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Self-Trapped States of an Electron in a Structurally Disordered System*

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Electrons injected into structurally disordered materials may occupy free-electron-like states in a conduction band, band-tail states, some of which will be nondiffusing and are thus localized in the Anderson sense, and, finally, self-trapped states. Eggarter has recently described the first two types of states with specific application to He gas. In the present work, the self-trapped states are discussed. Specific calculations are carried out for He, H_2, N_2, and Ne in the ideal-gas approximation. Virial corrections are demonstrated for He gas at 4.2 K. Available experimental results, for the four materials mentioned, are discussed in the context of the theory presented and it is shown that for certain regimes of density and temperature self-trapped states exist and play an important role in determining the observed transport parameters. Further calculations and experiments are suggested to probe in detail the characteristics of all the states available to electrons in the type of disordered materials discussed.

I. INTRODUCTION

Gases and liquids whose constituents repel electrons are examples of structurally disordered materials. The states available to electrons in such materials encompass a spectrum which includes delocalized states in a wide conduction band and states localized, in the Anderson sense,[1] by potential fluctuations (due to density fluctuations). These states have been recently discussed by Eggarter,[2] with specific application to He gas. A third class of states also exists which will be discussed at some length in this work: These states are due to self-trapped electrons. They have been called "electron bubbles," in the context of He, H_2, and Ne, and it will be shown that they are also expected in liquid N_2. Associating these states with the word "polaron" might be helpful in understanding their properties in a wider context.

Experimentally, gases and liquids whose constituents repel electrons (the common ones are[3,4] He, Ne, H_2, and N_2) offer quite attractive properties since they can be obtained with a high degree of purity. The equation of state of these materials and the interatomic (intermolecular) interactions have been deeply studied so that they are excellently characterized, in contrast to some other amorphous materials where the characterization is much more difficult. Variability in density, temperature, and the strength of the interatomic interactions afford the opportunity of being able to control which electron states, in these materials, will play a dominant role in determining transport characteristics. Some measurements of electron drift velocity have already been performed in experiments to be discussed in some detail later. Information can be obtained not only from zero-field drift-mobility measurements but also from higher-field effects and Hall-mobility determinations.

This paper will briefly review the formalism due to Eggarter[2] suggesting one change in his methods. Self-trapped electron states will be introduced and integrated into the above treatment. Zero-field drift-mobility formulas will be developed for a system in thermodynamic equilibrium including fluctuations which characterize the disorder. These formulas admit generalization to the case of non-negligible external fields. Calculations will be presented for specialization of the formalism to a virial fluid which interacts with electrons as a collection of hard-core scatterers (this characterization is probably quite appropriate in part of the region available experimentally for He, Ne, H_2, and N_2). Specific results are obtained for these four materials in the ideal-gas approximation, and improvements are examined in He gas as a particularly appropriate case. Finally, the available experimental results will be discussed in the context of the formalism developed.

II. MODEL

The material of interest is a structurally disordered one. Following Eggarter,[2] the material is imagined to be divided into cells of volume L^3, such that if an electron were added to the material it would interact within one cell with the remaining volume of the material $(\Omega - L^3)$ being unaware of the presence of the electron for all practical purposes. The L^3 localization is due to the fact that scattering forces the electron into a wave packet. Intrinsic potential fluctuations are taken into account by specifying a distribution of the number of cells with a given potential; by assumption the electron does not influence this distribution. Within a cell, intrinsic fluctuations are neglected on the assumption that the electron will adiabatically average over them and the only inhomogeneities will be due to electron-material correlations. However, it will be assumed that L^3 is large enough so that correlations within the cell are not apparent to the material outside the cell. The above model has decoupled the electron from the intrinsic fluctuations for purposes of finding the states of the electron, though the decoupling does not hold in calculating transport parameters where the cell environment may influence the transport.

The states of the electron-material system can now be specified by a list consisting of the cell (i), containing the electron, characterized by L and the interaction potential (V_i); the configuration of the material within the cell (labeled by R) which depends parametrically on the electron probability distribution (labeled by its energy E); the quantum numbers (K), if any, of the $\{E, R\}_i$ system, such as any center-of-mass motion; and the specification of the state of the material outside the ith cell, labeled by e.

By assumption e and V_i depend on the material properties only, and are uncorrelated; $\{E, R\}_i$ are to be determined self-consistently in the Born–Oppenheimer approximation, while K are to be determined by treating the $\{E, R\}$ system as an entity. Appropriate averages must be performed to calculate specific properties.

Assuming thermodynamic equilibrium, the density of states n will be populated in proportion to a Boltzmann factor B. Thus the partition function is

$$Z = \sum_{i,e,K,R,E} n(i, K, E, R, e) B(i, K, E, R, e) \tag{1a}$$

and, using the decoupling assumptions,

$$Z = \sum n(i, K, E, R) B(i, K, E, R) \sum_e n_e B_e \equiv Z_{\text{cell}} Z_{\text{out}} \ . \tag{1b}$$

The Boltzmann factor would also contain nonnegligible external fields, if any.[5] To calculate some observable property (A), such as the zero-field drift mobility, an average must be performed over all quantum numbers γ':

$$\bar{A} = Z^{-1} \sum_{\gamma'} A_{\gamma'} n_{\gamma'} B_{\gamma'} = Z_{\text{cell}}^{-1} \sum_{\gamma} \left(Z_{\text{out}}^{-1} \sum_e A_{\gamma'} \right) n_\gamma B_\gamma \ . \tag{2a}$$

The dependence of A_γ on e will account, in the case of the mobility, for percolation and such.[2] Since the cell i and its environment e are uncoupled, the sum over e may be in principle performed so that γ' contains e but γ does not. So that, with an obvious definition,

$$\bar{A} = Z_{\text{cell}}^{-1} \sum_{\gamma} A_\gamma n_\gamma B_\gamma \equiv \frac{I(A)}{I(A=1)} \ . \tag{2b}$$

