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Molecular-dynamics simulation of excess-electron transport in simple fluids

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This paper describes molecular-dynamics simulations of a collision-assisted transfer model of the excess electrons in a rare gas. In this model the effect of an external electric field applied to the fluid is taken into account by allowing the displacement of an excess electron from an atom to another if the modulus of the vector distance between the atoms and the angle between the vector distance and the field have prescribed values. The computed drift velocities are in reasonable agreement with the experimental ones for a large density domain (going from gas to liquid). Then, in spite of the simplicity of the studied model, our computation seems to show that the main features of the electron motion in argon and in other fluids originate in the dynamics of the molecules of these fluids.

I. INTRODUCTION

The status of an excess electron in a dense dielectric fluid is still a controversial problem. A theoretical calculation of the electron motion in this medium is very far from the first principles.

Fortunately a very complete set of drift velocities and mobilities in nonpolar as well as in polar fluids has been published in the last several years. In argon,[1] in argon and xenon,[2] in methane,[3] in ethane,[4] and in ammonia,[5] the mobility has the same variation versus the density. The most striking features of the excess-electron motion are the saturation of the velocity at high field at a value less than ten times the sound velocity[6] and the maximum of the mobility which occurs at a density between 1.5 and 2 times the critical density of the fluid. This feature is remarkable since, except in helium and neon, it exists in all the dielectric fluids though the magnitude of the mobility at the maximum is 4 orders of magnitude larger in spherical-particle fluids (argon, methane) than in a strongly dipolar one (ammonia). Hence beyond the details of the electron-molecule interaction this suggests that the motion of the electron reflects a characteristic behavior of the dynamics of the fluids. One can verify easily that for every gas the abrupt decrease of the mobility (less pronounced in methane) occurs at a density for which the onset of the localization is predicted by the Mott expression $\langle k\Lambda\rangle = k(n\langle\bar{\sigma}_m\rangle)^{-1}$, where k is the wave number associated with the electron in thermal equilibrium with the fluid, Λ is the mean free path, n the number density of the fluid, and $\langle\bar{\sigma}_m\rangle$ the thermal average of the momentum-transfer cross section at the fluid temperature.

Starting from this observation a model has been proposed[7] in which the excess electron is localized on one molecule. When the host molecule collides with a neighbor molecule at an energy sufficient to lower the potential barrier experienced by the electron under the energy of this one, the electron travels on both molecules at its own high velocity. In the absence of an applied field, at the end of the collision the electron is again localized on one of these two molecules. Applying an electric field increases the electron energy toward the opposite direction. Accordingly the electron will stay on the molecule which is in the position against the field. The increase of the energy of the electron in the field will lower the collision energy necessary for allowing its transfer.

Since the molecules interact through a distance-dependent potential, this lower energy will mean a transfer at a larger distance. Hence varying the electric field strength is equivalent to varying the transfer distance. The drift velocity of the electron is simply related to the motion of its successive host molecules. Besides the reasons leading to its elaboration, the interest of this model arises from its simplicity and from the possibility to test it by molecular dynamics.

A three-dimensional description of the model will be given first. Its adaptation to the molecular-dynamics simulation will follow. The results will be compared to the experimental ones. A discussion will conclude this paper.

II. THREE-DIMENSIONAL COLLISION-ASSISTED DRIFT MODEL

The one-dimensional model of the collision-assisted drift has been described in Ref. 7. It permits us to show that the drift velocities obtained by a one-dimensional simulation are quite satisfactory in magnitude at high field. This can be explained by different experimental results[8,9] showing that the diffusion at high field becomes extremely small which is equivalent to a quasirectilinear motion. The main shortcomings of the one-dimensional model are the difficulty in comparing densities at one and at three dimensions and the absence of damping of sound waves arising in the string.

In three dimensions one has to introduce new elements to the model. At zero field the electron should experience from its host molecule a spherical attractive potential. Between two collisions the electron is localized in a spherical volume. Its motion from molecule to molecule leads to a zero mean velocity.

When a finite field is applied, between two collisions the volume accessible to the electron is no longer spherical. It depends on the angle θ between the direction of the field and the distance vector from the host molecule to the colliding neighbor. For each applied field strength the volume in which the electron is localized is more or less ellipsoidal. Its exact shape could be calculated if the electron-molecule potential was known at such short distance and such high densities. The limits of this volume determine the "drift criteria" (r_1,θ), i.e., the larger distance r_1 for which the electron can spread on the next molecule located within the angle θ. Each set (r_1,θ) is associated with a given field strength. For the sake of simplicity the set of accessible volumes from a sphere at zero field to an oblong ellipsoid at high field is approximated by a set of spherical sectors of decreasing apertures θ and increasing radii r_1. This approximation is justified on the ground of the larger probability of transfer of the electron when it is far from the center of the host molecule in the direction against the field.

