Calculation of the mobility of electrons injected in liquid methane

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We report the calculation of the low-field mobility of electrons injected in liquid methane between the triple point and the critical point. The calculation was carried out as if methane were an atomic liquid resembling a rare gas. A good agreement with the experimental time-of-flight data is obtained by considering only the scattering of electrons by acoustical phonons and by static density fluctuations. The only arbitrary parameter that was used is an effective mass, $m^*=0.8m_0$. The good agreement between experiment and the model calculation is an indication that the optical modes arising from both the vibrational and rotational modes of the isolated molecules do not affect very much the mobility of thermal electrons.

I. INTRODUCTION

In this paper we will report the application to CH_4 of the formalism developed for the calculation of the mobility of electrons injected in simple liquids.[1,2] As in the previous cases, the calculation is limited to the liquid vapor coexistence line because of the availability of the necessary experimentally determined parameters. The reader is referred to Ref. 1 for a general literature background. The interest of this calculation, beside being another validation of the previously developed method, lies in the fact that CH_4 has both librational and vibrational modes that are absent in the rare-gas liquids. They have been detected in both the liquid and the solid phases.[3–6]

Both the vibrational and rotational modes should give rise to optical phonons that might be expected to influence the mobility of injected electrons. In the gas, the lowest vibrational mode of methane[6] is at 1306 cm^{-1} (1881 K) while the lowest rotational mode is at 10.5 cm^{-1} (15 K).

Recently several groups[7–15] measured the time-of-flight (TOF) mobility of electrons injected in liquid and fluid methane. Representative results will be compared with the calculation. From the comparison, it appears that neither the librational nor the vibrational modes are strongly coupled to thermal electrons.

II. MOBILITY CALCULATION

We shall not review details of the calculation insofar as it has been extensively described.[1,2] It suffices to say that the independent interaction of electrons with both acoustic phonons and static density fluctuations has been considered. The deformation potential and effective-mass approximations are used throughout. Phonon scattering is calculated using the classical deformation potential theory developed for semiconductors:[16]

$$\mu_0=\frac{3\times10^{-5}\left[\rho C_s^2\right]}{T^{3/2}\Xi^2}\left[\frac{m_0}{m^*}\right]^{5/2}. \tag{1}$$

Here ρ is the density in g/cm^3, C_s is the velocity of sound in cm/s, $\Xi=-n(dV_0/dn)$ is the deformation potential in electron volts, n is the number density, m^* is the effective mass, m_0 the free-electron mass, and μ_0 is the mobility in cm^2/V s .

This expression for μ_0 must be corrected by a factor $X\sim1$ that takes into account the value of the deformation potential, density, and phonon amplitudes where the electron is located. The electron is visualized as a wave packet whose dimensions are equal to its thermal wavelength. The factor X will become important and larger than 1 where $V_0\sim0$, i.e. near the mobility maximum, and smaller than 1, near the critical point. The phonon amplitude, the value of the density, and Ξ are all changed inside a density fluctuation:

$$X=1+\left[2n\frac{\left[\frac{d^2V_0}{dn^2}\right]}{\left[\frac{dV_0}{dn}\right]}+\frac{2n}{C_s}\left[\frac{dC_s}{dn}\right]+\frac{4n^2}{C_s}\frac{\left[\frac{d^2V_0}{dn^2}\right]}{\left[\frac{dV_0}{dn}\right]}\left[\frac{dC_s}{dn}\right]+\frac{n^2}{C_s^2}\frac{d^2C_s}{dn^2}+\left[\frac{dC_s}{dn}\right]^2\left[\frac{n}{C_s}\right]^2\right.$$
$$\left.+n^2\left[\frac{d^2V_0}{dn^2}\right]^2\left[\frac{dV_0}{dn}\right]^{-2}+n^2\left[\frac{d^3V_0}{dn^3}\right]\left[\frac{dV_0}{dn}\right]^{-1}\right]\left[\frac{\overline{(\Delta n)^2}}{n^2}\right] \tag{2}$$

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and

$$\mu = \mu_0 / X \ . \tag{3}$$

In the actual calculation of X the terms proportional to d^3V_0/dn^3 and d^2C_s/dn^2 were neglected because very near the critical point, where they are important, the accuracy of the experimental[17,18] data did not appear to warrant their use.