The sum over cells (i) can be transformed into an integral over the interaction potential (V) between the electron and the average material in the cell, if we assume a distribution function $P(V)$ for the probability of finding a cell with potential V:

$$\sum_i \to \int dV\, P(V) \frac{\Omega}{L^3} \ ,$$

where Ω is the total volume of the system. Along with Eggarter, we shall assume a Gaussian distribution for $P(V)$ about the average potential for the entire system $(\bar{V})$ with a mean deviation σ_V,

$$P(V) = (1/2\pi\sigma_V^2)^{1/2} \exp\{-\tfrac{1}{2}[(V - \bar{V})/\sigma_V]^2\} \ . \tag{3}$$

In the specific case where the material is a virial fluid, Eq. (3) corresponds to a Gaussian distribution of the number of particles (N) in the volume L^3. Then

$$\sigma_N^2 = \bar{N}kT \left(\frac{\partial P}{\partial \rho} \bigg|_{\bar{N},T} \right)^{-1} = \frac{\bar{\rho} L^3}{1 + 2B_V \bar{\rho}} = \sigma_\rho^2 L^3 \ , \tag{4}$$

where $\bar{N}/L^3$ is the average system density $\bar{\rho}$, P is the pressure, and B_V the virial coefficient. Therefore

$$\sigma_V = \frac{\partial V}{\partial \rho} \bigg|_{\bar{\rho}} \sigma_\rho = \frac{\partial V}{\partial \rho} \bigg|_{\bar{\rho}} \left(\frac{\bar{\rho}}{1 + 2B_V \bar{\rho}} \right)^{1/2} L^{-3/2} \ , \tag{5}$$

where V is the potential appropriate to the density ρ. It will be later shown that σ_V/kT is the crucial parameter. Clearly, it is necessary to choose L judiciously. It is in the choice of L that a change in Eggarter's treatment will be suggested.

Eggarter chose an energy-dependent function for L consisting of a constant times the de Broglie wavelength of an electron with energy E. The constant (c), assumed to be of order one, had to be varied with temperature in order to fit the experimental mobility measurements.[5] This variation

TABLE I. Density-dependent characteristics for He and N_2: $L_E(\bar{V}) = \lambda_{dB}(\bar{V})$; $L(\rho) = (\rho\sigma)^{-1}$; $\bar{V}$ is the Wigner–Seitz potential for the quoted density (ρ). σ_V are the rms variances of the potential fluctuations obtained using the two sampling lengths. A scattering length of 0.62 Å is used; see Ref. 3.

ρ ($10^{21}/\text{cm}^3$)	$\bar{V}$ (K)	$L_E(\bar{V})$ (Å)	$L(\rho)$ (Å)	$\rho L^3(\rho)$	$\sigma_V(\bar{V})/\bar{V}$ (10^{-2})	$\sigma_V(\rho)/\bar{V}$ (10^{-2})
1	422	64.4	207	8870	2.89	0.503
1.6	702	49.9	129	3440	3.40	0.815
2	896	44.2	103	2180	3.67	1.03
2.6	1200	38.2	79.6	1310	4.05	1.35
3	1400	35.3	69.0	986	4.27	1.57
4	1940	30.0	51.8	554	4.79	2.12
5	2500	26.4	41.4	335	5.25	2.67
6	3092	23.8	34.5	246	5.67	3.25

can be reinterpreted as a weak dependence of c on fluid density. The important length is L $(\bar{V})$ since the energy range of fluctuation is of order 1% $\bar{V}$ for the cases considered. For reasons to be discussed later, it seems more reasonable to choose as a sampling length one which depends on the scattering of the electron, rather than on its de Broglie wavelength. Such a length is the momentum-exchange mean free path $L(\rho) = (\rho\sigma)^{-1}$, where the length at the average conditions would be the important one. For densities of interest in He at 4.2 K, $L(\rho) \sim 2.5L$ $(\bar{V})$ $(c = 1)$ with a slightly different ρ dependence. Some specific numbers are given in Table I.

A. Density of States

Within a cell of volume L^3 a space-average potential $\langle V \rangle$ is felt by an electron. In the sense of the adiabatic Born–Oppenheimer separation, the average electron wave function will determine the configuration of the material within the cell (R). In turn, this configuration gives rise to a potential $V_R(r)$, which can vary as a function of position within the cell, which is felt by the electron. This description calls for a self-consistent adiabatic solution of coupled equations for the electron and the material within the cell, which shall be discussed later in a specific case. For now, assume that an envelope wave function for the electron can be found, $\psi_E(r)$, with eigenenergy E which depends on the equilibrium material configuration R.

As far as the electronic density of states is concerned, there are three interesting regimes.

(i) $E \gg \langle V \rangle$: It is reasonable to assume, subject to later verification, that the material configuration corresponds to the average one in the absence of the electron. Thus, the electron is delocalized within the cell. If L is large enough, the potential on any atom owing to the electron is weak. Hence, for this energy regime, the electron density of states, within the ith cell, is taken to be the one appropriate to a free electron:

$$2L^3 \frac{(2m)^{3/2}}{4\pi^2\hbar^3} (E - V_i)^{1/2} .$$

As shown by Eggarter[2] averaging the above over all cells gives rise to a conduction band with a low-energy tail. Then, invoking "percolation" theory, he shows that some of the states in the tail will not diffuse, so that they are localized in the Anderson sense. The extent of the band tailing depends on the mean intrinsic potential fluctuations from cell to cell as compared to kT; i.e., σ_V/kT is the crucial parameter.

