Quasifree electron mobility by the method of partial waves in liquid hydrocarbons and in fluid argon

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Applicability of the fluctuation model was tested in the case of *n*-hexane, *n*-pentane, *c*-hexane, 2,2-dimethylbutane, 2,2,4,4-tetramethylpentane, iso-octane, and neopentane. In our model, the quasifree electrons have been assumed to be scattered by the conduction state energy fluctuations of the liquid. These fluctuations are, in turn, described as a consequence of density fluctuations. The scattering potential is supposed to be square well like and the cross section is calculated in terms of partial waves. Averages due to the density fluctuations and the electron kinetic energy distribution are determined numerically. Except for the first three materials, the calculation reproduced the experimental mobilities with reasonable values of the square well radius, which is the only fitting parameter. Further extension of the description concerning the density dependence of the low field mobility of fluid argon has been performed. The estimated fluctuation size as a function of density increases monotonically at the minimum of the mobility in accordance with the monotonic behavior of the isothermal compressibility in the same region.

I. INTRODUCTION

In the calculation of excess electron mobility in molecular liquids such as hydrocarbons the Berlin–Nyikos–Schiller (BNS) fluctuation model[1] achieved considerable success.[2,3] The deformation potential theory developed by Basak and Cohen (BC)[4] was even able to describe the density dependence of excess electron mobility in fluid argon. Both models are based on the following physical picture.

(a) A considerable fraction of the excess electrons are moving in the quasifree state. The BNS theory assumes the coexistence of localized electrons although this distinction is not necessary in the case of fluid argon.

The Hamiltonian for quasifree electrons, $\hat{H}_{qf}$ has the following form:

$$\hat{H}_{qf} = \hbar^2 k^2/2m^* + V_0(r) \ , \tag{1}$$

where m^* and k are the effective mass and the wave number of electrons, respectively, and $V_0(r)$ is the energy of the bottom of the conduction band. This latter is a function of position coordinate having an origin in the local density fluctuations $\Delta n(r) = n(r) - \langle n \rangle$ around the average of the number density, $\langle n \rangle$ providing local deviations from the measurable mean value V_0.

(b) $V_0(r)$ can be expanded around its mean value:

$$\Delta V_0(r) = V_0(r) - V_0 = \frac{\partial V_0}{\partial n}\Delta n(r) + \frac{1}{2}\frac{\partial^2 V_0}{\partial n^2}(\Delta n(r))^2 + \cdots \ . \tag{2}$$

BNS truncate the series after the first term while BC deals with the first three terms. If the V_0 level is considered as the zero of the energy scale the Hamiltonian becomes:

$$\hat{H}'_{qf} = \hbar^2 k^2/2m^* + \frac{\partial V_0}{\partial n}\Delta n(r) + \frac{1}{2}\frac{\partial^2 V_0}{\partial n^2}(\Delta n(r))^2 + \cdots \ . \tag{3}$$

Thus the major scattering process in the description of mobility is the elastic scattering of thermal electrons by the potential fluctuations arising as a consequence of density fluctuations. Both mentioned theories handle the scattering problem with the aid of Born approximation.

(c) The derived cross section (BNS) or transition probability (BC) with thermodynamic averages over the fluctuations leads to the mean free path (BNS) or to the relaxation time (BC).

(d) Considering the thermal electron energy distribution and using the solution of the Boltzmann equation the zero field mobility can be evaluated.

A discussion of applicability of the outlined model follows.

II. CONSTRAINS FOR THE BNS AND BC THEORIES

A necessary condition for the application of fluctuation theories is to have scattering centers larger than single atoms or molecules. If the scattering objects are density fluctuations, their size must be large enough to define a local $V_0(r)$. In other words the average radius of fluctuations, A must exceed the Wigner–Seitz radius $r_s = (3\langle n \rangle/4\pi)^{1/3}$:

$$r_s \ll A \ . \tag{4}$$

The scattering potential (2) decays rapidly outside a sphere of radius A providing a cutoff for Hamiltonian (3). The electrons leaving this sphere perform quasifree translational motion eventually attaining a momentum eigenstate. This is an important condition for the application of Boltzmann equation. Furthermore, the thermal wavelength of the electrons λ_{th} has to be much smaller than their mean free path Λ. These two requirements can be stated in the form of inequalities:

$$2A \ll \Lambda \ , \tag{5}$$

$$\lambda_{th} \ll \Lambda \ . \tag{6}$$

Moreover, to use the Born approximation for the scattering, the following must prevail[5]:

