Calculation of the mobility of electrons injected in liquid xenon

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A model calculation is carried out in which we evaluate the mobility of thermal electrons injected in liquid xenon. Scattering by both phonons and static density fluctuations is taken into account. The calculation for the mobility limited by phonon scattering differs from the usual calculation in crystals by considering both the local changes in the deformation potential and the changes of the amplitude of the phonons that are caused by the existence of density fluctuations. The calculation of the mobility limited by scattering from density fluctuations is carried out assuming that they give rise to a square well (or barrier) potential that will scatter the electrons. The above perturbation, ΔV_0, is related to a density fluctuation Δn by $\Delta V_0 = V_o(\bar{n}+\Delta n) - V_0(\bar{n})$. The scattering volume Ω, where the density fluctuation Δn is located, is weighted by $\exp(-r/\xi)$ where ξ is the correlation length and r is the radius of Ω. The magnitude of the different density fluctuations are weighted by $\exp\{(\Delta n)^2\Omega/[2nS(0)]\}$, where $S(0)=nk_BTK_T$ and K_T is the isothermal compressibility. The calculation of the mean free path is carried out using partial waves. As in the case of argon, scattering by phonons and density fluctuations give comparable contributions to the mobility. However, contrary to the case of argon, a constant effective mass that is equal to the reduced mass obtained from exciton spectra, gives rise to a calculated mobility that is in excellent agreement with the available experimental data over the whole liquid-vapor coexistence range. There are therefore no adjustable parameters in the calculation.

I. INTRODUCTION

During recent years data on the mobility of electrons injected in insulating liquids has been accumulated.[1] Although one may question if most of the available time of flight (TOF) mobility data reflects the drift mobility that would be calculated using Boltzmann's equation,[2,3] it came originally as a surprise to this author that the TOF mobilities are frequently comparable to the mobilities observed in crystalline semiconductors. This must be contrasted with the enormous decrease of the mobility that is observed when one goes from a crystalline to an amorphous semiconductor.[4] In the case of electrons injected in several liquids near the triple point the TOF mobility is only about a factor of 2 lower than the mobility observed in the crystalline phase.[5,6]

One could imagine that the justification for the small effect that disorder has on the mobility is related to the van der Walls bonding in rare-gas liquids, in contrast to the covalent bonding in semiconductors. Only recently[7] a promising model has been developed that is capable of describing reasonably well the dependence of the experimental mobility on density. In this paper this model is applied to the case of liquid xenon without the use of adjustable parameters.

Basak and Cohen[8] (BC) calculated the mobility of an electron injected in a rare gas liquid assuming that a conduction band exists and that static density fluctuations represent the only scattering mechanism. BC related the scattering potential to the disorder produced by density fluctuations by introducing a deformation potential.

The deformation potential to be used in the calculation, dV_0/dn, is obtained from measurements[9] of the density dependence of V_0, where V_0 is the position of the conduction band minimum with respect to vacuum.

In the BC calculation, fluctuations corresponding to a local change of density Δn are considered and the change of energy of the minimum of the conduction band is expanded in series of Δn

$$\Delta V_0 = \left[\frac{dV_0}{dn}\right]_{\bar{n}} \Delta n + \frac{1}{2}\left[\frac{d^2V_0}{dn^2}\right]_{\bar{n}} (\Delta n)^2 + \cdots . \tag{1}$$

Successively Δn is expanded in Fourier series, the appropriate matrix elements between electronic plane wave states are evaluated and the thermal averages of the Fourier coefficients of Δn are used in the calculation. In the case of slow electrons this results in a scattering probability that is proportional to $S(q)$, the structure factor of the liquid for small momentum transfer. For slow electrons, BC approximated $S(q)$ by $S(0)=\bar{n}k_BTK_T$. Here K_T is the isothermal compressibility. Contrary to experimental evidence, the calculated mobility is zero at the critical point. Despite this difficulty, over a wide range of densities, the BC calculation[8,9] provides qualitative agreement with experiment.[10] It explains the observation[11] of a mobility maximum that coincides approximately with the density where $dV_0/dn = 0$ and, with $m^*=m_0$, it provides the correct order of magnitude of the mobility of electrons in both liquid argon and liquid xenon near the triple point.

The zero mobility predicted by the theory at the critical point is a serious difficulty, even more so when one considers the very small observed decrease from its maximum that is detected in the only available Hall mobility measurement.[12]

Finally, although scattering by static density fluctuations is important, in the absence of a numerical evaluation, it is difficult to imagine that other scattering mechanisms, like e.g. phonon scattering, should be ignored.

This is particularly evident when one realizes that both, scattered electrons and scattered light, which propagate in either a uniform or a periodic medium, can only give rise to constructive interference in the forward direction.[13] It is the inhomogeneities, both static and dynamic, that produce constructive interference, i.e., scattering, in other directions. In the case of light this corresponds respectively to Raleigh and Brillouin or Raman scattering.

The remainder of this paper will follow closely the previous discussion[7] for argon. The major difference between the results for xenon and argon is that in the literature there are higher frequency measurements of the velocity of sound for the former than for the latter and that reduced exciton mass values exist for liquid xenon while they are absent in the case of argon. As a result the free parameter that was used in the calculation of the mobility in argon is now fixed by experimental[14] data to $m^*=0.27m_0$ near the triple point. If this value of m^* had been used in the BC theory,[8,9] the resulting mobilities would have been about 25 times too large.

In Sec. II we shall see how a phonon scattering theory (deformation potential) used in semiconductors[15] must be modified in order to be applied to a liquid; the drift mobility due to phonon scattering will be calculated.

In Sec. III we will calculate the mobility due to scattering by static density fluctuations. Although the perturbation potential (ΔV_0) is similar to BC's, the details of the calculations permit us to take into account several points that they could not consider. In order to simplify the mathematics we shall assume that the potential resulting from the density fluctuations is a square well (or barrier).

