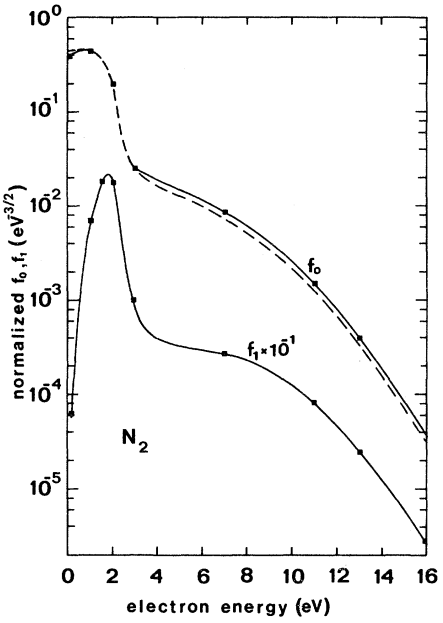

FIG. 1. Comparison of the first two normalized Legendre coefficients $f(\epsilon) = f_0(\epsilon)$ and $f_1(\epsilon)$ calculated using the Monte Carlo technique of Ref. 5 (solid curves), the conventional solution of the Boltzmann equation (dashed curves), and the six-term expansion solution to the Boltzmann equation (solid squares). The gas is N_2 at $E/N = 100 \times 10^{-21}$ V m^2.

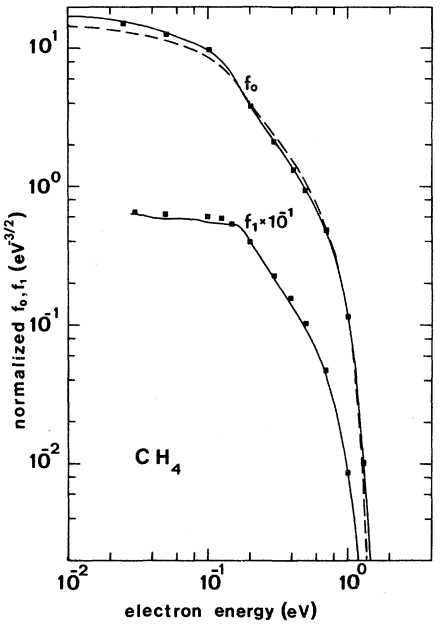

FIG. 3. Same quantities as in Fig. 1 but for CH_4 at $E/N = 2.42 \times 10^{-21}$ V m^2. The six-term data are from Ref. 2.

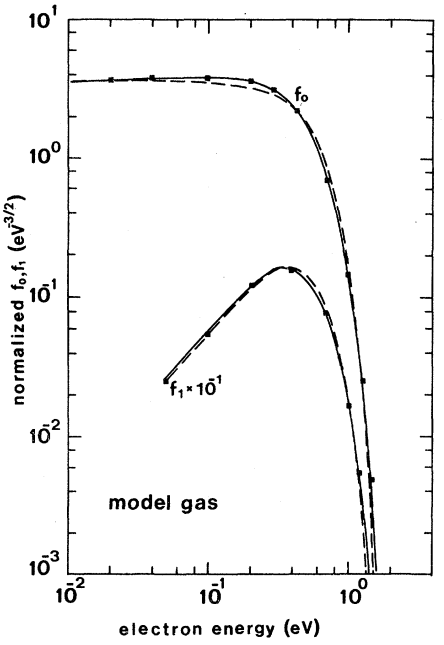

FIG. 2. Same quantities as in Fig. 1 but for the ramp-model gas at $E/N = 24 \times 10^{-21}$ V m^2. The six-term data are from Ref. 2.