(ii) $E \ll \langle V \rangle$: As will be shown, the equation for the electron in the cell demands that if states exist then they must be localized within the cell. It shall be assumed, in accordance with specific results to be obtained later, that the size of the localization region is small compared to L, but encompasses a region normally occupied by several atoms. Then, the envelope function and adiabatic potential concepts are still tenable with some reservations. This energy regime belongs to the self-trapped electrons ("bubbles" or polarons also being appropriate concepts). The density of states appropriate to this regime must take into account not only the electron, in a discrete eigenstate, but the fact that the localization may take place anywhere within L^3. If the localization region is small, then the entity may be characterized by a total effective mass m^* and a center-of-mass kinetic energy K. This characterization leads to a density of states within the ith cell of

$$2L^3 \frac{(2m^*)^{3/2}}{4\pi^2\hbar^3} K^{1/2}\delta(V_i - E - F_R - \alpha_R) .$$

Where the center of mass is treated as a point particle, F_R is the extra energy of the material due to the local distortion, and α_R is the total binding energy due to an electronic binding: $\alpha_R + F_R$, which must be positive by definition. $\alpha_R > 0$ corresponds to a stable self-trapped state, and $\alpha_R < 0$ to a metastable one which may be populated thermodynamically since it is, by definition, a self-consistent solution of the adiabatic equations if it exists at all. It shall be assumed, for simplicity, that there is only one bound state; otherwise, a sum over the possible values of α_R should be included. This part of the density of states, when averaged over all cells, gives rise to a distribution of states, since the δ functions are smeared by fluctuations over an energy range $\sim \sigma_V$.

(iii) $E \simeq \langle V \rangle$: This is a difficult regime to treat since, taking into account the motion of the atoms, the separation of electronic states into bound and unbound ones is not sharp. It will be assumed that this regime is narrow in energy, and thus that the errors introduced by its neglect will not cause serious error to properties depending on averages.

B. Formal Averages

In summary, the product of the cell density of states and the Boltzmann factor is

$$n_\gamma B_\gamma = \theta(E - V_i) 2L^3 \frac{(2m)^{3/2}}{4\pi^2\hbar^3} (E - V_i)^{1/2} e^{-E/kT} \delta_{R,0}\delta_{K,0} + \theta(V_i - E) 2L^3 \frac{(2m_R^*)^{3/2}}{4\pi^2\hbar^3} K^{1/2} \times \delta(V_i - E - F_R - \alpha_R) e^{-(E+F_R+K)/kT} \delta_{R,\alpha} . \qquad (6)$$

The Kronecker δ's in the first term indicate that the material configuration R is the uniform one and that the quantum number K is not applicable; in the second term, R is to be the self-consistent configuration having binding energy α.

To calculate averages one needs

$$I(A) = \sum_\gamma A_\gamma n_\gamma B_\gamma = \int_0^\infty dE \int_0^\infty dV P(V) \sum_{R,K} A_\gamma n_\gamma B_\gamma , \qquad (7)$$

where E includes F_R as well as the electronic energy. To do the algebra for the self-trapped states, a potential $V_p = E + \alpha_V$ may be defined such that it gives rise to a state bound by $V_p - E$. Further, since we are only interested in V close to $\overline{V}$ because $\sigma_V/\overline{V} \ll 1$, α_V may be expanded about $\overline{V}$ to terms linear in the deviation. The integral over V is used to eliminate the δ function and appropriate changes of variables yield a final result

$$I(A) = \left(2\Omega \frac{(2m)^{3/2}}{4\pi^2\hbar^3} (kT)^{3/2} e^{-\overline{V}/kT}\right) J(A) , \qquad (8a)$$

with

$$J(A) = \int_0^\infty y^{1/2} e^{-y} A\left(y = \frac{E - \overline{V}}{kT}\right) dy + \int_{-\infty}^\infty \left(\frac{\sigma_V}{kT}\right)^{3/2} e^{-x\sigma_V/kT} G(x) A\left(x = \frac{E - \overline{V}}{\sigma_V}\right) dx + \frac{\sqrt{\pi}}{2} \left(1 - \frac{\partial\alpha}{\partial V}\bigg|_{\overline{V}}\right) \exp\left\{\frac{\alpha_{\overline{V}}}{kT} + \frac{1}{2}\left[\left(1 - \frac{\partial\alpha}{\partial V}\bigg|_{\overline{V}}\right)\frac{\sigma_V}{kT}\right]^2\right\} H_{\overline{R}} . \qquad (8b)$$

The $G(x)$ describes the redistribution of states owing to intrinsic fluctuations,

$$G(x) = (1/2\pi)^{1/2} \int_0^\infty z^{1/2} e^{-(z-x)^2/2} dz - x^{1/2}\theta(x) ; \qquad (9)$$

it is shown in Fig. 1. Naturally, $\int_{-\infty}^\infty G(x)\, dx = 0$.

$H_{\overline{R}}$ is an average due to fluctuations of the properties of the self-trapped states:

$$H_{\overline{R}} = (1/2\pi)^{1/2} \int_{-\infty}^\infty [(m_R^*/m)^{3/2} A_R] e^{-z^2/2} dz , \qquad (10)$$

where R indicates a self-trapped state in a cell average potential V and

$$V - \overline{V} = \sigma_V \left[z - \left(1 - \frac{\partial\alpha}{\partial V}\bigg|_{\overline{V}}\right)\frac{\sigma_V}{kT}\right] . \qquad (11)$$

It has been assumed that A_R is independent of K and that $\overline{V}/\sigma_V \sim \infty$.

To recapitulate, the meaning of the three terms in $J(A)$ is physically interpretable. The first is the usual one for free electrons in a wide conduction band; the second is the result of a redistribution of states by intrinsic fluctuations—it gives the conduction-band "tail"; the last is the result of self-trapping appropriately averaged over intrinsic fluctuations. The first two terms are those obtained by Eggarter[2] and it can be seen that the influence of the second term depends very strongly on σ_V/kT as the crucial parameter. The term due to self-trapping depends on the self-consistently obtained binding energy α_V which we proceed to discuss. An observable is to be calculated with the above expressions:

$$\overline{A} = J(A)/J(A = 1) .$$

III. SELF-CONSISTENT EQUATIONS

The coupled material-electron equations, within a cell, will now be discussed. The discussion will be restricted to a virial fluid whose constituents interact with the electron as a system of hard-core scatterers.[6] The Schrödinger equation for the envelope function of an electron in a system of number density $\rho(r)$ is