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TABLE I. Characteristic lengths and experimental data used in the calculations for room temperature hydrocarbons.

	r_s (Å)	Right-hand side of Eq. (10) (Å)	Right-hand side of Eq. (11) (Å)	Λ (Å)	κ (10^{-11} cm^2/dyn)	$\frac{\partial V_0}{\partial n}$ (10^{-36} erg cm^3)	μ_F (cm^2/V s)
n-hexane	3.7	10.8	9.2	19.6	16.06	−700	27
n-pentane	3.6	9.1	10.9	30.7	24.00	−464	43
c-hexane	3.5	7.6	12.9	29.9	11.40	−573	42
2, 2diMe-butane	3.8	2.4	41.9	316	16.06	−334	440
2, 2, 4, 4-tetraMe-pentane	4.1	1.9	52.8	452	11.50	−465	630
2, 2, 4-triMe-pentane	4.0	3.3	29.6	103	14.01	−532	145
2, 2diMe-propane	3.6	1.0	98.5	317	29.40	−142	440

$$|\Delta V_0| \ll \hbar^2 k/m^* A \tag{7}$$

or

$$|\Delta V_0| \ll \hbar^2/m^* A^2 \ . \tag{8}$$

Far from the extrema of $V_0(n)$ the first term in the series (2) might be good approximation for ΔV_0. Δn can be estimated with the basic relation:

$$\frac{\langle \Delta n^2 \rangle}{\langle n \rangle^2} = \frac{k_B T \kappa}{V} \ , \tag{9}$$

where κ is the isothermal compressibility and $V = 4A^3\pi/3$ is the volume of the fluctuation. Combining Eqs. (2), (7), (8), and (9) either:

$$A \gg \frac{m}{4\pi\hbar^2}\left(\frac{\partial V_0}{\partial n}\right)^2 \langle n \rangle^2 \kappa \tag{10}$$

or

$$A \ll \frac{4\pi\hbar^4}{3k_B T\, m^2}\left(\frac{\partial V_0}{\partial n}\right)^{-2} \langle n \rangle^{-2} \kappa^{-1} \tag{11}$$

is required to justify the use of the Born approximation. However, when the Born approximation is used, A (the parameter characterizing the average extension of the fluctuation potential) vanishes from the final expressions. It is thus impossible, in general, to control the satisfaction of inequalities (10) and (11). m^*, the effective mass, is approximated by m, the rest mass of the free electron.

The constraints of the model are thus summarized in the inequalities (4), (5), (6), and (10) or (11). The characteristic lengths appearing in them are displayed in Table I. The semiempirical calculation of $\partial V_0/\partial n$ proposed by BNS[1] was applied. Similarly the characteristic lengths for liquid argon under a pressure of 70 atm studied by BC are surveyed in Table II. In this case the derivatives $\partial V_0/\partial n$ were obtained by numerical differentiation of the measured $V_0(n)$ relationship.[6] Values for the isothermal compressibilities are taken from Refs. 1 and 7. The mean free paths were calculated from quasifree mobilities for hydrocarbons and from experimental mobilities for argon[7] using the relation:

$$\mu = \frac{2e}{3}\left(\frac{2}{\pi m k_B T}\right)^{1/2} \Lambda \ . \tag{12}$$

Examining Table I, it is obvious that in case of n-hexane, n-pentane, and cyclohexane the applicability of Born approximation is in conflict either with the constraint (4) inherent in the fluctuation model or with the inequality (5), a necessary condition for the use of the Boltzmann equation. Concerning the other four hydrocarbons and liquid argon there is no conflict with the derived results and the system of inequalities in Eqs. (4), (5), (10), and (11). Thus the applicability of Born approximation can be justified only after estimating the average size of the fluctuations A.

The derivation of $\partial V_0/\partial n$ is the crucial point in both former models. The BNS theory starts from the semiempirical Wigner–Seitz method performing a straightforward derivation of $\partial V_0/\partial n$.[1] Using the polarizability of the molecules, the density and V_0 of the liquid the derivative can be estimated. In consequence the BNS theory has no fitting parameter.