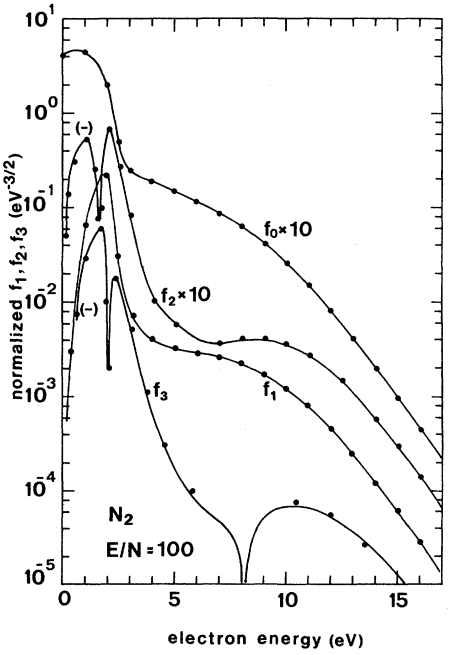

FIG. 4. Comparison between MC (points) and Boltzmann (solid curves) calculations of the Legendre expansion coefficients f_0, f_1, f_2, and f_3 in N_2 at $E/N = 100 \times 10^{-21}$ V m^2.

apart from the $f_1(\epsilon)$'s of Figs. 1–3 which have been calculated by the technique of Friedland.[8]

As one can see, we consider three gases, i.e., N_2, CH_4 and ramp model. In all cases the agreement between MC and theory is found to be so impressive that there are no doubts on the validity of the distributions of Pitchford and collaborators.[1,2] Only a slight discrepancy seems to be seen between the first Legendre expansion coefficients $f_1(\epsilon)$ in CH_4 which, however, does not seem to influence the calculation of the drift velocity, as we shall see below. This difference can also be due, at least in part, to a major difficulty to represent correctly $f_1(\epsilon)$ at low energy by the MC technique. Our results for $f(\epsilon)$ for the ramp model at $E/N = 24 \times 10^{-21}$ V m^2 are found to agree with corresponding MC results independently and simultaneously obtained by Skullerud[9] and Bardsley,[10] and with more recent results from Reid's code after the removal of the error referred to above.[7] On the contrary, no comparison has been possible between our results for $f_1(\epsilon)$ and corresponding MC results of other authors since calculations of $f_1(\epsilon)$ with the same accuracy of the curves reported in Figs. 1–4 have never been done before.

The second problem raised by Paper I concerns the small but significant (at least at $E/N = 100 \times 10^{-21}$ V m^2) disagreement between MC and six-term results for D_T in N_2. This more or less pronounced discrepancy can be seen in all the comparisons presented by Pitchfords and collaborators[1,2,11]; and in Paper I it is explicitly written that "this difference in the transverse diffusion coefficients calculated by the two techniques is not understood." On the basis of what we have said above it seems evident that the discrepancy is due to the error in Reid's code which was used by these authors. This conclusion is strengthened by the good agreement that Reid now finds, using his corrected code, with our results for his model gas. In this context it is worth noting that Reid's original results for $\langle\epsilon\rangle$ and W were generally not subject to significant error, and that his values of ND_T were subject to significant error (i.e., greater than the 2% statistical uncertainty stated by him) only when there were large differences between the MC results and those from the two-term Boltzmann code. [For example, with the ramp model at $E/N = 24 \times 10^{-21}$ V m^2, the error was 6% whereas the two-term and MC results differ by about 25%.] Nevertheless, it is important to assess the correctness of the multiterm calculations for transport and rate coefficients with our MC codes, particularly for the complex and realistic situations considered in Ref. 1. To this end, in Table I we report the results of our comparisons in N_2 and ramp-model gas. Data for CH_4 can be found in Ref. 4. As one can see, we do not observe any discrepancy between multiterm theory and MC in the model gas. The discrepancy between MC and theoretical values of ND_T is lower than 1% in the worst case which, for the model gas at $E/N = 24 \times 10^{-21}$ V m^2, agrees with the mentioned results of Skullerud[9] and Bardsley.[10] (It must be noted that with our code we obtain D_T with four different defin-

TABLE I. Comparison of Boltzmann (six-term) (Refs. 1 and 2) and Monte Carlo [Reid (Refs. 1 and 2) and present work (p.w.)] calculations of electron transport and rate coefficients for N_2 and the ramp-model gas, at different values of E/N. For N_2, the results of the conventional backward-prolungation (BACKPR) technique are also reported. The errors influencing our MC results are estimated to be of the orders of 0.5% for W and 1% for the diffusion coefficients.