An important result of the present calculation is that the mean free path due to scattering by density fluctuations does not become zero at the critical point. Furthermore there is a Ramsauer-like maximum of the energy dependence of the calculated mean free paths as well as evidence of sharp resonances that are assigned to the existence of metastable bound states.

II. SCATTERING BY PHONONS

The well known deformation potential theory that is used in the case of crystalline semiconductors[15] can be applied to the case of electrons injected into insulating liquids, provided that minor corrections are introduced.

In the case of semiconductors the deformation potential can be redefined in terms of changes of the edge of the conduction (or valence) band as a function of density, i.e.,

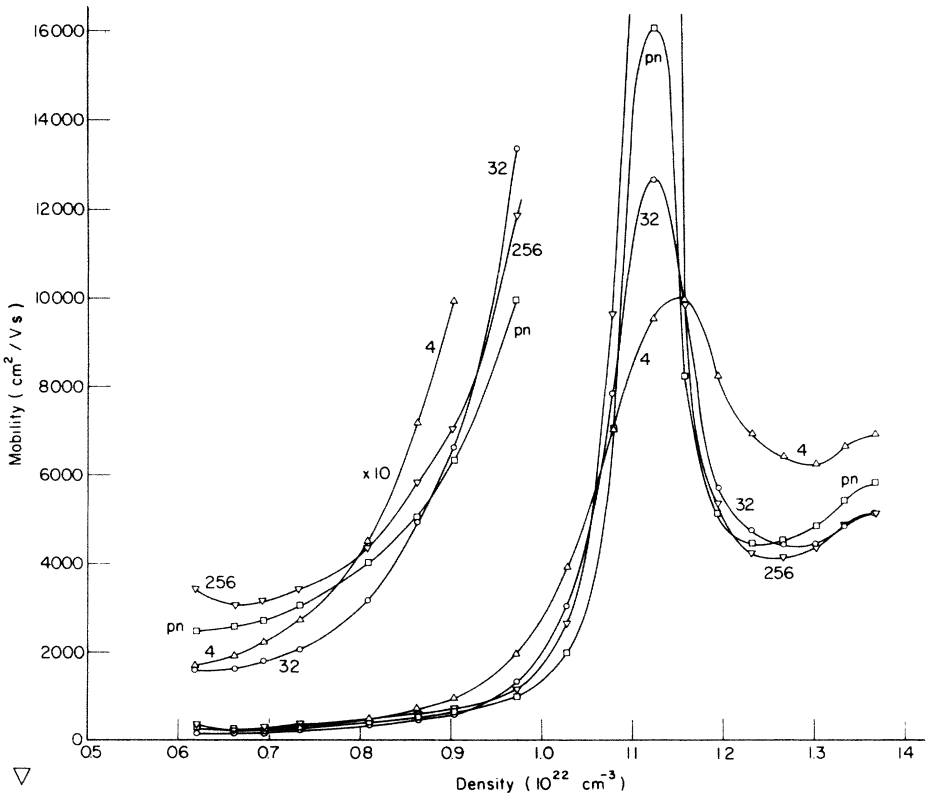

FIG. 1. Phonon limited mobility according to Eq. (4) (□). Mobility limited by scattering by density fluctuations when the effect of finite volumes is taken into account [Eq. (7)]; average number of atoms, N, contained in the volume $\Omega_{\min}$: $N=4$ (△), $N=32$ (●), $N=256$ (▽). The symbols on the graph correspond to the densities where the mobilities were calculated. An effective mass equal to $0.27m_0$ was used everywhere. The thermodynamic state of the liquid corresponds to the liquid-vapor coexistence line.

$\Xi = -n\,dV_0/dn$ rather than as a function of dilation as is usual in the theory of solids.[15]

In a crystalline solid Ξ is uniform and independent of position. In a liquid instead, density fluctuations will give rise to local variations of Ξ. Therefore, while in the theory of scattering of electrons in a solid one normally neglects to form an electron wave packet this will be important in the case of a liquid. The deformation potential that is important is obviously the deformation potential in the region where the electron is located.

As will be seen below this correction to Ξ is negligible everywhere except where Ξ is zero (and where we would have infinite mobility) and very close to the critical point where the velocity of sound becomes zero. We must however be cautious because of the observed dispersion of the sound velocity near the critical point.[16–22] In the case of xenon this means that corrections are important near ~ 220 K and near the critical point.

The expression[15] of the phonon limited electron mobility in a crystal whose density is ρ (g/cm^3) and at a temperature T is:

$$\mu_0 = \frac{2(2\pi)^{1/2} e\hbar^4}{3k_B^{3/2} m_0^{5/2}} \frac{\rho C_s^2}{T^{3/2}\Xi^2 (m^*/m_0)^{5/2}} . \tag{2}$$

In the case of liquid xenon

$$\mu_0 = \frac{(6.58\times 10^{-27}) C_s^2}{nT^{3/2}(dV_0/dn)^2 (m^*/m)^{5/2}} , \tag{3}$$

where n is in cm^{-3}, C_s is the velocity of sound in cm/s, V_0 in eV.

Corrections to the above expression arise because the value of n and dV_0/dn must be calculated at the location where the electron is scattered. Furthermore, if a phonon encounters a region of different density, the wave is partially reflected and the amplitude of the phonon inside the density fluctuation is lower than that in the uniform medium.

Since these corrections will be small almost everywhere, we shall not consider the full formalism of the Boltzmann equation. We shall instead assume that the electron can be localized in a volume Ω whose dimensions are the thermal wavelength of the electron, i.e., $\Omega = \lambda^3 = (2\pi m k_B T/h^2)^{-3/2}$ in which the density may differ from the average density $\bar{n}$, i.e., $n = \bar{n}(1+\Delta n/\bar{n})$. In this volume the amplitude of the incoming phonon differs from that in the homogeneous medium. Similarly we must consider the changes of the deformation potential in this volume. All of these changes give rise to corrections of the mobility. The significant quantity is therefore the probability of having a density fluctuation Δn in the volume λ^3.

