

Reply to "Comment on 'Molecular-dynamics simulation of excess-electron transport in simple fluids' "

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We agree with Gee and Freeman that our model could be improved to show better experimental agreement, but we believe that none of the points of the Comment by Gee and Freeman rests on quantitative grounds or justifies modification of the assumption of the model. On the contrary we underscore the reasonable quantitative agreement of our calculated v_{dsat} and even of dv_{dsat}/dn with experiment in the frame of one simple and clear assumption. Moreover, new very strong experimental evidence is given in favor of the localization of excess electrons in fluids and of the molecular-dynamics related drift: the similar density dependence of the inverse of the excess electron mobility and of the half width at half maximum of the ν_1 band of CH_4 related to the vibrational phase relaxation in methane [Echargui and Marsault-Herail, *Mol. Phys.* (to be published)]. It is the first time that such a similarity is found with the mobility.

The purpose of our paper¹ was to test numerically the model of collision-assisted transfer of localized excess electrons in dense dielectric fluids (excluding light elements). The assumption of the localization of the excess electron on one or several atoms has been proposed many times and criticized at least as many times. It appears that most of the arguments against the localization model and in favor of "free" electrons rest on feelings rather than on quantitative data.

In this Reply we will comment on the different points raised in the preceding Comment, and present and discuss a comparison between the inverse of the excess electron mobility and the width of a CH_4 vibrational line versus the density.

(1) Point (1) of the previous Comment describes the density range in which the saturation drift velocity exists. In the liquid phase at the triple point and at very high field a saturation of the drift velocity v_{dsat} is observed at $\sim 8 \times 10^3 \text{ ms}^{-1}$ in argon.² This implies that there is a dip at some place in the experimental v_{dsat} in Fig. 1 of the Comment. The point which is highly questionable in point (1) is the role of a Ramsauer-Townsend (RT) minimum in the density range of interest here [point (5) below]. At our knowledge the exact calculation of the electron momentum-transfer cross section σ is available for densities lower than one-tenth of the critical density.³ What occurs to σ at higher densities is in the nature of an assumption.

(2),(3) Point (2) raises the problem of the sign of dv_{dsat}/dn that we calculate. The first point to be stressed is the satisfactory value of v_{dsat} itself. Concerning the sign of the derivative versus the density, this sign is positive at least for the isotherms⁴ 155.8 and 156.8 at densities between 0.090 and 0.011 atoms \AA^{-3} . This leads to the S

curve in Fig. 3 of Ref. 1. This is what we have found in our computation. Our experimental S curve in Fig. 3 of Ref. 1 should be 100 ms^{-1} higher. Extrapolation toward lower densities of the isotherm was made following the general trend suggested by the v_d curves and their crossing over.

In the comment it is clear that the plotting of a "155 ± 3 K isotherm" in the high-compressibility range of interest here is not reasonable especially when starting from data given with a 0.1-K uncertainty.⁴ Hence the data of Gee and Freeman in Fig. 1 of their Comment have to be handled very cautiously since they do not follow isotherms. Experimentally the dip exists necessarily [point (1) above] and it is found in our computations.¹ The uncertainty has not allowed us to ignore it. Its extent as well as the shape of its sides might be influenced by the complete neglect of the evolution of the atom potential well versus the density in the model.¹ Meanwhile it cannot be excluded that another starting point for the model might give better agreement [point (5) below].

(4) The predicted value of v_{dsat} in liquid argon at the triple point by our model in one dimension⁵ is only 50% of the observed one; this is rather encouraging. Moreover, the model leads to the same agreement for krypton and xenon.⁴

(5) Our model assumes that the electron is localized on a single argon atom in liquid argon. It is clear that at low densities the collision-assisted transfer model is valid as far as the trapping duration of the electron is longer than the "free flight" of the host atom.⁵ Hence the model does not lead to the conclusion that v_{dsat} should necessarily be lower in the low-density gas than at higher densities.

All the arguments presented in this point of the comment are essentially qualitative. They do not lead to any

prediction. Our model does.

Since the drift velocity of the excess electron is the inverse of the sum of the durations it spends on its successive host atoms, v_d is simply related to the dynamics of the host atoms, the electron being just a marker. Hence it is interesting to find another physical effect closely related to the dynamics of the molecules. The vibrational phase relaxation (VPR) is a very interesting effect in this viewpoint. We have suggested to Marsault that in the density range between ρ_c and $2\rho_c$ the VPR of methane should show an effect quite comparable to the one observed on the mobility. Marsault has kindly provided the results of Fig. 1 prior to publication.⁶ This figure represents the width at half height ($\Delta\nu_{1/2}$) of the ν_1 band of methane on several isotherms. These isotherms have been obtained at temperatures above the critical one in the same conditions as the comparison between our computations and the experimental results.⁴ The shape of the isotherms is very striking with a maximum at ρ_c and a minimum at $2\rho_c$. It appears that $\Delta\nu_{1/2}$ is roughly proportional to the duration τ of the interaction between the vibrating molecule and the neighboring ones.⁷ For the mobility of excess electrons our model predicts a mobility μ inversely proportional to the duration τ of the trapping of the excess electron on its host molecule. In Fig. 1 μ^{-1} is drawn from Ref. 8. The similarity of variation of $\Delta\nu_{1/2}$ and μ^{-1} versus the density is striking. The "critical point" experienced by the mobility is different from the one experienced by $\Delta\nu_{1/2}$. This effect was already noted in Ref. 1 for the thermodynamical critical point and attributed to the excess electron which modifies the molecular-interaction potential of its host atom. We see in the similarity of behavior of μ^{-1} and $\Delta\nu_{1/2}$ a very strong confirmation of our model. We appreciate that the authors of the comment agree with the concept of temporary localization. We had ourselves proposed this approach in Ref. 9.

