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Semiclassical Theory of Electron Transport Properties in a Disordered Material*†

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We study the problem of an electron in a dilute gas of density ρ of hard spheres. The radius of the spheres is a. It is shown that a systematic expansion of the Green's function in a series involving the small parameter ρa^3 leads to inconsistencies at low energies. This is attributed to the existence of localized states. We then assume that the problem can approximately be reduced to the motion of a classical particle through a suitably defined smooth, random, energy-dependent effective potential. Physical arguments are given to justify this reduction, although a rigorous proof is lacking. The resulting classical problem is in complete agreement with the Mott–Cohen-Fritzsche-Ovshinsky model of disordered materials, and is simple enough to permit detailed calculations of all quantities of interest. As a test for the validity of our approximations, we apply the theory to compute the mobility of excess electrons in gaseous He. By adjusting two parameters of order unity we get a good fit to the experimental data; the remaining small discrepancies admit satisfactory explanations.

I. INTRODUCTION

The natural starting point for understanding the electronic properties of disordered materials is a knowledge of the one-electron energy spectrum and the nature of the associated wave functions in disordered potentials. In crystalline materials this task is enormously simplified by the Bloch-Floquet theorem which essentially reduces the study of the whole crystal to the study of one elementary cell. This theorem is the basis of the well-established band theory of solids. Unfortunately no analogous result exists for the disordered case, and in order to gain the desired information one is confronted, at least in principle, with the formidable task of diagonalizing a random matrix of order $\approx 10^{23}$, or of solving some equivalent problem.

Very few exactly soluble problems involving random media are thus far known. Most of these deal with one-dimensional situations and give only the energy spectrum but no information on the wave functions, and the methods of solution cannot be used in higher dimensions. Notable among these are the work of Dyson[1] on the frequency spectrum of a disordered chain of oscillators (equivalent to the electronic spectrum of a one-dimensional tight-binding alloy, since both problems consist in finding the eigenvalues of a tridiagonal matrix), and the electron spectrum in a random set of δ-function potentials, solved by Frisch and Lloyd.[2] For the last one Borland[3] proved also that all electronic wave functions are localized under quite general conditions. The same property has subsequently been shown to hold for other one-dimensional systems.[4,5]

Instructive as these problems may be, their usefulness as guidelines for realistic three-dimensional cases has to be questioned. From a physical point of view, waves can go around obstacles in three dimensions but not in one; mathematically there is considerable difference between the associated boundary-value problems for ordinary differential operators (one-dimensional case) and partial differential operators (three-dimensional case). It is therefore not surprising that the simplification achieved by studying a problem in one dimension is often accompanied by the loss of interesting phenomena. Examples of this situation are discussed by Lieb and Mattis.[6]

The only exactly soluble problem in three dimensions has so far been the density of states found by Lloyd,[7] who considers a tight-binding alloy in which the off-diagonal elements in the Hamiltonian have translational symmetry, while the diagonal elements $\{\epsilon_{\vec{n}}\}$ are independent random variables with a Lorentzian distribution $p(\epsilon)$. The average density of states $\langle n(E)\rangle$ turns out to be the convolution of the pure crystal density of states $n_0(E)$ with the probability distribution $p(\epsilon)$. Unfortunately, this elegant result is only valid for a Lorentzian probability distribution for the $\epsilon_{\vec{n}}$ and does not help one to understand other cases.

Among the approximate methods for the study of disordered materials, the most popular has been the perturbation expansion of the Green's function in the form $G = G_0 + G_0 V G_0 + \cdots$. Several choices of the unperturbed situation, and various renormalization procedures have been used. The literature on this point is so vast that it is impossible to select a reasonable set of references. The most successful of these approximations seems to be the "coherent-potential approximation" (CPA),[8,9] which uses as G_0 the propagator in a fictitious average medium that is determined self-consistently. The

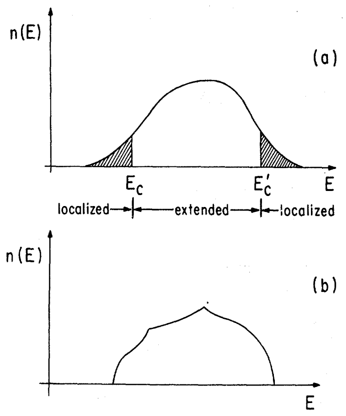

FIG. 1. Energy bands in (a) an amorphous material according to the Mott-CFO model, and (b) a perfect crystal.