The occurrence of multiple collisions, i.e., simultaneous collisions of more than two molecules, demands special care. During an efficient collision of two molecules in the forward direction, the excess electron gets from the field an energy about twice the potential energy it had gained on its host molecule. Accordingly its drift criterion is increased. An evaluation of the new drift criterion can be made in the following way. The computations show that for $\theta=\pi/2$ and some distance $r_1=r_0$ the drift velocity is very small (<3 m s^{-1} in the whole density and temperature range). Let us take this value as the zero field values of r_1 and θ. For a double collision between the molecules 1, 2, and 3, in the drift criteria between 2 and 3 the maximum transfer distance will be $r_2=r_0+2(r_1-r_0)$ if the maximum transfer distance between 1 and 2 is r_1.

These considerations have led to the semiempirical set of drift criteria given in Table I. For multiple collisions the θ angles are the allowed angles for the same transfer distance in a simple collision. The values in Table I have not been fitted for any experimental data and are used for all the densities. They have to be understood in the following way: for a given field, the collision will be efficient if it occurs at $r<r_1$ within the angle $\theta<\theta_1$ or $r<r_2$ and $\theta<\theta_2$ for a double collision. Simultaneous collisions of more than three atoms have very low probabilities and have been treated using the criterion for the double collisions. It appears that at large r_1 the allowed θ angle becomes very narrow and the probability of absence of one molecule in the field direction on the electron path is sufficiently large to prevent the drift velocity to increase indefinitely.

TABLE I. Criteria for the transfer of the excess electrons. The electric field is assumed to be parallel to the 0z axis. The criteria (Ref. 10) from 1 to 9 are used in a simple collision. These criteria mean that the excess electron moves according to the criterion i $(1<i<9)$ and goes from its host molecules to a neighbor molecule if the distance vector between the two molecules has a modulus smaller than r_1/σ and makes an angle with the 0z axis smaller than $\theta_{\max}$. The criteria from 10 to 15 are used for the double collisions (see text Sec. II). The criterion 0 corresponds to an almost zero drift velocity of the excess electron and so to zero electric field, if $\theta_{\max}$ was 90° for the criterion 8, v_d will be about four times larger than the experimental v_d.

c	r_1/σ	$\theta_{\max}$ (deg)
0	0.90	90
1	0.94	84
2	0.98	77
3	1.02	70
4	1.04	66
5	1.06	62
6	1.08	58
7	1.10	54
8	1.12	50
9	1.14	47
10	1.18	40
11	1.22	33
12	1.26	26
13	1.30	18
14	1.34	10
15	1.38	3

III. MOLECULAR DYNAMICS SIMULATION

In order to calculate the drift velocities of the excess electrons, we have performed a molecular-dynamics simulation of a system of $N=864$ particles. The particles are contained in a cubic volume with periodic boundary conditions, and they interact via a Lennard-Jones (LJ) potential which is well known for reproducing almost quantitatively the experimental properties of the fluid argon. The parameters σ and ϵ of the LJ potential are, respectively, 3.405 Å and 119.8 K. The molecular-dynamics method has been described many times,[11] so we only mention that we integrate the equations of motion by the Verlet's algorithm, with an integration step of 10^{-14} sec.

Owing to the fact that, in the studied model, the presence of the excess electrons is without influence on the motion of the molecules, we can associate one excess electron with each molecule of the fluid. Then the effect of an external electric field on the drift of the electrons is taken into account by an appropriate choice of the criteria determining the transfer of the electrons from one molecule to another. In addition as the velocity of the electron itself is very large compared to the velocity of the molecules, the transfer of the electron is considered to be instantaneous. At the initial time of the simulation, we look at the positions of the neighboring molecules of each molecule of the system. If the vector distance between a molecule and one of its neighbors satisfies the criterion currently associated with the transfer of the electrons, the electron carried by the molecule has access to this neighbor (if two distance vectors satisfy the criterion, the electron is moved on the nearest neighbor). Then the vector

TABLE II. Densities ρ in atoms/A^3, temperatures in Kelvin, pressures in pascal for the 15 thermodynamic states where the calculation of the drift velocities of the excess electrons was done.