Following the same steps as in Ref. 7 we find that the phonon limited mobility is:

$$\mu = \frac{\mu_0}{X} , \tag{4}$$

where μ_0 is the mobility calculated in the absence of density fluctuations. The correction factor X is

$$X = 1 + \left| 2n \frac{\left[\frac{d^2V_0}{dn^2}\right]}{\left[\frac{dV_0}{dn}\right]} + \frac{2n}{C_s}\left[\frac{dC_s}{dn}\right] + \frac{4n^2}{C_s}\frac{\left[\frac{d^2V_0}{dn^2}\right]}{\left[\frac{dV_0}{dn}\right]}\left[\frac{dC_s}{dn}\right] + \frac{n^2}{C_s}\frac{d^2C_s}{dn^2} + \left[\frac{dC_s}{dn}\right]^2\left[\frac{n}{C_s}\right]^2 + \left[\frac{d^2V_0}{dn^2}\right]^2\left[\frac{dV_0}{dn}\right]^{-2} + n^2\left[\frac{d^3V_0}{dn^3}\right]\left[\frac{dV_0}{dn}\right]^{-1} \right| \left[\frac{\overline{(\Delta n)^2}}{n^2}\right] \tag{5}$$

All quantities are calculated at the average density.

In contrast to the case of argon the velocity of sound in liquid xenon has been measured over a wide range of frequencies. Measurements of the velocity of sound at $\gtrsim 100$ MHz are appropriate for the calculation of the momentum exchanged by a thermal electron in an electron phonon collision.[16–22] The forementioned dispersion of the velocity of sound is not significant at these high frequencies for $T \lesssim 289$ K, the highest temperature considered in the calculation.

Data on the relation between temperature and density[23–26] in xenon appear to be of a quality similar to those for argon.

When both types of data are taken into consideration it is found that except near the mobilty maximum where $dV_0/dn = 0$, the value of X is extremely close to 1 for densities above 6.2×10^{21} cm^{-3}. As a reference, the critical density and the critical temperature of xenon are,[27] respectively, $n_c = 5.04\times 10^{21}$ cm^{-3} and $T_c = 289.734$ K.

The mobility of electrons limited by phonon scattering in liquid xenon along the liquid vapor coexistence line is shown in Fig. 1.

III. SCATTERING BY DENSITY FLUCTUATIONS

As in the case of Ref. 7, we calculate the density fluctuations contribution to the mobility of thermal electrons by considering the scattering of an electron by a square well (or barrier) using the technique of partial waves.[28,29]

Following the suggestion of Basak and Cohen[8] we shall

assume that if in a volume Ω the density differs from the average density n by Δn the scattering potential will be $\Delta V_0 = V_0(\bar{n}+\Delta n) - V_0(\bar{n})$. In our case we shall not assume that Δn is small and that ΔV_0 can be expanded in series. However, in order to simplify the calculation, we shall assume that the density in the volume Ω is uniform and equal to $\bar{n}+\Delta n$. Furthermore, we shall assume that the volume Ω is spherical.

Since the volumes Ω must fill all space (we neglect the fact that spheres cannot fill all space) their density is Ω^{-1}. This does not imply, however, that there will be a nonzero density fluctuation Δn in each one of the above volumes. However, the assumption of a uniform density fluctuation in the volume Ω implies unphysical discontinuities in the density.

Provided the radius of such a volume Ω is large in comparison with the correlation length ξ, the probability P_1 of finding a density fluctuation of magnitude[30] Δn in Ω is

$$P_1 \propto \exp - \frac{\Omega(\Delta n)^2}{2\bar{n}S(0)} . \tag{6}$$

Here $S(0)$ is the structure factor for zero momentum transfer. Amit[31] suggested that near the critical point, when ξ becomes comparable to the radius r of the volume Ω, because of finite size scaling, the compressibility should be

$$(K_T)_{\text{eff}} = K_T \left[\frac{\xi_{\text{eff}}}{\xi} \right]^{2-\eta} \tag{7}$$

where $1/\xi_{\text{eff}}^2 = 1/\xi^2 + 1/r^2$. The exponent[27] η is equal to 0.05. There is a corresponding change in Eq. (6).

The probability of choosing a radius r (and therefore a volume $\Omega = \frac{4}{3}\pi r^3$) is P_2, where

$$P_2 \propto e^{-r/\xi} . \tag{8}$$

There are clearly physical limitations on the possible values of Δn . The final density in the volume Ω cannot be either negative or larger than that of the solid at 0 K.

There are also limitations on the choice of Ω. Both P_1 and P_2 reflect results of statistical mechanics. Therefore the number of atoms contained in Ω must be sufficiently large to satisfy this requirement. Computer simulations in volumes containing at least 108 atoms (and periodic boundary conditions) succeed in reproducing several thermodynamic properties[32,33] of a fluid. Such a volume appears therefore sufficient to satisfy some of the limitations imposed by statistical mechanics.

We are however also using both an effective mass approximation and the concept of deformation potential. It is not clear what is the number of atoms that must be in Ω to satisfy the large orbit requirement implicit in the approximation. From the theory of shallow impurity states in semiconductors[34] this number appears to be of the order of 10^3.

Since we do not have good arguments for choosing a minimum size $\Omega = \Omega_{\text{min}}$ to which the calculation should apply, we carried out our calculation considering different Ω_{min} containing on average, at each temperature, from 4 to 256 atoms. The values of Ω_{min} at the lower limit are probably inappropriate while those containing $N \sim 256$ atoms might be satisfactory. We decided, however, to show the result corresponding to different values Ω_{min} so as to give the reader an impression on how the calculated mobility depends on this parameter. Despite the expected errors when $N = 4$ the result might give us a hint of what to expect in the case of small clusters. As will be seen subsequently the total mobility is not very sensitive to the choice of N.