The scattering due to density fluctuations is calculated in the effective-mass approximation using the phase shifts[19] associated with s to g partial waves. The scattering potential is assumed to be either an attractive or repulsive square potential of magnitude $V_0(\bar{n}+\Delta n) - V_0(\bar{n})$. Here Δn is the density fluctuation in a spherical volume Ω whose radius is r. The probability of finding a volume Ω with a uniform density is[20]

$$P_1 \propto \exp(-r/\xi) \ , \tag{4}$$

where ξ is the correlation length. The probability of finding a density $n = \bar{n} + \Delta n$ inside this volume is

$$P_2 \propto \exp\left[-\frac{(\Delta n)^2 \Omega}{2S(0)\bar{n}} \right] . \tag{5}$$

Eq. (5) is valid when $r \gg \xi$. $S(0) = k_B T K_T \bar{n}$ is the structure factor for zero momentum transfer and K_T is the isothermal compressibility. When $r \simeq \xi$ the bulk value of the compressibility is inappropriate and $S(0)$ must be modified in accordance with the theory of finite-size scaling[21] and should be substituted with[22]

$$S_{\text{eff}}(0) = S(0) \left[\frac{\xi_{\text{eff}}}{\xi} \right]^{2-\eta} , \tag{6}$$

where $\eta \simeq 10^{-2}$ and

$$\xi_{eff}^{-2} = \xi^{-2} + r^{-2} . \tag{7}$$

The energy-dependent mean free paths associated with scattering by density fluctuation were calculated for several thermodynamic states along the liquid vapor coexistence curve. These mean free paths are obtained by averaging the mean free paths appropriate for different volumes Ω, each one weighted by P_1. In each of these volumes there may be a density fluctuation Δn that is in turn weighted by P_2.

The volumes Ω are progressively doubled from a minimum value $\Omega_{\min}$ that contains N molecules up to when $\exp[-(r/\xi)] = 10^{-6}$. The value of N is made to vary between 4 and 256. The density of the liquid cannot be either larger than that of the solid (n_s) or negative. These give rise to physical limits to the possible values of Δn. For each volume Ω, Δn is varied between limits corresponding to when n is either equal to the density of the solid[23] (n_s), zero, or when $\exp[-(\Delta n)]^2 \Omega / 2S(0)\bar{n} = 10^{-6}$, between which ever upper or lower limits of Δn are most restrictive. The latter limit was chosen for practical reasons in order to limit computer time. In order to sample the range of densities between $n_{\max}$ and $n_{\min}$ the range of Δn is divided in 100 equal parts and the corresponding scattering is calculated at each one of the corresponding densities in each possible volume Ω . Each of