In contrast the BC model contains the derivative $\partial V_0/\partial n$ as an adjustable function of $\langle n \rangle$ providing significant flexibility in the description of the density de-

TABLE II. Characteristic lengths and experimental data used in the calculations for fluid argon at 70 atm.

T (K)	$\langle n \rangle$ (10^{22} cm^{-3})	r_s (Å)	Right-hand side of Eq. (10) (Å)	Right-hand side of Eq. (11) (Å)	Λ (Å)	κ (10^{-11} cm^2/dyn)	$\frac{\partial V_0}{\partial n}$ (10^{-36} erg cm^3)	μ_0 (cm^2/V s)
158.3	1.03	2.9	126	1	663	1955	−97	1266
157.3	1.09	2.8	104	2	761	1492	−94	1458
154.0	1.23	2.7	46	4	859	708.9	−84	1663
152.9	1.265	2.7	39	3	801	587.5	−80	1557
152.1	1.29	2.6	34	6	732	515.0	−78	1427
149.9	1.35	2.6	20	9	548	378.5	−67	1076
149.1	1.37	2.6	16	12	486	336.0	−61	957
142.1	1.51	2.5	10	20	253	179.2	62	510
121.1	1.80	2.4	5	53	155	54.36	63	340

pendent mobility. However, having an adjustable function may conceal the limitations of a model. Recently, the density dependence of V_0 in fluid argon was measured by Allen and Schmidt.[6] To obtain estimates for $\partial V_0/\partial n$ from their experimental data, we fitted a power function to the measured points and the derivative was evaluated using this empirical formula. This procedure helped to avoid the extreme fluctuations in the derivative.

Difficulties lying in the measurement of $V_0(\langle n\rangle)$ affect unfavorably the accuracy of $\partial V_0/\partial n$. The error of V_0 values measured in liquid argon is less than $\pm 4.8 \times 10^{-14}$ erg[6] which in consequence produces a 50% error in the derivative. Thus the values in Table II for the right-hand side of Eqs. (10) and (11) can only be expected to be order of magnitude estimates.

In the following section, a simple generalization of former models will be reviewed. Because the Born approximation is replaced with the method of partial waves, constraints (10) and (11) are eliminated. Moreover, this modification makes it possible to determine the average size of scattering density fluctuations, the only fitting parameter of present model. However, this parameter will be a function of density and will diverge at the singularity of the isothermal compressibility.

Analyzing Eqs. (10) and (11), one can predict where the Born approximation will break down. Near the extremum of the function $V_0(\langle n\rangle)$, Eqs. (10) and (11) become meaningless giving rise to constraints containing higher order derivatives of V_0. On the other hand, near the singularity of the isothermal compressibility, Eqs. (10) and (11) will conflict with Eqs. (5) or (4). Thus, near the critical point the Born approximation fails and the whole fluctuation theory approach breaks down.

III. MOBILITY OF QUASIFREE ELECTRONS WITH THE METHOD OF PARTIAL WAVES

The particular scattering problem involved in the above description is the elastic scattering of quasifree electrons with thermal wave number, k on a spherical potential well or barrier depending on the actual sign of ΔV_0

$$\Delta V_0(\mathbf{r}) = \begin{cases} \dfrac{\partial V_0}{\partial n}\,\Delta n(\mathbf{r}) + \dfrac{1}{2}\dfrac{\partial^2 V_0}{\partial n^2}\,(\Delta n(\mathbf{r}))^2 + \cdots, & \text{if } |\mathbf{r}| \le A \ , \\ 0 \ , & \text{if } |\mathbf{r}| > A \ . \end{cases} \tag{13}$$