ρ (atoms/Å^3)	T (K)	$P/\rho kT$	10^7 P_{pascal}
0.0144	156.2±0.5	0.36±0.02	1.117±0.05
0.0139	155.7±0.5	0.28±0.02	0.836±0.05
0.0134	156.2±0.5	0.24±0.02	0.693±0.05
0.0133	155.6±0.5	0.25±0.02	0.683±0.05
0.0132	155.8±0.5	0.24±0.02	0.681±0.05
0.0130	155.0±0.5	0.20±0.02	0.556±0.05
0.0129	155.6±0.5	0.21±0.02	0.581±0.05
0.0128	155.1±0.5	0.20±0.02	0.548±0.05
0.0127	156.7±0.5	0.21±0.02	0.576±0.05
0.0123	156.2±0.5	0.20±0.02	0.530±0.05
0.0116	155.5±0.5	0.18±0.02	0.448±0.05
0.0106	156.7±0.5	0.18±0.02	0.412±0.05
0.0096	155.8±0.5	0.21±0.02	0.433±0.05
0.0086	155.6±0.5	0.24±0.02	0.430±0.05
0.0076	155.8±0.5	0.31±0.02	0.506±0.05

distance between the new host molecule of the electron and its neighbors are analyzed, and if it is possible, the electron is displaced. The operation is repeated until all the electrons stop on a molecule such that the distances with its neighbors do not satisfy the transfer criterion. Then an integration step is made and so forth. Obviously the complete independence of the motions of the molecule and of the electrons permits an association with not only one, but several electrons on each molecule. In our computations we associate nine electrons at each molecule, and we have nine sets of 864 electrons which move following nine different transfer criteria.

We have performed 15 calculations of 2000 integration steps and also several others of 8000 integration steps in order to obtain a good estimation of our errors on the drift velocities. For these simulations the temperature is $T \simeq 156$ K and the density goes from 0.0076 atoms/Å^3 to 0.0144 atoms/Å^3. This isotherm is slightly below the critical point of the Lennard-Jones system.[12] Owing to finite value of N, it presents a Van der Waals loop. Our results concerning the pressure and other thermodynamic quantities are in good agreement with the values obtained by Adams.[12] One simulation run consumes about three hours of CPU (central processing unit) time on a UNIVAC 1110 computer on which these calculations have been done. We summarize the thermodynamic results in Table II.

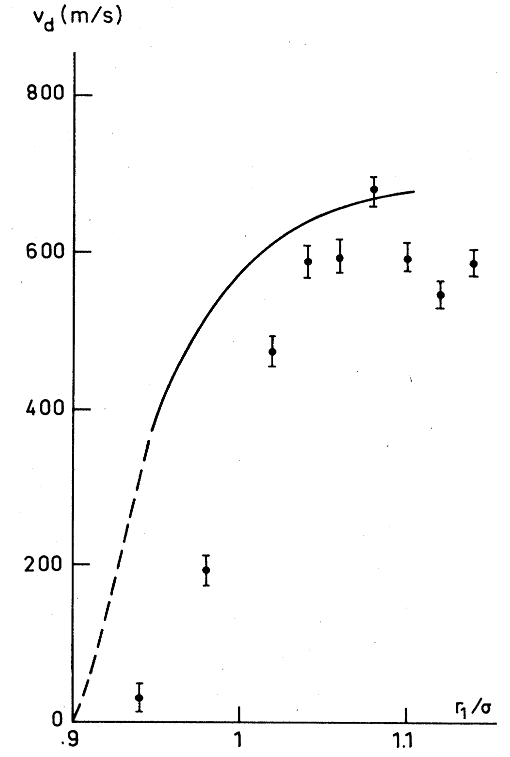

FIG. 1. Computed drift velocities (I) vs criterion r_1 compared to the experimental drift velocities (Ref. 1) (line) vs field strength at the temperatures $T=156.4$ and 152.8 K and at the density 0.012 67 atoms/Å^3. The dashed line is a linear extrapolation of the experimental result to zero drift velocity. (Note: the computed drift velocities depend also on the values of $\theta_{\max}$.)

In Table III we give typical results for the drift velocities v_d associated with the nine sets of excess electrons in the system. Typical uncertainties on v_d are about (8–10)% after 2000 integration steps. d_j is the mean distance covered by an excess electron during a move from its host molecules to the neighboring molecule; for a given transfer criterion it can exceed the maximum distance covered in a transfer by an electron; this fact means that some displacement corresponds to one, two, or more transfers.