CPA is not restricted to small values of some parameterlike impurity concentration or scattering strength, and gives reasonable results at most energies. But the CPA gives energy bands with sharp edges, such as those one finds in a perfect crystal, while it is known that in a disordered medium the band edges are smeared out into tails, as shown in Fig. 1(a). That the theory is incorrect near the band edges is a serious failure, since this is the most interesting region. In many cases all transport properties are determined entirely by states in the tails of $n(E)$. Feynman path integrals[10] and integration in other function spaces,[11] as well as variational calculations,[12] have also been used in connection with random media. In spite of all these efforts our understanding of disordered materials is still in a very primitive stage. A comprehensive review of the present situation is given in Ref. 13.

In recent years a model of the electronic structure of disordered systems known as the Mott-Cohen-Fritzsche-Ovshinsky (Mott-CFO) model[14,15] has emerged. Its basic assumption is that there are certain universal features shared by all disordered materials: The energy eigenvalues are grouped in bands [Fig. 1(a)] but, in contrast to the crystal case sketched in Fig. 1(b), both the Van Hove singularities and the band edges are smeared out. Inside each band there exist critical energies E_c, E_c' which separate electron states of completely different natures. The states between E_c and E_c' are extended, while those in the tails of the density of states [shaded area in Fig. 1(a)] are localized. (In a perfect crystal all states are extended according to the Bloch-Floquet theorem.) The energies E_c and E_c' are called mobility edges; the mobility $\mu(E)$ is zero for states outside these points. If the disorder is increased the mobility edges move towards the center of the band, and the region of extended states may eventually disappear. This is known as the Anderson transition.[16]

The Mott-CFO model is based on and unifies a considerable amount of information on disordered materials, both theoretical and experimental, which is at present available. Its assumptions, however, have not yet been derived in general from first principles; it differs in this sense from the band theory of crystalline solids. The main obstacle for such a first-principle derivation is the extreme mathematical complexity of the problems under consideration.

In the present paper we study one of the simplest imaginable three-dimensional problems: an electron in a low-density gas of hard spheres. In Sec. II we discuss the difficulties encountered by using the "most natural" approach to the problem: to expand the Green's function in a series involving the small parameter $\rho a^3 \ll 1$. We find that there is always a region around the origin on the energy axis where such an expansion is not possible; we relate this to the existence of localized states.

In Sec. III we examine the problem from a completely different point of view. We use physical arguments to construct a semiclassical model for our system. The set of randomly located hard spheres is replaced by an equivalent, random, smooth effective potential, and classical mechanics is then assumed to be approximately valid. The physical picture so obtained is in complete agreement with the Mott-CFO model and illustrates many of its concepts, for example, the existence of a mobility edge follows naturally from the existence of a percolation threshold, localized states are the result of unusually deep fluctuations in the random effective potential, etc. Our semiclassical approach has pedagogical value, since it can be easily understood and still exhibits all the physical properties postulated by the Mott-CFO model. More important, it is accurate enough for approximate calculations of several quantities of interest. In Sec. IV we apply it to compute the mobility of excess electrons in gaseous helium. By adjusting two parameters of order unity we obtain a very good fit to the experimental data of Levine and Sanders.[17] Sections III and IV are an expanded version of earlier work by Eggarter and Cohen.[18,19]

To simplify our equations, units such that $\hbar = 1$ and $2m_e = 1$ will be used.

II. FORMULATION OF THE PROBLEM; ATTEMPT AT SOLUTION BY GREEN'S-FUNCTION TECHNIQUES; DIFFICULTIES; SOME ONE-DIMENSIONAL RESULTS

A. Problem

We want to study an electron in the presence of a gas of hard spheres. Let a be their radius, and $\{\vec{x}_i\}$, $i = 1, 2, \cdots$, the random positions of their centers. The spheres are assumed to be motionless. The Green's function for this problem is the solution of

$$\nabla_{\vec{x}}^2 G(\vec{x},\vec{x}'|E) + E\,G(\vec{x},\vec{x}'|E) = -4\pi\delta(\vec{x}-\vec{x}') \qquad (1)$$

with the boundary conditions $G(\vec{x},\vec{x}'|E)=0$ when either $\vec{x}$ or $\vec{x}'$ are on the surface of one of the spheres, and G bounded for $|\vec{x}|\to\infty$ or $|\vec{x}'|\to\infty$.

We will restrict our attention to low energies $E \ll a^{-2}$ in which case the scattering by a hard sphere is dominated by s waves; p-wave scattering is smaller by a factor Ea^2 and will be neglected. The Green's function can then be expanded in the usual way

$$\begin{aligned} G(\vec{x},\vec{x}'|E) &= G_0(\vec{x},\vec{x}'|E) \\ &\quad + \sum_i G_0(\vec{x},\vec{x}_i|E)(-\tilde{a})G_0(\vec{x}_i,\vec{x}'|E) \\ &\quad + \sum_i \sum_{j\neq i} G_0(\vec{x},\vec{x}_i|E)(-\tilde{a}) \\ &\quad \times G_0(\vec{x}_i,\vec{x}_j|E)(-\tilde{a})G_0(\vec{x}_j,\vec{x}'|E) + \cdots, \qquad (2) \end{aligned}$$

where $G_0(\vec{x},\vec{x}'|E) = e^{iE^{1/2}|\vec{x}-\vec{x}'|}/|\vec{x}-\vec{x}'|$ is the free-particle propagator and $\tilde{a} = e^{-iE^{1/2}a}$ is the s-wave scattering amplitude.