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \frac{V_\infty}{\rho_\infty}\rho(r)\right)\psi(r) = E\psi(r) . \qquad (12)$$

ρ_∞ is the density far from the electron and V_∞ the interaction potential corresponding to that density (we shall use the Wigner–Seitz potential[2] determined by the scattering length of the material). It should be noted that collective polarization terms

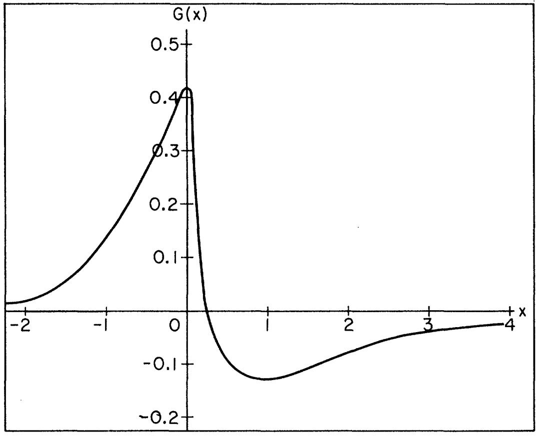

FIG. 1. Function $G(x)$ describing the redistribution in energy of unbound states, within cells, due to fluctuations.

have been neglected for simplicity, which should not be a serious omission if the density and polarizability of the material are small. With the electron now specified, the potential energy of an atom at r, due to the electron, is given by $(V_\infty/\rho_\infty)|\psi_E(r)|^2$. The equation of state for the material is taken as the virial one,

$$P(r)=\rho(r)kT[1+B_V\rho(r)] \,. \tag{13}$$

So that requiring that the chemical potential be constant yields

$$\ln\frac{\rho(r)}{\rho_\infty}=-\frac{V_\infty}{\rho_\infty}\frac{|\psi_E(r)|^2}{kT} + B_V\rho_\infty\left[1-\exp\left(-\frac{V_\infty}{\rho_\infty}\frac{|\psi_E(r)|^2}{kT}\right)\right] , \tag{14}$$

with the virial corrections assumed small. This equation states that the ratio of the number of atoms in two small volume elements is given by the Boltzmann factor.

The density far from the electron is not the same as the average density in the cell in the absence of an electron (a similar remark applies to the potential),

$$\langle\rho\rangle=\rho_\infty(1-\delta)\,;\qquad \delta=L^{-3}\int[1-\rho(r)/\rho_\infty]\,d\vec{r} \,. \tag{15}$$

But it shall be assumed, and verified later, that $\delta\ll 1$ in the cases of interest. The excess energy of the material due to the density distortion, caused by the electron, is

$$F_R=\rho_\infty kT\int\left[\frac{\rho(r)}{\rho_\infty}\ln\frac{\rho(r)}{\rho_\infty}+\left(1-\frac{\rho(r)}{\rho_\infty}\right)\right]d\vec{r} , \tag{16}$$

which does not include any collective terms other than those implicit in the equation of state.

Solutions to the equations may now be investigated. (a) $E>V_\infty$: The wave function is delocalized over the cell, $|\psi|^2\sim L^{-3}$, and the potential felt by an atom is $V_\infty/\rho_\infty L^3$. If this potential is small compared to kT a uniform fluid density results, in agreement with that assumed to obtain ψ. The sampling length L is clearly important here as well as in determining the importance of fluctuations [see Eqs. (5) and (8)]. Using the numbers in Table I, it can be shown that for He at 4.2 K this energy of interaction per atom (in K) corresponds to values of 1.6–5.2 K for $\rho=10^{21}$ to $2\times10^{21}/\mathrm{cm}^3$ if $L(\overline{V})$ is used, but has values of 0.05–0.41 K if $L(\rho)$ is used. The quoted density range is the important one in dealing with the observed mobility edge. Thus, the choice of the de Broglie length leads to interactions which are not negligible with respect to kT. This is inconsistent with the neglect of interactions in writing a free-particle density of states. There is no such objection in using the somewhat larger sampling length $L(\rho)$.

(b) $E<V_\infty$: The approach followed was to choose a two-parameter trial function for $\rho(r)$:

$$\frac{\rho_0(r)}{\rho_\infty}=1-\frac{C}{\cosh^2 br} \,. \tag{17}$$

This choice has the great advantage, aside from an intuitive density profile, that the Schrödinger equation can be solved, for all C and b, in closed exact form.[7] For the ground state, defining

$$s=\frac{1}{2}\left[\left(1+\frac{8mV_\infty}{\hbar^2b^2}C\right)^{1/2}-1\right];\quad \beta=\frac{\hbar^2b^2}{2mV_\infty} \tag{18}$$

[note $C=\beta s(s+1)$], the eigenstate and its energy are given by

$$\psi_0=\left(\frac{b^3C_s}{4\pi}\right)^{1/2}\left(\frac{1}{br}\frac{\sinh br}{\cosh^s br}\right);$$
$$\frac{E_0}{V_\infty}=1-\beta(s-1)^2 \tag{19}$$

with

$$C_s^{-1}=\int_0^\infty\left(\frac{\sinh x}{\cosh^s x}\right)^2 dx \,.$$

The two parameters (β, s) can now be chosen by the self-consistency requirement, i.e., by demanding that the equilibrium equation (14) for the density of the host material be exactly satisfied at two points ($br=0$, 1 were chosen). The solutions obtained in this manner can be examined to determine the adequacy of the self-consistency for all r. In the cases examined the self-consistency for all r was quite good. It is now fairly trivial to improve the electronic energy by first-order perturbation theory. It is also fairly trivial to calculate the excess energy of the host material using the model den-

TABLE II. Wigner–Seitz potential T_∞(K) for various densities ($10^{21}/\text{cm}^3$). For H_2 two values of a were used, $a_1 = 0.85$ Å and $a_2 = 0.74$ Å (Refs. 3 and 8); for Ne the value $a = 0.21$ Å was used (Refs. 4 and 8). See Table I as well.