The mean free path Λ appropriate for the electrical conductivity is:

$$\Lambda^{-1} = \sum_{\Delta n}\sum_{r} \left[(e^{-\Omega(\Delta n)^2/2\bar{n}S(0)} e^{-(r/\xi)}) \frac{1}{\Omega} \left[\int_0^{\pi}\int_0^{2\pi} \sigma(\theta,\Delta n,\Omega,q)(1-\cos\theta) d\phi \sin\theta \, d\theta \right] \right] \times \left[\sum_{\Delta n}\sum_{r} e^{-\Omega(\Delta n)^2/[2\bar{n}S(0)]} e^{-(r/\xi)} \right]^{-1} , \tag{9}$$

where

$$\sigma(\Delta n,\Omega,q) = 2\pi \int_0^{\pi} \sigma(\theta,\Delta n,\Omega,q)(1-\cos\theta)\sin\theta d\theta = \frac{4\pi}{q^2}[\sin^2\delta_0 + 3\sin^2\delta_1 + 5\sin^2\delta_2 + 7\sin^2\delta_3 + 9\sin^2\delta_4 - 2\sin\delta_0\sin\delta_1\cos(\delta_1-\delta_0) - 8\sin\delta_1\sin\delta_2\cos(\delta_2-\delta_1) - 12\sin\delta_2\sin\delta_3\cos(\delta_3-\delta_2) - 16\sin\delta_4\sin\delta_3\cos(\delta_4-\delta_3)] . \tag{10}$$

Here s to g waves are considered with phase shifts labeled δ_0 to δ_4. The latter are calculated as in Refs. 28 and 29.

The first term in parentheses in Eq. (9) is proportional to the probability, P_1P_2 , of having a volume Ω in which there is a density fluctuation Δn. The last term is the normalization of the above probability.

In the case of argon,[7] we limited ourselves to g waves because it was found that their introduction did not change significantly the electron mobility. Similar conclusions are applicable to xenon. The high angular momentum waves (primarily f waves) are the source of the "spikes" and resonances seen in the Λ vs E curves (Figs. 2–4). For the purpose of comparison the constant mean free path associated with scattering by phonons is also indicated in the figure.

High angular momentum waves arise either from high

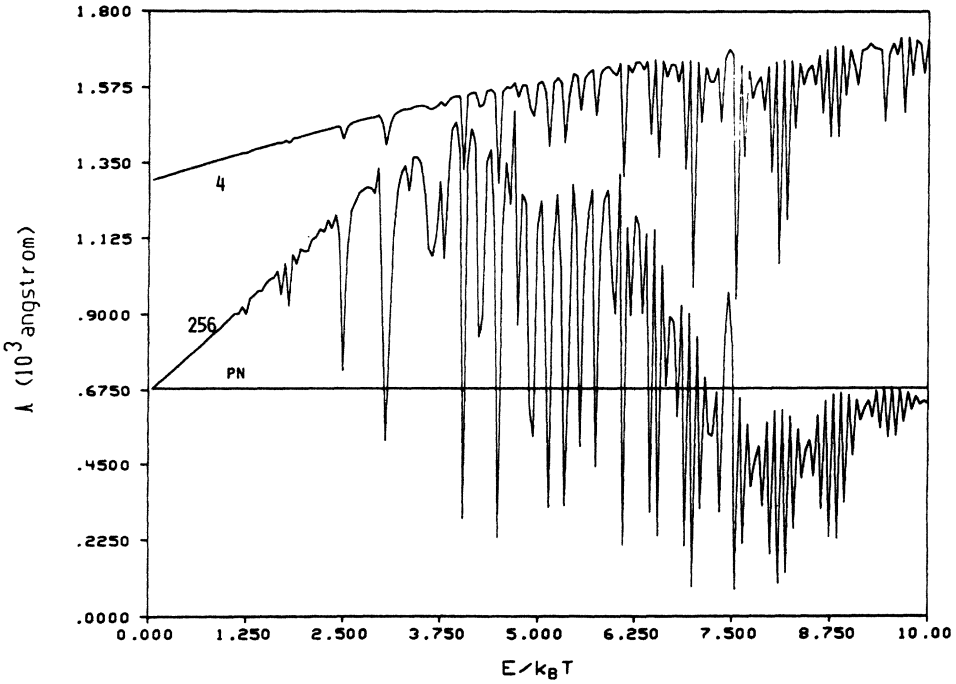

FIG. 2. Mean free path Λ as a function of electron energy. Average number of atoms in volume $\Omega_{\min}$, $N=4$ and 256. The line labeled pn indicates the mean free path associated with phonon scattering; $m^*/m_0 = 0.27$. The density is $1.302\times10^{22}\,\mathrm{cm}^{-3}$, $T=180$ K.

energy electrons or large Ω. Electrons whose energy is large compared with k_BT give minor contributions to the mobility of thermal electrons. Large volumes, Ω, are weighted by the factor P_2 that is small when $r \gg \xi$. The values of $(\Delta n)^2$ in these volumes will be significantly smaller than those corresponding to smaller radii because of the form of P_1. As a result of these considerations the effect of g waves becomes important only towards the highest electron energies we considered when the temperature is near T_c.

We have chosen to carry out sums rather than integrals because the integrals cannot be carried out analytically.