By solving the radial Schrödinger equation, the phase shifts, δ_l can be derived[8]

$$\delta_l(E, \Delta V_0, A) = \mathrm{arc}\,tg\left[\frac{kj_l(k^*A)\,j_l'(kA) - k^*j_l(kA)\,j_l'(k^*A)}{kj_l(k^*A)\,y_l'(kA) - k^*j_l'(k^*A)\,y_l(kA)}\right] , \tag{14}$$

where l is the angular momentum quantum number, j_l and y_l denote spherical Bessel functions of the first and second kind, respectively, and j_l', y_l' stands for their derivatives. E is the thermal kinetic energy of the electrons and $k^* = (2m(E - \Delta V_0))^{1/2}$ may be real or imaginary. The scattering amplitude for the transition between states of momentum k and k′ is

$$f_{\mathbf{k},\mathbf{k}'} = \frac{1}{k}\sum_{l=0}^{\infty} \sqrt{4\pi(2l+1)}\, e^{i\delta_l} \sin\delta_l\, Y_l^0(\theta) \ , \tag{15}$$

where the scattering angle, θ is related to the momentum transfer, $\mathbf{k} - \mathbf{k}'$ by

$$1 - \cos\theta = 2\left(\frac{k' - k}{2k}\right)^2 , \tag{16}$$

$Y_l^0(\theta)$ denotes the usual spherical harmonics. Making use of the orthogonality relations for the spherical harmonics, the total cross section $\sigma(E, \Delta V_0, A)$ appears in the usual form:

$$\sigma(E, \Delta V_0, A) = \frac{4\pi}{k^2}\sum_{l=0}^{\infty} (2l+1)\sin^2\delta_l \ . \tag{17}$$

Averaging the cross section over the fluctuations yields the mean free path, Λ for electrons with kinetic energy E:

$$\Lambda^{-1}(E, A) = \frac{1}{(2\pi\langle n\rangle^2 k_B T \kappa V)^{1/2}} \times \int_0^{\infty} \sigma(E, \Delta V_0, A)\exp\left(-\frac{(\Delta n)^2 V}{2\langle n\rangle^2 k_B T \kappa}\right) dn \ . \tag{18}$$

Far from the critical point, the exponential decays rapidly allowing the truncation of the series in Eq. (17) at less than ten terms.

The low field mobility is calculated so the electron energy distribution is not far from the Maxwell distribution. Thus the mobility will have the form[10]

$$\mu = \frac{2e}{3}\left(\frac{2}{\pi m k_B T}\right)^{1/2} \int_0^{\infty} x\Lambda(x, A)\, e^{-x}\, dx \ . \tag{19}$$

The notation $x = E/k_B T$ has been introduced.

The average radius of the fluctuations was determined by the method of successive approximation. Starting from a suggested value of A the electron mobility was calculated and compared to the experimental value. The input data of the calculation were the following. The density, temperature, and isothermal compressibility of the liquid and the density derivative of the energy of conduction band, $\partial V_0/\partial n$ which was estimated semiempirically as above. In order to obtain the electron mobility first the scattering problem had to be solved. Supposing that electrons with energy E are scattered on potentials generated by density fluctuations, Δn the nonvanishing phase shifts were determined. The scattering cross section calculated on this basis was a function of the extension and amplitude of the density fluctuations and the energy of electrons. Averaging this cross section throughout the V_0 fluctuations generated by density variations provided the mean free path of the electrons. This mean free path was still a function of electron energy which was eliminated by averaging over the Maxwell distribution. Finally the mean free path was converted to mobility by Eq. (12) depending on a single parameter A.

IV. DISCUSSION

Extensive calculations were carried out to determine error bounds for the estimated A values. If the experimental mobilities were distorted with 10% error, the induced change in the corresponding A never exceeded 5%. This means that the estimated fluctuation radius is not extremely sensitive to possible errors in mobility.

Comparison of the calculated and measured mobilities provides the possibility to estimate A. The values obtained for the seven hydrocarbons are summarized in Table III. As expected, values for n-hexane, n-pentane, and cyclohexane do not meet the requirements stated in Eqs. (10) or (11), therefore negating the applicability of the Born approximation. In the case of the other four hydrocarbons, Eq. (10) is fulfilled thus justifying the use of the Born approximation.

It is worthwhile here to draw attention to an interesting qualitative correlation. If Eq. (11) is satisfied then the potential well is too shallow to accommodate bound states. Comparing this condition and the localization probabilities P one can find a correlation between the violation of Eq. (11) and the deviation of P from unity. The localization probabilities[1] are displayed in Table III. n-hexane, n-pentane, and cyclohexane show high localization probabilities while 2, 2-dimethyl-propane has a relatively low value of P and good fulfilment of Eq. (11). This correlation may refer to the mechanism of trap formation. In other words, the temporary existence of negative energy states in fluctuating potential wells serves as necessary condition for electron trapping.