TABLE III. At the density $\rho=0.0132$ atoms/A^3, and at the temperature $T=156.2$ K, estimations of v_d, for the nine transfer criteria (c: 1,2,3, . . . ,9), obtained after 1000 or 2000 integration steps. n_s is the number of electron displacements done according to the different criteria, during these integration times, and d_j is the mean distance covered by an electron in a transfer in Å.

c	1	2	3	4	5	6	7	8	9	Average on
$v_d^{m/s}$	30	204	568	646	708	660	660	616	616	1000 steps
d_j	3.37	4.25	4.93	5.10	4.90	4.50	4.19	3.88	3.78	
n_j	1329	6487	13 838	14 653	16 343	16 119	17 133	16 908	16 934	
$v_d^{m/s}$	30	201	541	623	660	636	633	550	560	2000 steps
d_j	3.37	4.25	4.90	5.00	4.73	4.46	4.19	3.91	3.78	
n_j	2704	13 093	26 827	28 824	31 787	31 445	32 917	29 753	30 605	

IV. RESULTS

The computed drift velocities v_d obtained for nine values of the criteria and the corresponding experimental one are shown in Fig. 1 for a typical thermodynamic state. In order to compare the computed and experimental velocities we suppose that the criteria is a monotonic function of the field strength hence the abscissa of the computed v_d is arbitrarily adjusted for the coincidence of the two graphs at their maximum. The drift velocities are in fair agreement at high field for the absolute value at the maximum and for the decrease at higher field.[2] At low field the shapes of the two graphs are quite different since the v_d derivative at low r_1 tends to zero as r_1 decreases, whereas this derivative in the experimental graph is assumed to be not null.[1] In fact it is to be noticed that the "experimental" graph under the sound velocity is the result of an interpolation between zero and 25 V cm^{-1} fields, with the implicit assumption that this part of the graph is more or less linear. Though the relation between the field and the transfer criteria is not incompatible with the respective aspects of the experimental and computed graphs, we would say that further experimental investigations at lower field are necessary before a definitive acceptance of this interpolation.

If new experimental graphs are drawn with a zero slope at zero field, the field at which the electron reaches the sound velocity v_s is practically constant for the whole density range. This is in good agreement with the computed drift velocities which give $v_d = v_s$ for $r_1 \simeq \sigma$.

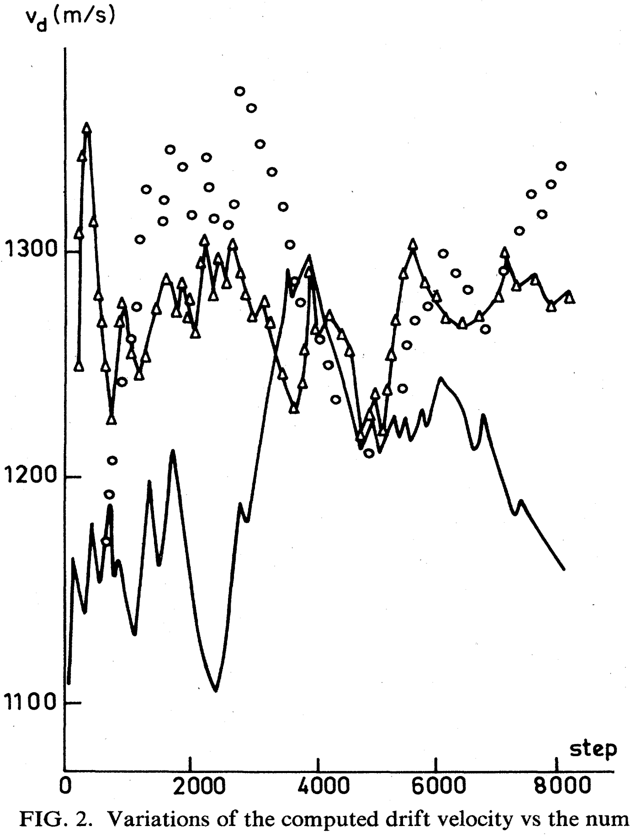

FIG. 2. Variations of the computed drift velocity vs the number of integration steps for three criteria at the density 0.0106 atoms/Å^3 and the temperature $T = 156.7$ K. Line: criterion $r_1 = 1.04\sigma$, line with △: criterion $r_1 = 1.08\sigma$, open circles ○: criterion $r_1 = 1.10\sigma$.