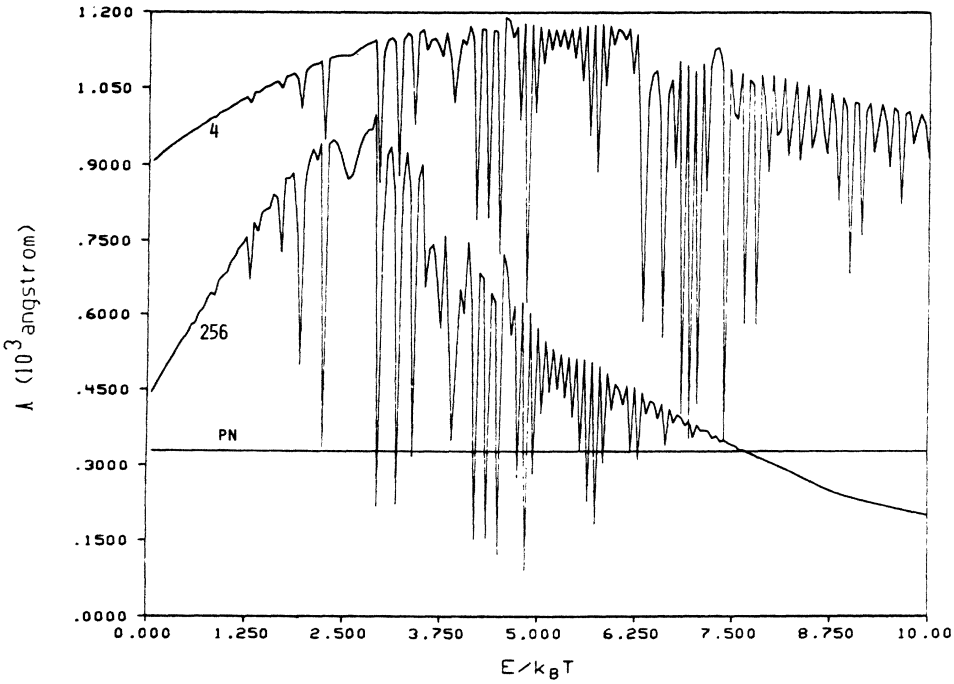

FIG. 3. Same as Fig. 2 with $T=250$ K. Density $1.028\times10^{22}\,\mathrm{cm}^{-3}$.

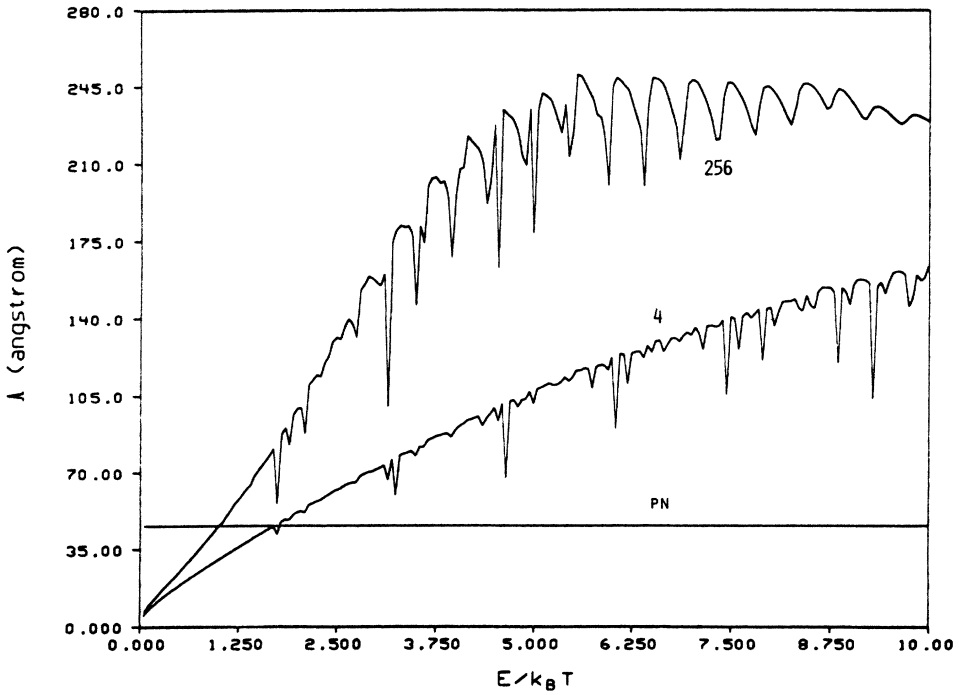

FIG. 4. Same as Fig. 2 with $T=289$ K. Density, $6.19\times10^{21}\,\mathrm{cm}^{-3}$.

The sums are instead ideally suited for a computer calculation. The chosen limits for r are such that $e^{-r_{\max}/\xi}=10^{-6}$ while $r_{\min}$ is given by $\Omega_{\min}=\frac{4}{3}\pi r_{\min}^3$.

There are physical limits on the possible densities in the volume Ω: n_s and 0. Here n_s is the density of the solid. The limits chosen for Δn are therefore either $\Delta n = n_s - n$ and $\Delta n = -n$ or a value of Δn such that P_1 decreased by 10^6, whichever is smallest. The values of r were chosen so as to progressively double Ω to $e^{-r/\xi} = 10^{-6}$. The chosen values of Δn were such that the interval between $(\Delta n)_{\max}$ and $(\Delta n)_{\min}$ was divided into 100 equal intervals. The values of q were chosen in such a way that the energy was incremented in intervals of $k_B T/20$ up to $10\,k_B T$.

The values of the correlation length ξ are known[35] above ≈ 273 K. Theory predicts[36] that

$$\xi = \xi_0 t^{\nu}(1+At^{1/2}) \tag{11}$$

where $t = (T_c - T)/T_c$. Both the exponent ν and the value of ξ_0 have been measured.[35] Their values are respectively 0.57 and 1.8 Å. The constant A is expected[36] to be ~ 1. The choice of A can only affect the mobility near the triple point.

Despite the small range of temperatures over which ξ has been measured in xenon, we shall use Eq. (11) down to the triple point. It may be worthwhile to point out that, despite the expected universality of the exponent ν its value for xenon (0.57) differs from the value measured for argon[37] (0.63). The coefficient ξ_0, although it is not supposed to be a universal constant, is nearly twice as large for xenon as for argon. The ratio of the values of ξ_0 is however much larger than what one would intuitively expect, i.e., equal to the ratio of $n_c^{1/3}$ for the two substances. The use of a critical exponent ν equal to either 0.57 or 0.63 does not however qualitatively change the calculated mobilities.

Minimal differences were obtained when comparing calculations carried out, in double precision using either the Control Data Corporation CDC 6600 (120 bits) or the Digital Equipment Corporation PDP 11-44 (64 bits). This indicates that round-off errors are not significant. The computing times for the calculation were near 13 min for the CDC when the temperature of the fluid is assumed equal to 289 K. The time on the PDP is about 7 times longer. Near the triple point the times are decreased by a factor of approximately 2.