The terms in the series (2) can be represented by graphs in the usual way; for example, Fig. 2 stands for

$$\begin{aligned} &G_0(\vec{x},\vec{x}_1|E)(-\tilde{a})G_0(\vec{x}_1,\vec{x}_3|E)(-\tilde{a})G_0(\vec{x}_3,\vec{x}_2|E)(-\tilde{a}) \\ &\qquad \times G_0(\vec{x}_2,\vec{x}_1|E)(-\tilde{a})G_0(\vec{x}_1,\vec{x}'|E). \qquad (3) \end{aligned}$$

Several quantities can be obtained from a knowledge of the Green's function. To be specific, let us assume that we want the average density of states per unit volume $n(E)$, which is given by

$$n(E) = \frac{1}{4\pi^2} \lim_{\epsilon\to 0^+} \lim_{|\vec{x}-\vec{x}'|\to 0} \operatorname{Im} G(\vec{x},\vec{x}'|E+i\epsilon)\,. \qquad (4)$$

Let us consider one graph $\mathcal{G}$ linking r scatterers and having $r+s+1$ free-propagator lines (for example, $r=3$, $s=1$ in Fig. 2), and call $I(\mathcal{G})$ the contribution it makes to $\langle G\rangle_{\vec{x}=\vec{x}'}$. $I(\mathcal{G})$ is given by an integral of the form

$$\begin{aligned} I(\mathcal{G}) &= \rho^r(-\tilde{a})^{r+s} \int\cdots\int d\vec{x}_1^3\cdots d\vec{x}_r^3 \\ &\quad \times \frac{\exp(i\sqrt{E}\,|\vec{x}-\vec{x}_3|)}{|\vec{x}-\vec{x}_1|}\cdots\frac{\exp(i\sqrt{E}\,|\vec{x}_r-\vec{x}|)}{|\vec{x}_r-\vec{x}|}, \qquad (5) \end{aligned}$$

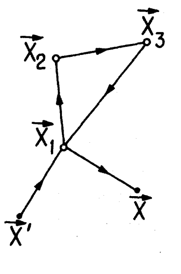

FIG. 2. Typical diagram in the expansion (2) of the Green's function.

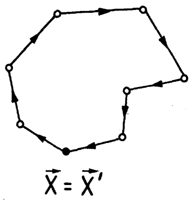

FIG. 3. Ring diagram giving contribution of order zero in the small parameter $(\rho a^3)^{1/2}$ to the Green's function.

where the integrand has $r+s+1$ free-particle propagators. The change of variables $\vec{\xi}_i = \sqrt{E}\,\vec{x}_i$ reduces this to

$$I(\mathcal{G}) = \sqrt{E}\,(\rho\tilde{a}^3)^{s/2}(\rho a/E)^{r-s/2}\quad, \qquad (6)$$

where $I_0(\mathcal{G})$ is a definite integral (i.e., a number) depending only on the topology of $\mathcal{G}$ but not on parameters ρ, a, or E.

If we are interested in a low-density situation $\rho a^3 \ll 1$ and in energies $E \approx \rho a$ (this is the physically interesting energy region, as will soon become apparent), Eq. (6) suggests a natural way of organizing the perturbation series for $n(E)$. It consists in taking as a first approximation the sum of all $s=0$ graphs, which do not contain the small parameter $(\rho a^3)^{1/2}$, as a second approximation the sum of all $s=1$ graphs, which contain one factor $(\rho a^3)^{1/2}$, and so on. What one expects to obtain is an expansion of the form

$$\begin{aligned} n(E) &= \sqrt{E}\,[F_0(\rho a/E) + (\rho a^3)^{1/2}F_1(\rho a/E) \\ &\qquad + \rho a^3 F_2(\rho a/E) + \cdots]\,. \qquad (7) \end{aligned}$$

We will now discuss briefly the first two approximations, which are easy to compute.