	H_2		Ne	
ρ	$T_{\infty 1}$	$T_{\infty 2}$	ρ	T_∞
1	631	526	15	2070
2	1380	1140	20	2810
3	2210	1800	25	3560
4	3120	2510	30	4340
5	4090	3270	35	5130

sity (17) in zero order, or, as an improvement, the better density obtained by using the electronic wave functions in Eq. (14) which defines the density variation. In the cases examined, the corrections to the model were all small, indicating that the lowest order of perturbation theory is quite adequate. The host material is specified in relating V_∞ to ρ_∞ and by specifying B_V. It is the virial coefficient which makes the calculations tiresome since its variations prevent one calculation from having wide applications. The binding-energy result using the corrections is

$$\frac{\alpha_V}{V_\infty} \equiv \frac{V_\infty - E - F_R}{V_\infty} = \beta(s-1)^2$$

$$+ \frac{C_s kT}{V_0(0)} \int_0^\infty dx\, x^2 \left[y\left(1 - \frac{\beta s(s+1)}{\cosh^2 x}\right) + e^{-y} - 1 \right] , \quad (20)$$

where

$$y = \frac{V_0(0)}{kT} \left(\frac{1}{x} \frac{\sinh x}{\cosh^s x} \right)^2 ,$$

$$\frac{V_0(0)}{kT} = \frac{V_\infty}{\rho_\infty} |\psi_0(0)|^2 ,$$

and $\{\beta, s\}$ are to be determined from solving the transcendental equation (14),

$$\ln\left(1 - \frac{\beta s(s+1)}{\cosh^2 a}\right) = -y(a) + B_V \rho_\infty (1 - e^{-y(a)})$$

at $a = 0, 1$. It should be noticed that y also depends on s and β, that $V_0(0)$ is the electron-atom interaction potential at the origin while $y(x)$ is the position-dependent electron-atom interaction energy divided by kT (where $x = br$). The above expression for α_V includes corrections due to B_V only implicitly, through the values of β and s.

A. Ideal-Gas Results ($B_V = 0$)

The model does not admit consistent solutions for ρ_∞ smaller and/or T larger than a line in (ρ, T) space specified by

$$T_\infty (T_\infty / nT)^{2/3} = 1.12 \times 10^4 , \quad (21)$$

where n is the number density, in molecules/cm^3 $\times 10^{-21}$, and $kT_\infty = V_\infty$. This limit line has solutions $s = 1.728$, $\beta s(s+1) = 1 - e^{-1}$. Using the model density dependence leads to $E_0 / V_\infty = 1 - 0.0710$, $F_{R,0} / V_\infty = 0.0972$. The first-order perturbation-theory correction to the electronic energy is $+0.0040 V_\infty$, and using the density profile defined by the wave functions decreases the extra free energy of the gas by $0.0027 V_\infty$ from that calculated in zero order. Thus the zero-order α_V is $-0.0262 V_\infty$ and the improved one is $-0.0275 V_\infty$. The gas density at the origin is 37% of that far from the electron. The above results only depend on the host material through the scattering length in V_∞. A modest table (Table II) of V_∞ versus ρ_∞ is given for He, N_2, H_2, and Ne[3,4,8] in regions accessible to experiment (see also Table I). Graphs of the limit lines for these materials are given in Fig. 2.

For lower densities or higher temperatures than the limit line, the two-parameter model is too inflexible to admit solutions. However, it is a fair inference that in that region the binding will be weakened from that at the limit lines (which are already metastable since α is a negative although the electronic part of the system is well bound).

Continuing the discussion of the model, deeper binding than that at the limit line can be examined. Such increased binding results from using higher densities or lower temperatures. Table III lists five curves, plotted for He and N_2 in Fig. 3, specifying their definition, the potential felt by an atom at the origin divided by kT for all points on each curve, the gas density at the origin relative to infinity, zero-order electronic binding energy, perturbation-theory corrections to it, zero-order extra energy of the gas due to the density change, corrections to this energy, and total binding energies. It can be seen that as the binding increases the atoms are increasingly excluded from the region in which the electron is localized. For the five curves quoted, one can compute the number of atoms displaced by the correlation. This number, divided by the ratio of V_∞ / kT, along the entire curve 1 is given by 0.85 and slowly decreases, becoming 0.57 on curve 5. Specifically, for He at 4.2 K, ~100 atoms are displaced on curve 1 ($\rho = 1.28 \times 10^{21}/\text{cm}^3$) and this number slowly increases, becoming ~140 on curve 5 ($\rho = 2.25 \times 10^{21}/\text{cm}^3$). Also for He, by 30 K the above numbers of atoms are approximately halved, i.e., ~50 on curve 1 ($\rho = 3.65 \times 10^{21}/\text{cm}^3$) and ~65 on curve 5 ($\rho = 6.55 \times 10^{21}/\text{cm}^3$). It should be remarked that, consistent with the assumption ($\delta \ll 1$), those numbers of atoms are quite small compared with the number of atoms in the cell [$\rho L^3(\rho)$; see Table I]. Also, the distance over which the density varies

TABLE III. Characteristics of five curves in (ρ, T) space $(B_V=0)$. $T_\infty(K)$ is the Wigner–Seitz potential for the density $n\times 10^{21}/\text{cm}^3$; it is obtained from using the scattering length. Row 1 is the limit lines. See text for details.

	$T_\infty(T_\infty/nT)^{2/3}$	s	β	$V_0(0)/kT$	$1-\rho(0)/\rho_\infty$	$\beta(s-1)^2$	$\Delta E/V_\infty$	F_{R0}/V_∞	$\Delta F/V_\infty$	α/V_∞
1	11 200	1.728	0.1341	1.00	0.632	0.0710	+0.0040	0.0972	−0.0027	−0.0275
2	13 500	2.200	0.1282	2.33	0.902	0.1846	−0.0050	0.1720	−0.0031	+0.0207
3	16 200	2.500	0.1100	3.28	0.962	0.2475	−0.0219	0.1862	+0.0065	+0.0767
4	19 200	2.735	0.096 30	3.63	0.973	0.2900	−0.0129	0.1900	+0.0164	+0.0965
5	22 800	3.000	0.082 91	5.28	0.995	0.3311	−0.0675	0.1811	+0.0264	+0.1916

because of the correlation is correspondingly small compared to L.