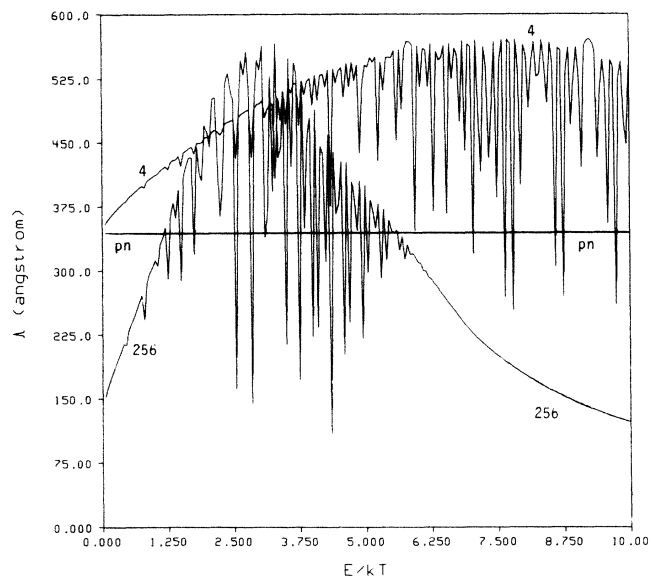

FIG. 1. Mean free path of electrons injected in CH_4 when the scattering mechanism is due exclusively to density fluctuations. The state of the liquid is characterized by a temperature $T = 133.15$ K, and a density $n = 1.46 \times 10^{22}$ cm^{-3}. The parameter N equals either 4 or 256. It indicates the number of molecules in the volume $\Omega_{\min}$. The line labeled pn indicates the mean free path when the electrons are scattered exclusively by acoustical phonons. In all three cases $m^* = 0.8 m_0$.

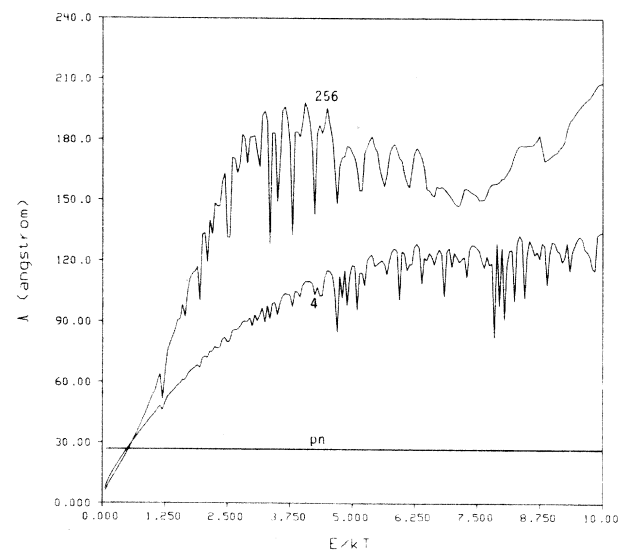

FIG. 2. Mean free path of electrons injected in CH_4 when the scattering mechanism is due exclusively to density fluctuations. The state of the liquid is characterized by a temperature $T = 188.65$ K, and a density $n = 7.805 \times 10^{22}$ cm^{-3}. The parameter N equals either 4 or 256. It indicates the number of molecules included in the volume $\Omega_{\min}$. The line labeled pn indicates the mean free path when the electrons are scattered exclusively by acoustical phonons. In all three cases the effective mass is chosen as equal to $0.8 m_0$.

these calculations is carried out for 200 equally spaced electron energies between $kT/20$ and $10kT$. At each temperature, this requires the calculation of between 10^5 and 10^6 scattering cross sections. Details are given in Refs. 1 and 2.

Examples of the calculated mean free paths due to scattering by density fluctuations in the cases when $N=4$ and $N=256$ are given in Figs. 1 and 2. For purposes of comparison the phonon limited mean free path, labeled pn, is given as well. A physical interpretation of the results will be given under point (3) below. To ascertain that the "spikes" seen in Figs. 1 and 2 are not numerical artifacts, the calculation was carried out using double-precision arithmetic using both a Digital Equipment Corporation PDP11/43 computer with 64-bit (binary digit) accuracy and a Control Data Corporation CDC-6600 computer with 120-bit accuracy. No difference was found between the results obtained from both machines.

Figure 3 shows the mobilities calculated when either only acoustical phonon scattering, or scattering by density fluctuations, is active. In the latter case the data in Fig. 3 corresponds to a choice of the parameter N equal to 4, 32, or 256. Finally, the combined mobility is obtained[1] from an appropriate average of the combined mean free paths:

$$\Lambda=\frac{\Lambda_{\rm pn}\Lambda_{\rm df}}{\Lambda_{\rm pn}+\Lambda_{\rm df}} . \tag{8}$$

The combined mobilities are shown in Fig. 4 in the case when N is either 4 or 256. Experimental data from several authors[9–13,15] are plotted in the same figure.