Gas	E/N 10^{-21} V m^2	Technique	W 10^4m sec^{-1}	ND_T 10^{24}m^{-1} sec^{-1}	ND_L 10^{24}m^{-1} sec^{-1}	$\bar{\epsilon}$ eV	$\frac{\alpha}{N}(v=0\rightarrow 1)$ 10^{-20}m^2	$\frac{\alpha}{N}(A\,^3\Sigma)$ 10^{-22} m^2
Ramp model	1	six term	1.272	0.975		0.1015		
		MC Reid	1.255	0.986		0.1013		
		MC p.w.	1.272	0.975		0.1014		
	12	six term	6.84	1.134				
		MC Reid	6.87	1.168				
		MC p.w.	6.84	1.136		0.269		
	24	six term	8.88	1.132		0.408		
		MC Reid	8.89	1.194		0.413		
		MC p.w.	8.88	1.134		0.408		
N_2	40	BACKPR	5.62	1.741	0.667		3.06	
		six term	5.56	1.614	1.094		3.14	
		MC Reid	5.42	1.604				
		MC p.w.	5.52	1.66	0.67	1.09	3.1	
	100	BACKPR	11.24	2.09	1.088		3.12	6.29
		six term	10.95	1.941	1.383		3.12	7.68
		MC Reid	10.90	2.01			3.09	7.67
		MC p.w.	10.9	1.947	1.18	2.1	3.11	7.66

itions including that adopted in the MC code used in Paper I.) In N_2 the agreement is perfect at $E/N = 100 \times 10^{-21}$ V m^2. Only at $E/N = 40 \times 10^{-21}$ V m^2 a discrepancy is systematically found of the order of 2–3% which is greater than the 1% statistical uncertainty we expect to influence our results for D_T.

The third problem we are almost forced to mention is stimulated by the same results of Table I and concerns the calculation of the diffusion coefficient D_L parallel to the electric field. Pitchford and Phelps[1] have found that a large discrepancy exists between the values of D_L in N_2 as obtained by the six-term and conventional two-term solution of the Boltzmann equation. On the basis of the results reported in Paper I, the conventional values of D_L in N_2 are in error of about 39%, 48%, 21%, and −9.5% at $E/N = 40$, 70, 100, and 200×10^{-21} V m^2, respectively. However, it is emphasized that the six-term values of ND_L are "very sensitive to the choice of the energy grid, the details of the integration procedure, etc." Since Paper I does not present a comparison with MC results for D_L we have considered it useful to extend our calculations and obtain this quantity. Surprisingly enough, as reported in Table I, our results do not agree with those of Paper I. The disagreement with the conventional data is much less pronounced than indicated by the six-term solution. In fact, errors of about the same order seem to influence the conventional diffusion coefficients D_T and D_L. Really, at least for the values of E/N considered here, D_L seems even better calculated than D_T when using the conventional two-term theory. As clearly shown by the results of Figs. 5 and 6 relative to N_2 at $E/N = 40 \times 10^{-21}$ V m^2, we have tried in different ways to find if this discrepancy between MC and six-term values of D_L could be due to imperfections of our MC codes. To this end, we have used both the (quite different) codes mentioned above.[4,5] However, in any case, we always have found the data reported in Table I to be confirmed. In virture of the proved correctness of our calculations of D_L also in a number of other gases,[3–5,12] this discrepancy does not seem to be due to errors in our codes and remains for us unexplained.[13]

The fourth question which is mentioned in Paper I concerns the angular distributions of the electrons in the velocity space. In fact, it is indicated that, in contrast with the multiterm theory, the MC angular distributions are found to present a disturbing minimum at 90°, an effect which also was observed by Sakai[14] and co-workers some years before. The problem is to see if this minimum is real or not. To this end, having recourse to the electron velocities just before each (real and null) collision,[5] we have been able to obtain very accurate angular distributions. The results for N_2 at $E/N = 40$ and 100×10^{-21} V m^2 are reported in Fig. 7. In both cases, we have obtained two distinct angular distributions, one relative to low-energy electrons (i.e., with $\epsilon < 0.2$ eV) and one integrated over all values of ϵ. As one can see, we do not observe minima near 90°. Since this same conclusion was reached in several other cases, we believe that MC angular distributions leading to a different conclusion are in error. So, we share the opinion of Sakai and co-workers[14] that the depression they observe in the velocity distribution when $\theta > \pi/2$ is probably due to their method of tracing electron motions which gives "a smaller chance of sampling electrons with θ a little larger than $\pi/2$."