Initially disregard the sharp spikes in the Λ vs E curves (Figs. 2–4). An overall maximum is noticeable. It moves to lower energies both with increasing the size of $\Omega_{\min}$ and with increasing temperatures. It becomes less pronounced when the temperature approaches the critical point. Similar results were found for argon[7] and were interpreted as a Ramsauer effect produced by the scattering from a density fluctuation in the volume $\Omega_{\min}$. The same interpretation applies here.

When ξ becomes comparable to r, several volumes larger than $\Omega_{\min}$ are weighted with comparable probabilities P_2. They give contributions to the mean free path whose maxima correspond to different energies. The resulting Λ vs E curve has a much less well defined extremum. This maximum disappears near the critical point if one does not use a finite size scaling correction of a form similar to that suggested by Amit.[31] Notice, however, that the pseudo Ramsauer maximum appears at energies of a few tens of meV, i.e., 10 times smaller than what is observed in the case of gases.[38]

The mobility was calculated from the above Λ vs E data using a Boltzmann distribution, i.e.,

$$\mu = \frac{21.28}{\sqrt{T}} \frac{m_0}{m^*} \frac{\sum_i \left[\frac{E_i}{k_B T}\right] \Lambda_i \exp(-E_i/k_B T)}{\sum_i \left[\frac{E_i}{k_B T}\right]^{3/2} \exp(-E_i/k_B T)} . \quad (12)$$

Figures 1 and 5 display the mobility calculated using Eq. (12) and $m^*/m_0 = 0.27$ for several values of $\Omega_{\min}$. Figure 1 corresponds to the case when $S(0)$ is calculated with the correction for finite size scaling suggested by Amit[31] [Eq. (10)]. It is instead ignored in the calculation leading to Fig. 5. The symbols on each one of the curves correspond to the densities where the mobility was calculated. In between the mobility was freely interpolated. The growth of the maximum of the mobility in correspondence to the density where $dV_0/dn = 0$ is clearly shown in both sets of curves. Although the calculation has not been extended to the critical point on account of the divergences of $S(0)$ and ξ, there is no indication that the mobility should be zero at $T = T_c$.

The fact that the mobility does not go to zero at the critical point can be understood qualitatively. The most probable value of the volume in which there is a density fluctuation is $\Omega \sim \xi^3$. In this volume, the average of the square of the density fluctuation is

$$\overline{(\Delta n)^2} \sim \frac{\bar{n} S(0)}{\Omega} . \quad (13)$$

Since near the critical point $S(0) \propto \xi^{2-\eta}$ it is clear that $\overline{(\Delta n)^2} \propto \xi^{2-\eta}/\xi^3$. Thus although both ξ and $S(0)$ diverge near the critical point, the rms fluctuation that is important for the calculation of the mobility does not diverge. What becomes large instead is the rms fluctuations in a fixed volume. Thus the scattering cross section remains finite although much larger than e.g. near the triple point where the value of $|dV_0/dn|$ is comparable. A further contribution to the finite cross section are the previously mentioned limits on the possible values of the density fluctuations.

We should consider the errors intrinsic in this kind of calculation. The use of square wells and barriers implies unphysical discontinuities of the density. This author believes that this approximation may overestimate the scattering cross section. The regular increments of Ω give rise to some periodicity in the "spikes" seen in Figs. 2 to 4. It was previously seen with the calculation of the mobility of injected electrons in argon, that if the sizes of r [Eq. (9)] are obtained from random increments of Ω, this periodicity disappears, although the calculated mobilities are not significantly affected. The use of the effective mass precludes the consideration of scattering by spatially small density fluctuations like e.g. those that would result

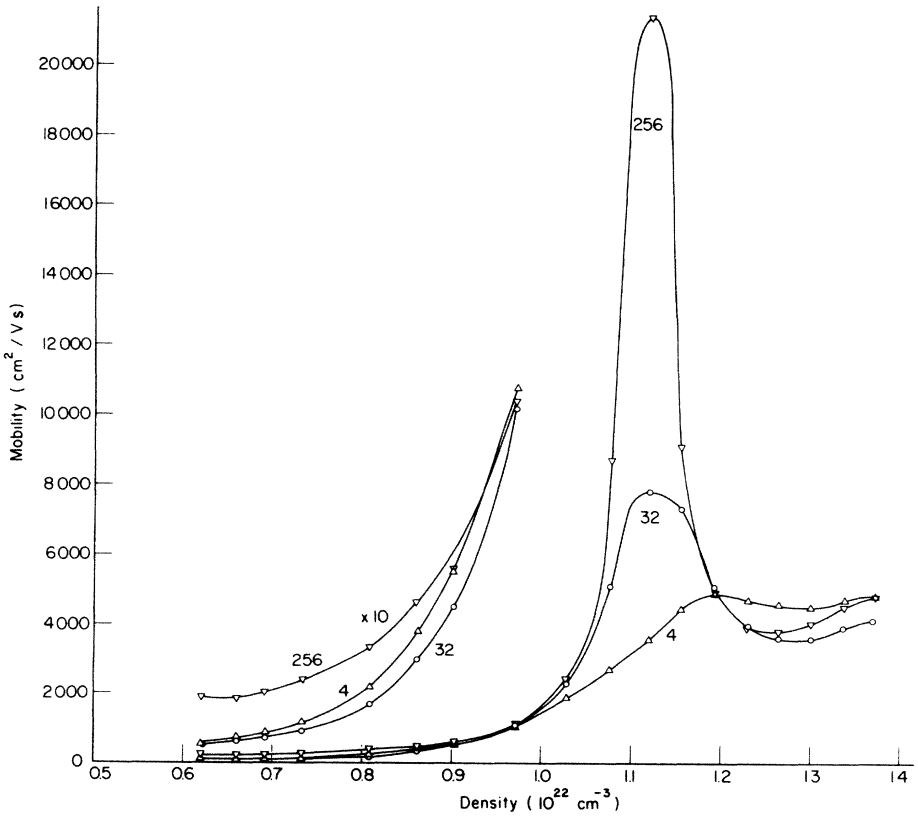

FIG. 5. Density fluctuation limited mobility corresponding to volumes $\Omega_{\min}$ containing on average $N=4$ ($\triangle$), 32 ($\bullet$), 256 (∇) atoms. No correction for small volumes; $m^*/m_0 = 0.27$. The symbols on the graph correspond to the densities where the mobilities were calculated. The thermodynamic state of the fluid corresponds to the liquid-vapor coexistence line.