In order to carry out these calculations we used data from several sources. At each temperature the velocity of sound (measured at ~ 1 MHz), the density, as well as $S(0)$ were mostly taken from Gammon and Douslin.[18] Data for two points below 113 K were taken from Straty.[24,25] The values of V_0 were taken from the results of

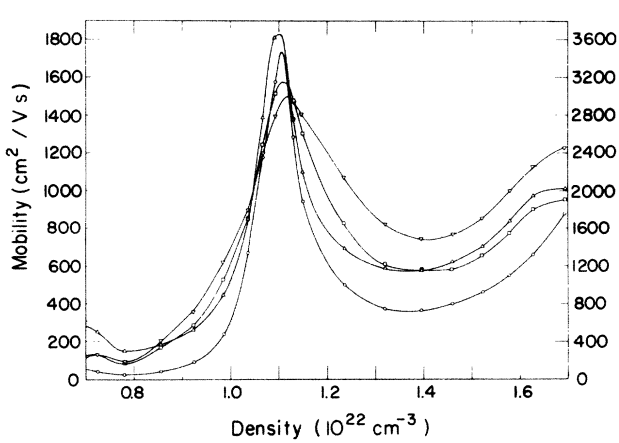

FIG. 3. Mobility of thermal electrons injected in liquid methane when the only scattering mechanism is due to density fluctuations. The parameter N is chosen to be 4 (▽), 32 (□), or 256 (△). The curve labeled ○ (right scale) indicates the mobility of thermal electrons scattered exclusively by acoustical phonons. The electron effective mass was chosen as equal to $0.8m_0$.

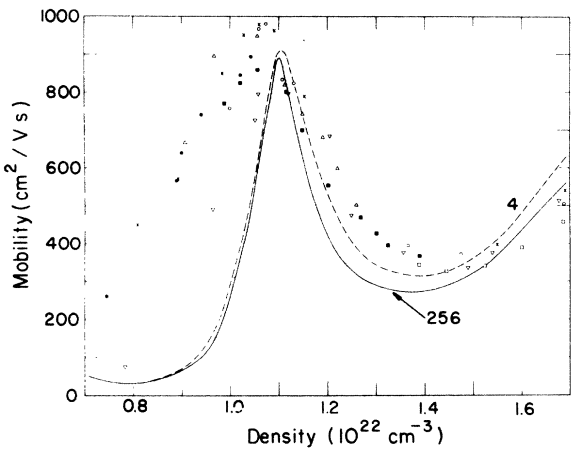

FIG. 4. Mobility of thermal electrons injected in CH_4 subject to scattering by both acoustical phonons and density fluctuations. The value of N was taken as equal to either 4 (dashed line) or 256 (solid line). The effective mass is chosen as equal to $0.8m_0$. The experimental data shown is from TOF mobility measurements taken by several authors: Gee and Freeman (Ref. 12), × ; Engels (Ref. 10), □ ($p<1.35$ MPa), ■ ($p=3.58$ MPa), △ ($p=5.08$ MPa), and ● ($p=6.08$ MPa); Floriano and Freeman (Ref. 15), ○; Nakamura *et al.* (Ref. 13), ▽.