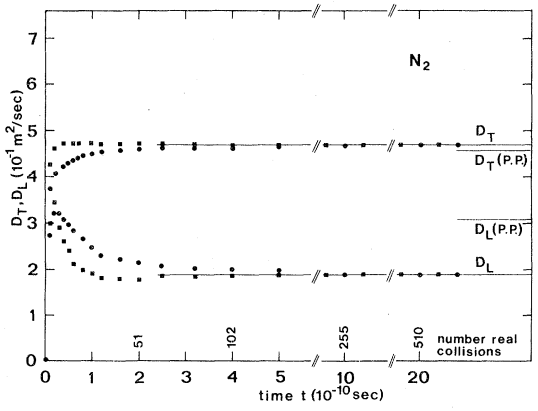

FIG. 5. Temporal behaviors of the correlation functions $\tilde{D}_T(t) = \langle \vec{v}^*(0) \cdot \vec{r}^*(t) \rangle$ (points) and $\tilde{D}_L(t) = \langle \vec{r}^*(t) \cdot \vec{r}^*(t) \rangle / 2t$ (squares) used to obtain $D_T = \tilde{D}_T(t \to \infty)$ and $D_L = \tilde{D}_L(t \to \infty)$ in N_2 at 100 Torr 0 °C and $E/N = 40 \times 10^{-21}$ V m^2. Here $\vec{v}^*(t) = \vec{v}(t) - \vec{W}$ and $\vec{r}^*(t) = \int_0^t \vec{v}^*(t')\,dt'$. Values quoted as P.P. are from Ref. 1.

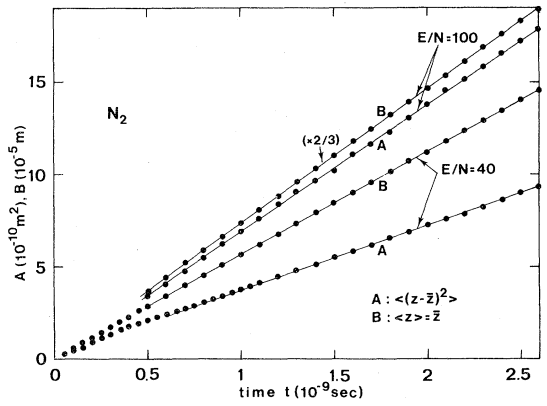

FIG. 6. Temporal behaviors of $\langle z \rangle \equiv \bar{z}$ and $\langle (z - \bar{z})^2 \rangle$ in N_2 at 100 Torr 0 °C and $E/N = 40$ and 100×10^{-21} V m^2. The reported asymptotic linear behaviors of $\langle (z - \bar{z})^2 \rangle$ and $\langle z \rangle$ perfectly agree with the results of Table I and Fig. 5, according to the definitions $2D_L = d\langle (z - \bar{z})^2 \rangle / dt$ and $W = d\langle z \rangle / dt$. The MC points have been obtained with a swarm of 3250 electrons released at $t = 0$ from the origin with steady-state mean energy and isotropic Maxwellian energy distribution.

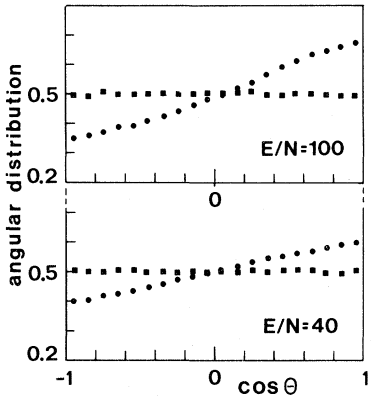

FIG. 7. Normalized angular electron distributions in N_2 at $E/N = 40$ and 100×10^{-21} V m^2. The solid circles report the angular distributions integrated over all values of ϵ while the solid squares refer to electrons with $\epsilon < 0.2$ eV, only. The observed isotropy at low energy agrees with the corresponding very low values of $f_1(\epsilon)$ reported in Fig. 1.