B. Inclusion of B_V (Helium 4.2 K)

To estimate the virial corrections, the densities appropriate to the first three curves examined in the ideal-gas case were reexamined for He gas at 4.2 K. The method used was to begin with the ideal-gas values of (s, β) and to iterate the self-consistency transcendental equations (for s and β) which include the virial corrections. Three iterations were needed in the cases examined to obtain self-consistency to four figures. The results are quoted in Table IV. It might be noted that the effects of B_V tend to cancel somewhat in computing α_V.

Given the uncertainty in m^* discussed below, it was not felt it would be fruitful to further pursue virial corrections.

C. Return to Fluctuations and Calculation of Averages

Having quoted the results of calculating α_V, the points which remain to be discussed are $\partial\alpha/\partial V$, the variation of binding with density; σ_V/kT, the crucial parameter for fluctuations; and m^*, the effective mass of self-trapped entity. All of these points have already been touched on either explicitly or by implication. The reader should refer to the expression derived previously for $I(A)$, Eq. (8), which is to be used in the calculation of averages.

The density variation of the binding energy for helium can be obtained from the quoted results. It was found that the binding increases with density at a fixed temperature. From examining curves 1–5 for He (Fig. 3 and Table III), $\partial\alpha/\partial V$ was of order 0.3 at the limit line with very small temperature dependence. By curve 4 it had

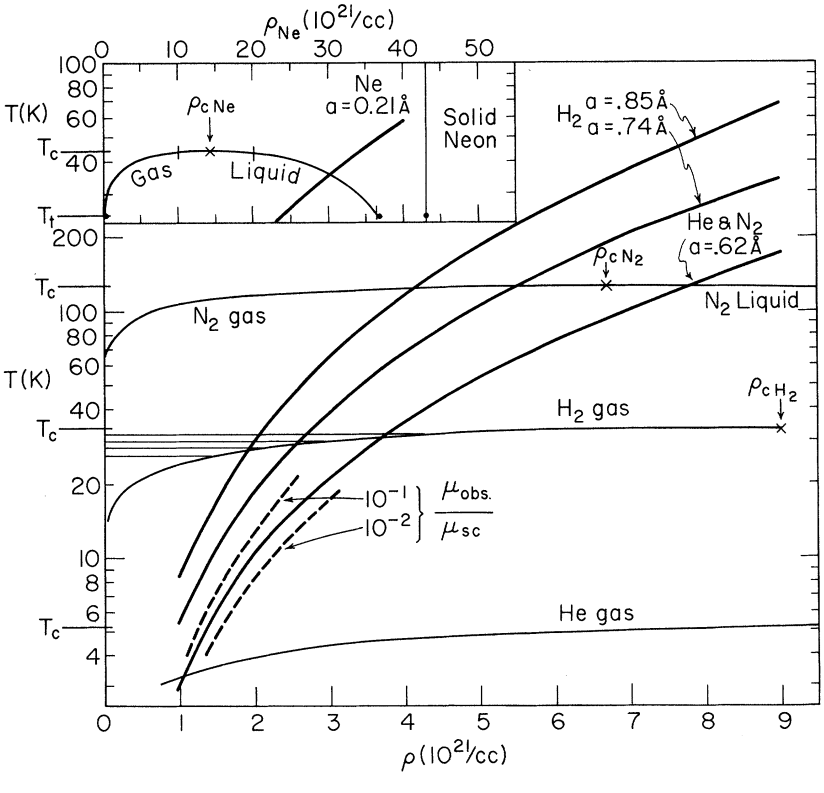

FIG. 2. Limit lines for He, N_2, H_2, and Ne (insert) in the ideal-gas approximation. See Table II and row 1 in Table III. The density of the saturated vapor in these materials is also shown, as is that of the liquid of Ne and N_2 under the saturated vapor pressure. Density measurements are from Ref. 17. Observed drift mobility divided by the semiclassical value expected for He gas is shown from Refs. 9 and 10. The four isotherms noted for H_2 correspond to those where the mobility was measured, from Refs. 14 and 10. The mobilities were measured in Ne, Refs. 4 and 12, along the saturated liquid and vapor lines.

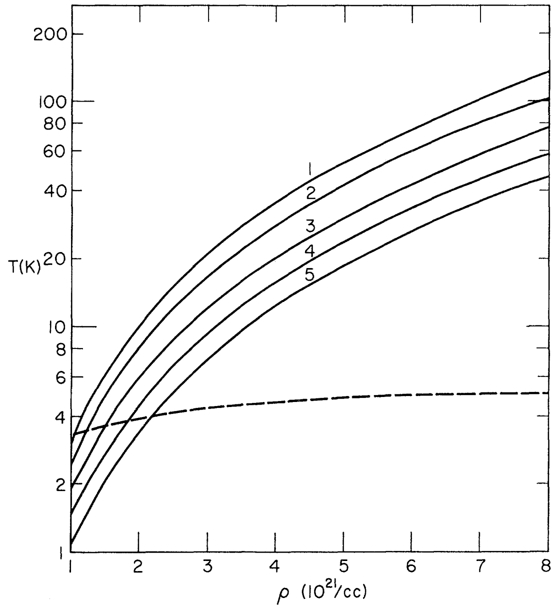

FIG. 3. Curves 1–5 from Table III are shown for H_2 (N_2 also) denoting increasing binding as specified in the table. Calculations were in the ideal-gas approximation.

typically changed to 0.2. Thus the parameter of importance, namely, $1-\partial\alpha/\partial V|_{\bar{V}}$, is 0.7–0.8 and increasing towards unity with density.