Improvements in the theory of the interaction potential of the excess electron in a fluid are highly desirable and will probably lead to a volume of interaction following a density behavior close to the VPR one¹⁰ and consequently the excess electron localization on one molecule will be the high-density limit of the description which will definitely rest on molecular-dynamics ground which is the main claim of Ref. 1.

The statement that "the methane vibration-phase-relaxation results of Marsault⁶ are reminiscent of the bulk viscosity of argon" in the comment is not correct. It comes from an exaggerated extrapolation of the results of Cowan and Ball.¹¹ These results are only partial since they concern only the high-density range of the 50-atm isobar. The Enskog theory which is very powerful in determining the transport coefficients in dense fluids predicts a monotonous variation of the bulk viscosity in all the density and temperature range.¹²

Hence there is no common point between the behavior of the bulk viscosity and that of the excess electron mobility. The results displayed in Fig. 1 are indicative not only of the ability of our model to describe the drift of excess

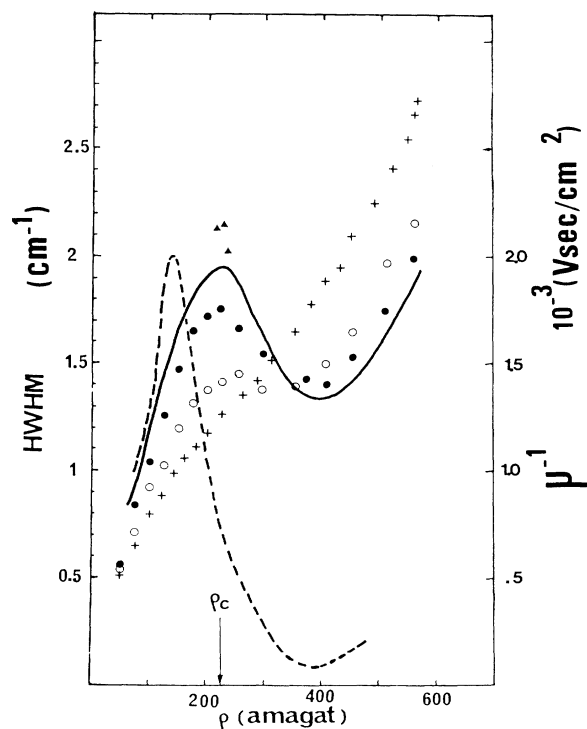


FIG. 1. Half width at half height vs density of the ν_1 band of methane along the isothermal lines: +, 298 K; o, 225 K; ●, 200 K; △, 191.4 K estimated at 196 K from Ref. 5; — —, inverse of the mobility μ^{-1} at 196 K from Ref. 8.

electrons in fluids (except light and very polar ones) but also to predict new properties of these fluids.

(6) The fact that the Mott expression or the Ioffe and Regel one do not apply "cleanly" to the determination of the density at which the excess electrons localize obviously does not mean that the excess electrons do not localize.

The order of magnitude as well as the derivative density behavior of v_{dsat} calculated from our extremely simple collision-assisted transfer model are in agreement with the experimental data of Jahnke *et al.* These data have never been contested.

We have found what we feel are many incorrect statements in the Comment of Gee and Freeman, but not valid reasons demonstrating the "untenable" aspect of the model. On the contrary, our model has suggested the interest of measuring the density dependence of $\Delta\nu_{1/2}$ for the vibrational phase relaxation in methane. The density behavior is strikingly similar to the μ^{-1} one. No fluid transport phenomena has such a behavior. The success of our prediction reinforces our confidence in the interpretation of the drift velocity in terms of molecular dynamics rather than in terms of electron-molecule collisions. This does not exclude an evolution of the model especially in the light of new experimental information on the molecular-dynamics behavior as has been shown here.

- ¹A. Leycuras and D. Levesque, *Phys. Rev. A* **32**, 1180 (1985).
- ²L. S. Miller, S. Howe, and W. Spear, *Phys. Rev.* **166**, 871 (1968).
- ³T. F. O'Malley, *J. Phys. B* **13**, 1491 (1981).
- ⁴J. A. Jahnke, L. Meyer, and S. A. Rice, *Phys. Rev.* **3**, 734 (1971).
- ⁵A. Leycuras and J. Larour, *J. Phys. C* **15**, 6765 (1982).
- ⁶M. A. Echargui and F. Marsault-Herail, *Mol. Phys.* **60**, 605 (1987).
- ⁷F. Marsault-Herail (private communication).
- ⁸N. E. Cipollini and R. A. Holroyd, *J. Chem. Phys.* **67**, 4636 (1977).
- ⁹A. Leycuras and J. Larour, *J. Phys. (Paris) Colloq.* **39**, C1-213 (1978).
- ¹⁰J. Chesnoy, *Chem. Phys.* **125**, 267 (1986).
- ¹¹J. A. Cowan and R. M. Ball, *Can. J. Phys.* **50**, 1881 (1972).
- ¹²J. O. Hirschfelder, C. F. Curtiss, and R. Byron Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1962), p. 648.