from the displacement of a single atom with respect to its neighbors. It is hoped however that the results corresponding to values of Ω_{min} containing e.g. either four or eight atoms may give an indication of the possible trends. On the basis of our results, it appears that the principal effect will be a broadening of the mobility maximum possibly accompanied by a small shift towards higher densities. The errors are however difficult to quantify.

Despite the fact that both ξ and K_T are taken from experimental data[18,35,39] there are errors due to uncertainities of T_c as well as discrepancies in the relation between n and T quoted by different authors.[23–26] These errors appear to be much smaller in the case of xenon than in the case of argon. When we were in doubt about the choice between different sets of data we preferred those that better matched an extrapolation, using the theory of critical phenomena, of similar data that had been measured near the critical point.

Finally the expression for ξ_{eff} suggested by Amit is at best valid only in the vicinity of the critical point. It was however used in the calculation of P_1 down to the triple point. Its effect on the mobility can be gauged by comparing Figs. 1 and 5.

The present calculation does not take into account the coherent scattering by several density fluctuations. We do not know how to estimate its importance, but we suspect it is small on account of the long mean free paths that are calculated.

A partial justification for the choice of the effective mass and its comparison with experiment appears appropriate. The reduced mass obtained from the binding energy of the $n=1$ exciton[14] is $0.27m_0$. To assume that the reduced mass is equal to the electron mass implies the existence of a very large hole mass. Furthermore the question arises if the reduced mass obtained from the $n=1$ exciton state without the use of a quantum defect is only an upper limit of the reduced mass of the exciton.

The only guide we have for these considerations arises from calculations in solids. Resca *et al.*[40] found that for the $n=1$ uv exciton in xenon the quantum defect is nearly 10 times smaller than for higher s-like exciton states. However, when considering a similar calculation for core excitons[41] (p- and d-like as in contrast to the s-like excitons produced in the uv range), they not only find a much larger quantum defect but also a reduced mass nearly twice as large as for the s excitons. If this conclusion would be correct it would imply that the electron and hole effective masses in the solid are similar and near $0.65m_0$.

Reilly[42] estimates the effective band at the top of valence band of xenon to be near $4m_0$, while Fowler[43] calculates that for krypton the heavy hole mass is very anisotropic and varies between $3.4m_0$ and $7.1m_0$. A large hole mass is necessary to understand the existence of a self-trapped exciton[44–46] that resembles the corresponding case in alkali halides. This is particularly plausible when one recalls that e.g. xenon is isoelectronic with CsI.

Near the triple point, in order to get agreement between the calculated mobility and the experimental data,[5,47,48] the electron effective mass must be between $0.26m_0$ and $0.28m_0$. On the other hand to get agreement with the data from Ref. 49 an effective mass $\sim 0.23m_0$ is required.

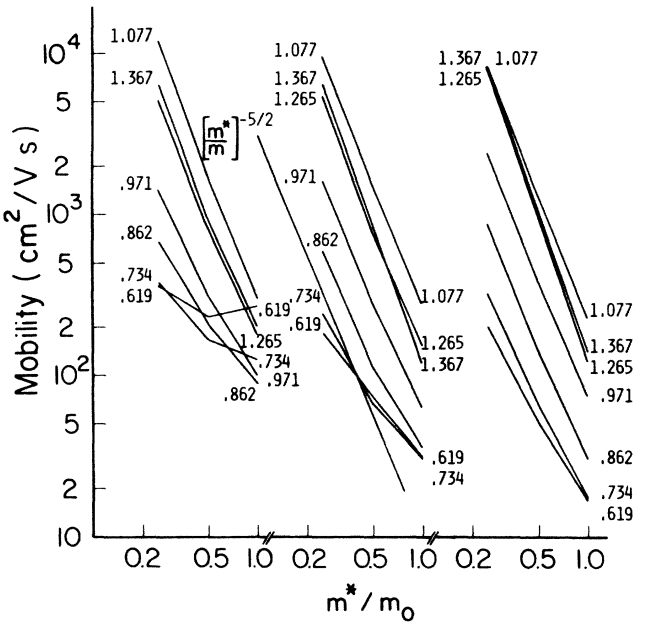

FIG. 6. Variation of the mobility as a function of effective mass for selected densities. The correction characterized by Eq. (7) has been taken into account. The different "curves" correspond to the cases when Ω_{min} contains on average $N=256$, $N=32$, or $N=4$ atoms (left to right). The mobilities were only calculated in correspondence to m^*/m_0 equal to 1, 0.5, and 0.25. The lines are just a guide for the eye. The states of the fluid correspond to the liquid-vapor coexistence line. The numbers next to each line correspond to densities in units of 10^{22} cm^{-3}.

Overall, considering the errors in the calculation of the reduced mass from exciton spectra,[14] it appears that in the liquid, the electron mass must be near $0.27m_0$ and the hole mass must be much larger to explain the observed self-trapping.[46] This does not exclude that the electron effective mass will be a function of density, that may well resemble the density dependence of V_0. Clearly the electron mass in the dilute gas must equal m_0.

The reader should refer to Ref. 7 for a further discussion comparing the results of this kind of calculation with others in the literature.