Asaf *et al.*,[17] who fitted their measurements of the density dependence of V_0 to an equation of the form suggested by Basak and Cohen.[26] Data for the velocity of sound and the structure factor corresponding to two points near the mobility maximum were calculated by interpolating between values given by Gammon and Douslin.[18] The interpolation for $S(0)$ was obtained by keeping in mind that[27]

$$K_T n^2 \propto (n-n_c)^{1-\delta}(1+\cdots) \tag{9}$$

with $\delta=4.352$. The value of the correlation length,[27]

$$\xi=\xi_0 t^{\nu}(1+At^{1/2}) , \tag{10}$$

where $t=(T_c-T)/T_c$, was calculated taking for ν and ξ_0 the values given by Sengers and Levelt Sengers.[28] The constant A was taken[27] to be equal to 1. The values of the critical temperature T_c, critical pressure P_c, and critical density n_c came from the IUPAC (International Union of Pure and Applied Chemistry) compilation of the properties of methane.[29] Finally, the value of $m^*=0.8m_0$ was chosen arbitrarily so as to get an approximate agreement between the calculated mobilities and the experimental TOF mobilities near the triple point. This author is unaware of any estimates of the effective mass of electrons in the conduction band of either liquid or solid methane.

The data can easily be scaled to take into account other effective-mass values. From previous results[1,2] we know that the combined mobility dependence on effective mass is near $(m_0/m^*)^{5/2}$.

Several points are clear from the figures.

(1) As in the case of argon[1] and xenon,[2] the phonon limited mobility is comparable to the density fluctuation limited mobility. The former will dominate the combined

mobility near the critical point on the low-density side of the mobility maximum.

(2) The density fluctuation limited mobility is not very sensitive to the choice of N. This quantity determines the smallest volume Ω_{min} considered in the mobility calculation. As pointed out in previous publications,[1,2] a choice $N=4$ is incompatible with both statistical mechanics and the effective mass theory, both of which are used in the calculation. A choice $N=256$ appears to be compatible with both.

(3) As can be seen by reference to Figs. 1 and 2, there is a pseudo Ramsauer resonance of the mean free path that arises on account of resonant s wave scattering by density fluctuations contained in Ω_{min}. Higher angular momentum waves give rise to sharp resonances similar to those observed in the cases of argon[1] and xenon.[2]

There are clear discrepancies between the experimental data and the calculated mobility. Part of these discrepancies probably arise from the oversimplified model we used. Examples are the way the effect of density fluctuations was taken into account in the calculation of the phonon limited mobility and the use of square wells in the calculation of the density fluctuation limited mobility. The errors introduced by the latter are difficult to estimate. Those due to the calculation of X are, in general, small because $X \sim 1$. Where X differs significantly from 1, the errors arising from the method of calculation appear to be overshadowed by the estimates of the errors associated with the higher derivatives of both V_0 and the velocity of sound. The errors of C_s are not only of experimental origin; the measured values were obtained near 1 MHz while the values appropriate for the mobility calculation are in the GHz range. The known dispersion of the velocity of sound[30] gives rise to significant differences that very close to the critical point may affect the mobility by as much as a factor 2.

Another source of discrepancies arises if the TOF mobility is not measured along the coexistence curve. The calculated mobility, is quite sensitive to both the value of $S(0)$ and C_s. If the thermodynamic state of the liquid corresponds to a state removed from the coexistence curve, $S(0)$ is decreased and the mobility increases. Similarly the rapid changes of the velocity of sound near the critical point will drastically affect the phonon limited mobility. This conclusion is graphically illustrated in the case of liquid Ar where the mobility increases the further the state of the fluid is from the liquid vapor coexistence line. This is more accentuated in the vicinity of a density equal to the critical density.[31]

Most of the data of Engels and Van Kimmenade[9–11] displayed in Fig. 4 was taken at isobars above the liquid vapor coexistence line. In the case of the data from Freeman and collaborators,[12,15] the fluid was condensed in the sample holder and only the temperature of the vessel was measured. In these conditions, it is difficult to assure that the correct amount of fluid is being used so that the fluid will always follow the coexistence line when its temperature is varied. Furthermore, near the critical point, small temperature errors can give rise to large changes in density. As an example,[29] the density changes from ~ 10.1 mole/l to ~ 12.5 mole/l when T varies between the critical point (T = 190.555 K) and 190 K.