However, the breakdown of the Born approximation is not the only limitation for the calculation of electron mobility in n-hexane, n-pentane, and c-hexane. The average diameter of potential fluctuations $2A$ cannot be neglected compared to the mean free path or else the inequality (5) would be violated. This means that within the fluctuation approach, the Boltzmann equation cannot be applied. Equation (6) cannot be satisfied with a λ_{th} of 60 Å for room temperature electrons.

V_0 measurements in fluid argon,[6] krypton, and xenon[10] show a reasonable displacement in the position of minimum of the $V_0(\langle n\rangle)$ curve from the maximum of the $\mu(\langle n\rangle)$ data. Thus, the position of maximum in $\mu(\langle n\rangle)$ is not exclusively governed by the shape of $V_0(\langle n\rangle)$, i.e., by the electronic structure of the liquid but also by the $A(\langle n\rangle)$ relationship, i.e., by the dynamic geometrical structure of the liquid. As an example in the case of liquid argon under a pressure of 70 atm the maximum in the mobility is at a number density of 1.2×10^{22} cm^{-3},[7] the minimum in $V_0(\langle n\rangle)$ is at 1.4×10^{22} cm^{-3},[6] while the extremum of the isothermal compressibility is at $<0.94\times10^{22}$ cm^{-3}. Apparently the extremum of $\mu(\langle n\rangle)$ occurs between those of $V_0(\langle n\rangle)$ and $\kappa(\langle n\rangle)$.

TABLE III. Average size of fluctuations and the localization probability in various hydrocarbons.

	A (Å)	P
n-hexane	11	0.998
n-pentane	14	0.997
c-hexane	13	0.995
2, 2-diMe-butane	28	0.972
2, 2, 4, 4-tetraMe-pentane	30	0.962
2, 2, 4-triMe-pentane	18	0.952
2, 2-diMe-propane	18	0.841

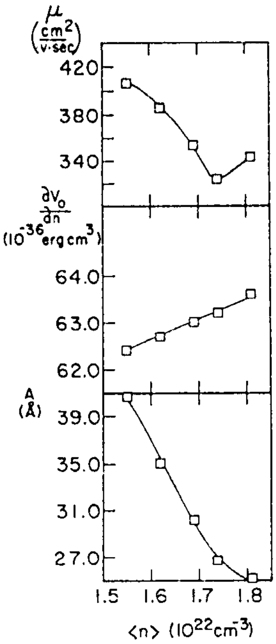

FIG. 1. Number density dependence of mobility, $\partial V_0/\partial n$, and the average fluctuation size in fluid argon at 70 atm.

To demonstrate the effect of fluctuation size, the mobility was calculated in the density range $(1.55-1.81)\times10^{22}$ cm^{-3}. In this range $\mu(\langle n\rangle)$ curve displays a *minimum*, however, $\partial V_0/\partial n$ is a monotonic nonzero function. Since κ in this region is monotonic as well, one expects to describe the minimum in $\mu(\langle n\rangle)$ with a monotonic average fluctuation size (as a function of density). The results are shown in Fig. 1. Restricted experimental data on $\partial V_0/\partial n$ may cause errors in the actual value of $A(\langle n\rangle)$ but it will not change the monotonicity of the function. Approaching the maximum of $\mu(\langle n\rangle)$ the number of partial waves which must be involved will increase sharply. This and the sparse information available about $\partial V_0/\partial n$ are the current limitations on the domain of investigations.

V. SUMMARY

After a critical survey of the applicability of the Born approximation in fluctuation models of quasifree electron mobility, simple constraints have been established far from the extrema of $V_0(\langle n\rangle)$. This allowed the prediction of the inappropriateness of the above-mentioned approach in the case of n-hexane, n-pentane, and c-hexane. The introduction of the method of partial waves instead of the Born approximation allow the estimation of an average fluctuation size. Calculations around the mobility minimum in liquid argon provided a monotonic average fluctuation size function according to expectations.

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