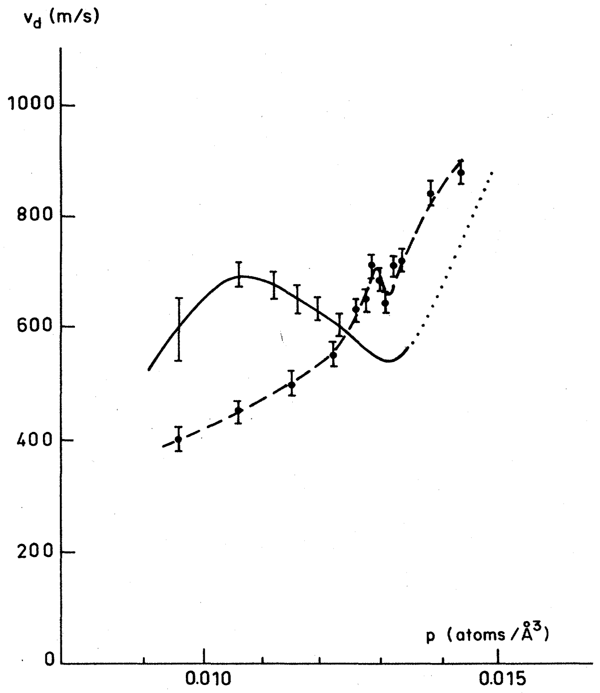

FIG. 3. Comparison between the experimental maximum drift velocities (Ref. 1) and the computed maximum drift velocities vs the density at $T \sim 155$ K. Line and I, experimental values; dashed line and Ī, computed values (the dotted line is an interpolation between the density domains where the drift velocities are experimentally known).

A new mobility could be defined between two values of the field for which the drift velocity has been measured. But here we encounter a very surprising dispersion of the computed $v_d \pm 0.02$ at $r = 1.04$ and ± 0.005 at $r_1 = 1.10\sigma$ in comparison with what is found at $r_1 = 1.08\sigma$ as it is shown in Fig. 2. This behavior is not found at all the densities. For the densities at which it occurs one can suggest that a temporary locally ordered structure has main directions which strongly favor the transfer. The time necessary for reaching a stable mean value at these points would be far too long for the present investigation.

This leads us to use a remarkable feature of the experimental results[1] which had not yet been evidenced. The maximum of the experimental v_d at high field exhibits a general increase with the density as shown in Fig. 3 with a relative maximum and minimum. The computed graph on the same figure has quite a comparable trend.

V. DISCUSSION

Several points entering the simulation of the model should be improved in order to allow complete comparison between computed and experimental results. Among these points the following are to be noted.

The Lennard-Jones potential is only an approximation to the molecular interactions in the fluids, but overall, here it is modified by the presence of the excess electron on one of the molecules. The magnitude of this influence is not known but even if it were, the real local potential could not be taken into account. Actually it is not possible for any reasonable computing time of any computer to compute the general dynamics of a large amount of particles interacting through a given potential and a few of these particles interacting through another potential.

Obviously the presence of a few excess electrons does not modify significantly the thermodynamical critical point of the fluid but can markedly influence locally the environment of the host molecules and consequently the densities and temperatures at which the experimental drift of the excess electrons reflects this critical point. A similar remark applies to the discrepancy between the experimental and computed extrema in the drift velocity.

The relation between r_1 and E is not known which prevents a complete comparison between computed and experimental v_d in the whole field range. There is no doubt that the information contained in Table I could be improved by using the ellipsoids themselves rather than crude approximations to them.

The accuracy of the simulation is limited by the statistics of the molecular-dynamics runs (Fig. 2).

The range of validity of the model is limited to the densities higher than the density of the onset of the localization and lower than the metalization density.

In spite of these problems a quite satisfactory agreement is found between the experimental and computed drift velocities in the whole density range. It must be emphasized that these computed results have been obtained without any fit to experimental data.

We conclude that for argon most of the drift properties of the excess electron reflect the dynamics of the fluid inducing the motion of the electron from atom to atom. This behavior is the same for most of the gases.

For nonspherical molecules the volume accessible to the electron is no longer spherical even at zero field and can be strongly orientation dependent. In this case the rate of the transfer which has been computed previously is strongly affected by the probability of finding a favorable coincidence between the orientation of the host molecule and the colliding one. For NH_3, for instance, the number of transfers per step of integration can become extremely low and thus would demand extremely long computing times for a reasonably accurate determination of the drift velocities.

We would like to emphasize that in all the situations where the excess electron is localized with a weak bound[13,14,5] either on a molecule, a group of molecules, or a fluctuation of density, the most powerful method for describing its motion is certainly the molecular-dynamics method when computing method and computing times are not excessive.

The dynamical behavior of the fluids around $2\rho_c$ which is evidenced by these calculations should be observed in other fields of molecular physics particularly on phenomena strongly influenced by the close environment of the active molecule. Among these phenomena one can think of vibrational relaxation, light depolarization, and collision-induced far-infrared spectra. Very few of such data are available in this density and temperature range. New experimental results on vibrational phase relaxation in methane[15] confirms the peculiar dynamical behavior of the fluids for density $\sim 2\rho_c$ and $T > T_c$.

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