The importance of fluctuations, then, depends only on σ_V/kT which, in turn, only depends on the choice of L since $\sigma_V \propto L^{-3/2}$. It has already been implied that choosing the de Broglie wavelength of an electron of an energy equal to the average potential ($\bar{V}$) for L seems too small since it is the lower limit specified by the uncertainty principle; this choice also seems somewhat inconsistent with the free-electron density of states within the cell; its choice leads to correlation energies, for unbound states, which are comparable to kT at the densities where the mobility edge is observed, which in turn implies that density variations within a cell are not negligible. All of the above objections can be removed if L is chosen as the mean free path for momentum-exchange scattering at the average density for the system. This mean free path choice, for L, allows the good agreement between theory and experiment obtained by Eggarter[2] to stand by decreasing (though not denying) the role of fluctuations in the mobility drop observed experimentally. The burden of returning the theoretically predicted mobilities to the experimental values is then passed on to the self-trapped states.

To calculate mobilities in a system in thermodynamic equilibrium, for He, for example, the partition function previously described is to be used. The mobility to be averaged has already been discussed by Eggarter[2] for the unbound states including "pseudobubbles," localized states due to intrinsic density fluctuations rather than self-induced trapping. For the self-trapped electrons a mobility formula also exists[6]:

$$\mu_R = \frac{1}{6\pi\eta R}\left(1+\frac{9\pi\eta}{4\rho R(2\pi MkT)^{1/2}}\right), \tag{22}$$

where η is the viscosity of the host material, R the effective radius of the entity, and M a reduced mass:

$$\frac{1}{M}=\frac{1}{m^*}+\frac{1}{M_{\text{host}}}. \tag{23}$$

In the case of strong binding, a hydrodynamic regime, m^* is half the mass of the excluded atoms[6]; thus $m^* \gg M_{\text{host}}$, $M = M_{\text{host}}$, and R might be taken as the classical turning point for host atoms (i.e., the r at which a host atom would feel a repulsion of $\frac{3}{2}kT$ due to the localized electron; for He at 4.2 K the ideal-gas curves 3–5 yield $R \sim 15$ Å using this prescription). In the case of weak binding, the above interpretation of R is not tenable since, for example, on curve 1 (our limit line) the maximum repulsive potential felt by a host atom is kT (at $r = 0$), so that there is no classical turning point for an atom with the average kinetic energy. A second problem is m^* at small binding, which may not be large compared to M_{host} since for very weak binding one should expect that m^* goes smoothly to the electron mass.

To obtain an estimate for m^*, experimental results[6,9] for an isothermal mobility edge (He, 4.2 K) and theory can be compared. Let us assume μ_R is small compared to the semiclassical

TABLE IV. Role of the virial coefficient B_V in He gas at 4.2 K.

ρ		$V(0)/kT$	$1-\rho(0)/\rho_\infty$	$\beta(s-1)^2$	α/V_∞	α/kT
1.20×10^{21}	ideal gas	1.000	0.6321	0.0710	−0.0275	−3.36
	with B_V	1.544	0.8102	0.1385	−0.0212	−2.59
1.38×10^{21}	ideal gas	2.328	0.9025	0.1846	+0.0207	+2.94
	with B_V	2.293	0.9135	0.2078	+0.0166	+2.36
1.65×10^{21}	ideal gas	3.283	0.9625	0.2475	+0.0767	+13.2
	with B_V	3.199	0.9665	0.2866	+0.0750	+13.0

free-electron mobility μ_{sc}. Further, neglect fluctuations, which can only reduce the mobility from the semiclassical value. With these assumptions the mobility drop is due to self-trapped electrons and an upper limit for $(m^*/m)^{3/2}$, the only unknown parameter in the partition function, can be obtained. To fit the experimentally observed mobility at $\rho = 1.38\times10^{21}/\mathrm{cm}^3$ (curve 2, Fig. 3) in He for 4.2 K (a value of $10^{-2}\times\mu_{sc}$)[10] a maximum value of $m^*/m \simeq 6$ is required. Hence, for weak binding (a few kT) the effective mass of the self-trapped electron is of order $10m$ and not $50M_{\mathrm{He}}$. This value will change rapidly with increased binding since the hydrodynamic regime must be approached (again for He, $m^* \gg M_{\mathrm{He}}$ for the liquid[11]). Thus m^* will vary by $\sim 10^6$ between weak and strong binding. Concurrently the fraction of electrons in self-trapped states, which is already non-negligible at the weak binding of a few kT, will increase by 10^9 $[(m^*/m_e)^{3/2}]$ due to the mass factor alone.

In the absence of detailed knowledge of m^* it seems fruitless to attempt a *detailed* comparison of theory with the mobility-edge experiments. At this time it might also seem indicated to again make the reader aware of other problems that exist for quantitative purposes. In each cell, when the electronic energy $E \simeq \langle V\rangle$, the density of states and mobilities being used are hardly exact because the separation of electrons into bound and unbound ones is not sharp. It has been assumed that errors introduced are not serious in computing properties which depend on averages, but quantitatively this is not precise. Further, in the case of self-trapped electrons, when the linear dimension of the localization region is only a few average interatomic distances the replacement of these atoms by a potential depending only on the local density is an approximation of uncertain precision. However, since the *detailed* comparison of theory and experiment is being abandoned, the experiments will be examined in the context of the theory taken at face value.

IV. DISCUSSION OF EXPERIMENTS

For He gas,[9,10] the mobility experiments seem to fit quite well into the framework developed in this paper. At constant temperature, for low helium density the observed mobility is due to free electrons. This is as expected since, in this regime, $\bar{V}$ and σ_V/kT are quite small (see Table I) and α_V/kT will also be negligible. As the helium density is increased, σ_V/kT increases and the low-energy states brought about by the fluctuation-induced redistribution of states begin to trap a non-negligible fraction of electrons in nondiffusing states (whose mobility must be very small). The net result is that the observed mobility, while remaining fairly high, steadily falls with increasing density below the value calculated semiclassically for free electrons. The steepness of the drop in mobility with density decreases with increasing temperature as expected. Eventually self-trapping will begin to play a significant role leading, after a sharpened drop of mobility with density, to mobilities of order 10^{-1} cm^2/V sec rather than the value of $\sim 10^3$ expected for free electrons. Measurements in helium gas are also indicated in Fig. 2. This general behavior is also to be expected in the other materials discussed below. Measurements at constant density and decreasing temperature should show the same type of behavior.