In Fig. 6 we compare the mobilities associated with scattering by density fluctuations when the effective mass is either m_0, $0.5m_0$, or $0.25m_0$. The points have been joined by lines so as to guide the eye. It is seen that, except in the case when the volume Ω_{min} contains 256 atoms, and the temperature is very near the critical temperature, the mobility varies approximately as $(m_0/m^*)^{2.5}$. This is the dependence calculated by BC using the Born approximation.

In Fig. 7 we give the combined mobility considering scattering by both phonons and density fluctuations. These are the values that must be compared with experiment.

The combined mobilities are calculated using the combined mean free paths, i.e.

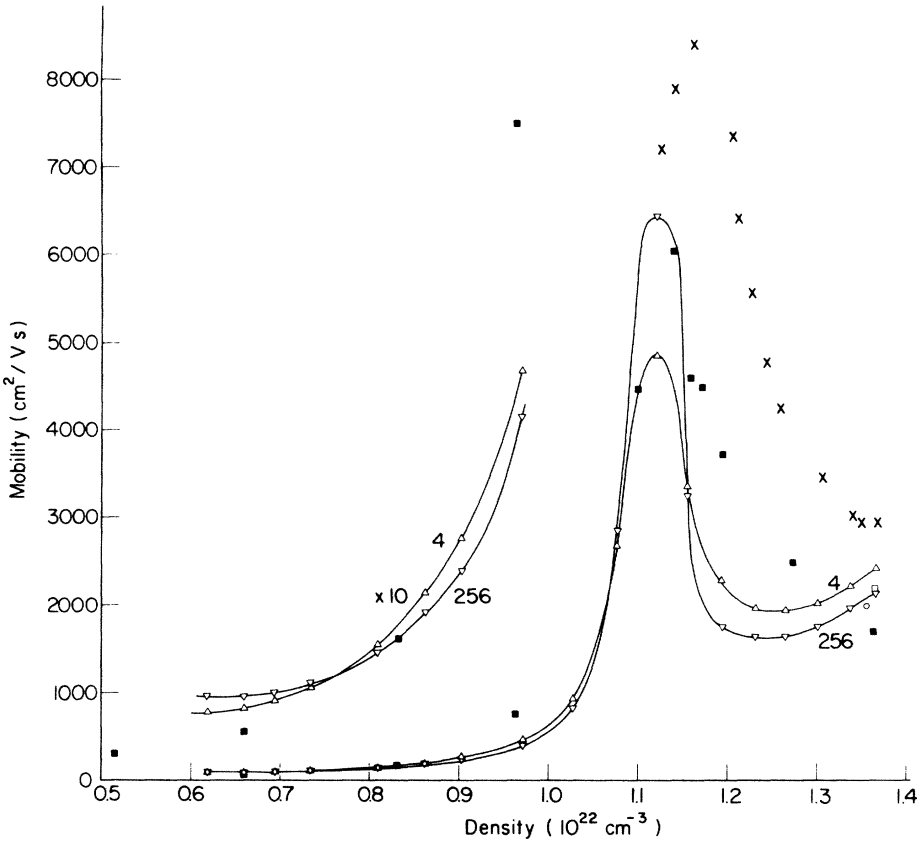

FIG. 7. Mobility calculated considering both scattering by phonons and by density fluctuations for the cases when Ω_{min} contains on average 4 (△) or 256 (▽) atoms while $m^*/m_0=0.27$. Each of the symbols corresponds to a density where the mobility was calculated. The experimental data of Ref. 47 is represented by ■, that of Ref. 5 by □, that of Ref 48 by ○, and that of Ref. 49 by ×. The state of the fluid corresponds to the liquid-vapor coexistence line.

$$\Lambda'(q) = \frac{\Lambda_p \Lambda(q)}{\Lambda_p + \Lambda(q)} \tag{14}$$

in Eq. (12). Here $\Lambda(q)$ is the mean free path arising from density fluctuations while Λ_p is the energy independent mean free path[50] arising from phonon scattering that can be calculated from Eq. (3):

$$\Lambda_p = \frac{3}{4}\left[\frac{2\pi m^* k_B T}{e^2}\right]^{1/2} \mu \, . \tag{15}$$

Experimental measurements of the time of flight mobility[5,47–49] are indicated in Fig. (7). Discrepancies between the experimental results are obvious. Insufficient information on the experimental procedures in Ref. 49 makes it difficult to judge the reliability of the data. However, the mobility of electrons in liquid xenon near the triple point was measured by other authors[1,5,48] who found results close to those in Ref. 47. The data of Ref. 47 may have experimental errors arising from the measurement of temperature, insofar as the temperature of the outer wall of the thick glass ampoule containing the sample was measured instead of the temperature of the fluid itself. If such errors are significant, they may influence the agreement between theory and experiment. The scatter of the data from Ref. 47 from those from Ref. 5 and 48 may give an indication of the experimental errors.

A better agreement between experiment and the calculation can be obtained by considering a density dependent effective mass. The presently available data does not however justify the introduction of four additional parameters to describe a variation of m^* with density of the kind found for the variation of V_0 with density.

Besides some support for the existence of localized states that influence time of flight measurements, the present calculation provides another explanation for the apparent saturation of the time of flight velocity observed at high electric fields.

In the usual theory of phonon scattering the mean free path is independent of the electron energy and the resulting drift velocity is proportional to the square root of the applied field ($F^{0.5}$).

The existence of a maximum in the variation of Λ with E due to scattering by density fluctuations implies that above a certain energy, Λ is a decreasing function of energy. Therefore, particularly at energies where the scatter-

ing by density fluctuations is dominant, the drift velocity should vary with field more slowly than $F^{0.5}$. The existence of the spikes in Figs. 2 to 4 that we interpreted as resonances associated with high angular momenta,[28] would presumably form a continuum if the radii of the density fluctuations would be varied continuously. These resonances should further decrease the mean free path of high energy electrons. The localized states that give rise to these resonances should also significantly influence the energy relaxation. A more precise statement requires a much better knowledge of the processes involving energy losses that have been completely neglected in the present calculation.

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