In the course of their TOF measurements, Nakamura *et al.*[13] measured both the temperature and the pressure of the fluid. Inspection of their original data indicates that their sample was frequently measured at a pressure that is a large fraction of an atmosphere above the liquid vapor coexistence line given in Ref. 29. Although these pressure differences are a small fraction of the total pressure, they give rise to significant changes of the sound velocity, the density, and the structure factor when the temperature is near the critical point. The data of Nakamura *et al.*[13] is replotted in Fig. 4. It is the experimental data that is the closest to the calculated mobility.

Although the density is the thermodynamic coordinate present in the equation of state that changes the most near the critical point, it was not measured in any of the experiments giving the TOF mobility. The knowledge of both the density and the temperature would be important in order to characterize the thermodynamic state of the fluid. Finally, the errors that arise from transferring the data plotted in the original publications into Fig. 4 cannot be neglected.

Even when all these considerations are taken into account and even if the calculations would be perfect, it is clear that the calculated mobility has a maximum at densities above that corresponding to the experimental data. The value of the calculated maximum mobility is a little smaller than the experimental values.

It would be astonishing if the effective mass of the electrons did not change while the density of the fluid varies by ≈ 2.75 between the triple and the critical point. A likely density dependence of m^* is similar to that of V_0. It would decrease from the triple point towards a density near where V_0 has a minimum and increase thereafter towards m_0 in the dilute gas limit. Such a behavior would increase the calculated mobility minimum near 1.35×10^{22} cm^{-3}, increase the value of the mobility maximum and shift it towards lower densities. This might decrease the discrepancy between the experimental and calculated data. However, in order to make such a fit, we would require five adjustable parameters as opposed to the single one that was used. This appears unjustified because of all the uncertainties of both the data and the calculation. It is, however, reassuring that overall there are no large discrepancies between the measurements and the calculated mobilities.

III. CONCLUSIONS

From this calculation we conclude that optical phonons do not have a large influence on the mobility of thermal electrons injected in liquid methane. On account of their large energies, few 1306 cm^{-1} (1881 K) phonons are excited at the temperatures of interest and their energy is about 10 times the average energy of the electrons. As a consequence, they are not expected to greatly influence the mobility of thermal electrons. However, the fact that the mobilities that are calculated are close to the experimental ones indicates that also the phonons that arise from rotations of the free molecule are weakly coupled to the electrons.

This is not astonishing. The librational modes of methane are optically active and contribute to the dielectric constant of the fluid.[4,32] Therefore a polaron theory is appropriate to take into account their contribution to the mobility.[33] In this case the square of the matrix element for the calculation of the scattering probability of electrons by optical phonons is proportional to[33] $\omega(\epsilon_\infty^{-1}-\epsilon^{-1})/q^2$ where $\hbar q$ is the electron momentum, ω is the phonon frequency, while ϵ_∞ and ϵ are, respectively, the high-frequency and low-frequency dielectric constants. In the case of rotational modes these correspond, respectively, to frequencies much higher and much lower than 10.5 cm^{-1}. The near equality[4,32] of ϵ and ϵ_∞ and the small value of ω assure that the coupling of the electrons with modes that originate from the rotational states of CH_4 is small.

The results of this calculation give further support for the formalism developed to explain the mobility of electrons in nonpolar liquids of highly symmetric molecules. Both scattering by phonons and scattering by density fluctuations must be considered.

A single parameter, the effective mass, was used to "fit" the calculated values to the experimental results near the triple point. The discrepancies between experiment and the calculation that are found near the critical point may be assigned in part to the inappropriateness of the velocity of sound that was used in the calculation. Probable changes of the effective mass with density, as well as an insufficiently well-characterized thermodynamic state of the fluid where TOF mobilities were measured should also contribute to the discrepancies between experiment and the calculation.

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