As indicated by Fig. 2, self-trapping in neon is expected at densities above the critical density, i.e., in the liquid for the saturated vapor pressure. Measurements in Ne gas[4] and liquid[4,12] are also consistent with the picture developed here. The high mobilities measured in the saturated vapor fall below the free-electron values and the low mobilities found in the liquid are typical of self-trapped electrons. More detailed calculations should probably include polarization effects and density-dependent atom-atom interactions which were neglected in plotting the appropriate curve in Fig. 2. Miyakawa and Dexter[8] obtained results in substantial agreement with experiment for liquid Ne. They considered a square well for the electron-induced density disturbance and neglected unbound electrons and fluctuations.

For N_2, Fig. 2 shows that self-trapped electrons are to be expected quite close to the critical density at the saturated vapor pressure. The available mobility measurements in the liquid[13] indeed show that the negatively charged species has the expected low mobility. However, the experimental results cannot be unambiguously identified with self-trapped electrons though the possibility exists. A substantial amount of both detailed calculations and extended experimental measurements remain to be done.

Measurements in H_2 gas and higher-temperature He gas are quite interesting and are discussed below.

Nonequilibrium Cases

There have been mobility measurements in H_2 (~ 30 K)[10,14] (for the isotherms denoted in Fig. 2) and in He (77 and 160 K)[15] where two coexisting mobility branches have been observed, indicating a lack of thermal equilibrium. The high-mobility branch seems excellently described by the semiclassical treatment augmented by fluctuations (trapping by intrinsic density fluctuations or "pseudobubbles"). That is, the observation on the high-mobility branch shows the semiclassical values at low densities, dropping slowly from those values with increasing density by factors of as much as 2 or 3 at the highest density where the high-mobility signal is observable. This behavior is completely consistent with some of the electrons being trapped by intrinsic fluctuations, a process which is not extremely effective at these high temperatures.

The low-mobility branches show all the characteristics of self-trapped electrons where the trapping time is comparable to the transit time of free electrons under the experimental conditions ($\sim 10^{-5}$ sec). Owing to the measurement method, trapping almost anywhere in the drift space leads to the low-mobility value since the inverse of the drift time is measured and the fast and slow times are in ratio of $\sim 10^3$. The influence of impurities can be ruled out in both experiments. The low-mobility signal strength is transit-time dependent[15] indicating a lifetime effect, and is also density dependent[14,15] as would be expected for an increasing trapping probability. The time required for an electron to self-trap must be extremely long for very low gas densities ($m^* \sim m$ and $\alpha < 0$) and is known to be quite short ($\sim 10^{-12}$ sec) for liquid He[16] at ~4 K. There must be a temperature- and density-dependent transition regime where the trapping time is comparable to the experimental transit time. This effect is dynamic and thus cannot be probed in detail with the formalism which has been developed—it can only be made plausible.

The observation of a low mobility occurs at lower density for H_2 gas (30 K) than for He gas (77 K) and at yet higher densities (for the same transit time) for He at 160 K. This is as expected in the context of this work since the limit line, Fig. 2, for H_2 at 30 K is at lower density than for He at 77 K and is at higher densities yet for He at 160 K. It should be noted that Fig. 2 would predict a higher density ratio between He (77 K) and H_2 (30 K) than that observed experimentally for the stable existence of self-trapped electrons. However, the double-gate technique used for He[15] is more sensitive to a low-mobility species than the single-gate technique used for H_2.[14]

To further uphold the interpretation given here, it should be noted that measurements for H_2 were made along four isotherms (noted in Fig. 2). The isotherms terminate at the density of the saturated vapor and density fluctuations beyond this point cannot be expected because of the liquid-gas phase separation. The two higher-temperature isotherms terminate at higher densities than the limit line; these were the isotherms on which a low-mobility branch was observed. No low mobilities were observed on the two lower-temperature isotherms. It is assumed that density fluctuations play a role in this experiment, not because intrinsic fluctuations trap electrons (to account for the low mobilities) but because density fluctuations will provide a few cells where conditions are favorable for self-trapping even when the average density is below that at which self-trapped electrons will be stable on the average. The observations of low mobilities are at average densities lower than the limit lines of Fig. 2. Favorable conditions for self-trapping are high-density regions which would lead to a reasonable binding (not too small α) and a reasonably high m^* (large density of self-trapped states within the cell). The above discussion shows that all expectations, within the context of this work, are fulfilled if the low mobilities observed in H_2 and He are interpreted as due to self-trapped electrons.

V. SUMMARY

A formalism has been developed for electrons in some structurally disordered materials. It includes a wide conduction band, band-tail states which include localized states owing to random potential fluctuations, and self-trapped states. Specific results have been obtained for an ideal gas interacting with electrons through a potential linearly dependent on the local density. Appropriate parameters to represent He, H_2, N_2, and Ne were introduced (the scattering lengths) and predictions resulted. Corrections were examined due to the virial coefficient and they were estimated for He gas at 4.2 K. The effective mass of a self-trapped electron was introduced and shown to be important and quite sensitive to the experimental situation. Semiquantitative comparison of the theory and the available experimental results showed good agreement for the four materials considered in the regimes where measurements are available. More detailed calculations should be made for Ne and N_2. Also, further experimental measurements should be quite rewarding, especially if they chart the regions near the limit lines, where the mobilities will drop, and investigate the effects of high fields in influencing the distribution of electrons among the available states.

ACKNOWLEDGMENTS

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