The last question we intend to mention concerns the observation reported in footnote 28 of Paper I, that is, "our result that for N_2 the MC calculation yields higher rates of electronic excitation than does the two-term calculation is the opposite of that found for" CO_2:N_2:He:CO in Ref. 14. In this context, we must note that some time ago we found that this first simulation[15] in laser mixtures could be improved. In fact, further results were obtained more recently.[3(c)] However, in this latter paper which was mainly concerned with pure (molecular) gases, the excitation rates were not considered. Then the problem remains to be seen if the slightly lower rates in laser mixtures mentioned above are real (i.e., due to the fact that they were obtained in a gas other than pure N_2) or if they have to be ascribed to the accuracy of MC simulations. To this end, the simulation of Ref. 15 in CO_2:N_2:He:CO (6:34:54:6) at $E/N = 50 \times 10^{-21}$ V m^2 has been repeated. Because of the difficulty we found in the past to obtain converged macroscopic parameters for mixtures, the simulation has been repeated with an improved and faster code, i.e., with an increased number of collisions ($> 10^7$), also in the attempt to reduce the observed (unexpected) difference of the order of 2–3% between conventional and MC values of the drift velocity we still observed in the simulation of Ref. 3(c). The new rates we have obtained are compared with those provided by the conventional theory in Table II. As one can see, the MC rates really are closer to the expectations, at least on the basis of the comparisons reported in Figs. 1–3. In particular, the MC excitation rates which mainly depend on the tail of $f(\epsilon)$ tend to be slightly, but systematically, higher. The differences, however,

TABLE II. Comparison of (conventional) Boltzmann and Monte Carlo calculations of electron excitation rates in the laser mixture CO_2:N_2:He:CO (6:34:54:6) at $E/N = 50 \times 10^{-21}$ V m^2. For the sake of comparisons with the results of Ref. 14, the same cross sections have been used. In particular, in this case the cross sections for N_2 are from Ref. 16.

Process	Gas	Threshold	B(%)	MC(%)
Vibrational (010)	CO_2	0.083		
Vibrational (020) + (100)	CO_2	0.167		
Vibrational ($v=1$)	CO	0.266	14.05	13.85
Vibrational ($v=1$)	N_2	0.29		
Vibrational (001)	CO_2	0.291		
Vibrational ($v=2$)	CO	1.266		
Vibrational ($v=3$)	CO	1.382		
Vibrational ($v=4$)	CO	1.514		
Vibrational ($v=5$)	CO	1.608		
Vibrational ($v=6$)	CO	1.504		
Vibrational ($v=2$)	N_2	1.7	41.79	40.57
Vibrational ($v=3$)	N_2	1.7		
Vibrational ($v=7$)	CO	1.79		
Vibrational ($v=4$)	N_2	1.9		
Vibrational ($v=5$)	N_2	2.0		
Vibrational ($0n0$) + ($n00$)	CO_2	≥ 2.03		
Vibrational ($v=8,9,10$)	CO	≥ 2.3	8.49	8.31
Vibrational ($v=6,7,8$)	N_2	≥ 2.2		
Vibrational (?)	N_2	5.00	7.96	8.18
Electronic excitation	N_2	≥ 6.7	18.18	18.6
Electronic excitation	CO	≥ 6.22	7.59	8.0
Electronic excitation	CO_2	≥ 7.0		

are generally small and need an elevated number of collisions to be correctly displayed. An insufficient number of events tends to alter the conclusion as the tail of $f(\epsilon)$ tends to be insufficiently populated. Finally, it must be mentioned that even the agreement between the transport coefficients obtained via MC simulation and via conventional solution of the Boltzmann equation has been found to be better than it was found in all previous simulations. In fact, the MC results (at 1 Torr 0 °C) are now found to converge to $W(\mathrm{MC}) = 8.45 \times 10^4$ m sec^{-1}, $D_T(\mathrm{MC}) = 0.730 \times$ m^{2}s^{-1}, and $\bar{\epsilon}(\mathrm{MC}) = 2.01$ eV, while $W(B) = 8.55$, $D_T(B) = 0.735$, and $\bar{\epsilon} = 2.00$. No special problem of convergence has been found in this case. This is further confirmation of the validity of our new technique of MC simulation for the study of electron transport in complex gases.

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