B. Ring Approximation; Optical Potential

The only $s=0$ diagrams are the rings, Fig. 3. The integrals they give, Eq. (5), are convolutions of free-particle propagators, which are easily evaluated through the use of Fourier transforms. The sum of all ring diagrams turns out to be

$$\begin{aligned} &\sum_{r=1}^{\infty} I\ (\text{ring with } r \text{ scatterers}) \\ &\qquad = i\,[(E-4\pi\rho a)^{1/2} - E^{1/2}]. \qquad (8) \end{aligned}$$

To be consistent with the neglect of terms in $(\rho a^3)^{1/2}$, we must set $\tilde{a}=a$, since $e^{-iE^{1/2}a} = e^{-i(E/\rho a)^{1/2}(\rho a^3)^{1/2}} \approx 1$. The density of states that results within this ring approximation is

$$n(E) = \begin{cases} (E-4\pi\rho a)^{1/2}/4\pi^2 & \text{for } E \geq 4\pi\rho a \\ 0 & \text{for } E < 4\pi\rho a\,, \end{cases} \qquad (9)$$

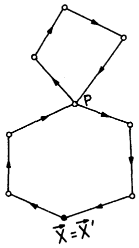

FIG. 4. Double ring giving a contribution of first order in $(\rho a^3)^{1/2}$.

consistent with Eq. (7) with $F_0=(1-4\pi\rho a/E)^{1/2}/4\pi^2$ for $E \geqslant 4\pi\rho a$ and zero otherwise. The physical interpretation of (9) is simple: The gas of hard spheres represents a potential barrier of height $V=4\pi\rho a$ for the electrons. This $V=4\pi\rho a$ is called the optical potential, and the above result has been known for a long time[20,21] and can be derived in a number of ways. There is one alternative derivation,[22] which we would like to sketch briefly; it is called the Wigner-Seitz method and gives the optical potential at low densities, but includes repeated scattering corrections for higher ρ's. The idea is to derive the effective potential barrier represented by the gas, $V_{WS}=k_0^2$, from the conditions that the wave function of the electron in its ground state must be s-like close to any one of the scatterers,

$$\psi_i \approx \sin[k_0(r-a)]/r, \quad r=|\vec{x}-\vec{x}_i| \text{ small}, \tag{10}$$

and the wave function must be smooth when going from any scatterer to its neighbors. Associating with each scatterer a "Wigner-Seitz sphere" of radius r_s defined by

$$\tfrac{4}{3}\pi r_s^3 \rho = 1 , \tag{11}$$

we have to impose the boundary condition

$$(\partial\psi_i/\partial r)\,|_{r=r_s}=0$$

or

$$k_0 r_s = \tan[k_0(r_s-a)] . \tag{12}$$

Equations (11) and (12) determine k_0 and hence V_{WS} as a function of ρ and a. At low density one can expand $\tan x \approx x+\frac{1}{3}x^3$ and recapture the optical potential. The argument can be generalized[23] to construct traveling wave states and gives a dispersion law $E(\vec{k})=V_{WS}+\vec{k}^2/m^*$. The effective mass $m^*(\rho,a)$ differs from 1 by less than 2% for all (ρ,a) values to be considered in this work, and we will neglect these effective-mass corrections.

C. Double Ring Approximation

The first correction to the ring approximation consists in taking the $s=1$ graphs. These are the double rings shown in Fig. 4. The sum of all these graphs can be obtained by a straightforward but rather lengthy calculation and is

$$\sum I(\text{double rings}) = 2\pi\rho\tilde{a}^2[E/(E-4\pi\rho\tilde{a})^{1/2}-1] . \tag{13}$$

For the same reasons discussed before, we can set $\tilde{a}=a(1-ia\sqrt{E})$, which is correct up to order $(\rho a^3)^{1/2}$. Putting $\langle G\rangle \approx G_0+\langle G\rangle_{\text{rings}}+\langle G\rangle_{\text{double rings}}$ we get as our second approximation

$$n(E)\approx\frac{1}{4\pi^2}\Bigg(\operatorname{Re}(E-4\pi\rho a+i4\pi\rho a^2\sqrt{E})^{1/2} + 2\pi\rho a^2 \operatorname{Im}\Bigg\{(1-2ia\sqrt{E}) \times\Bigg[\bigg(\frac{E}{E-4\pi\rho a+i4\pi\rho a^2\sqrt{E}}\bigg)^{1/2}-1\Bigg]\Bigg\}\Bigg) . \tag{14}$$

If our approximation procedure makes sense, it should be possible to rewrite (14) in the form (7) and extract the first-order coefficient $F_1(\rho a/E)$ from the expansion. An elementary analysis shows that the right-hand side of (14) admits an expansion like (7) if and only if

$$E-4\pi\rho a > 4\pi\rho a^2\sqrt{E} , \tag{15}$$

which is approximately equivalent to

$$E > 4\pi\rho a[1+(4\pi\rho a^3)^{1/2}] , \tag{16}$$

and $F_1(\rho a/E)$ turns out to be zero for these energies. [Consideration of terms with higher s will restrict the validity of the perturbation series (7) to still higher energies. This must be so since the Wigner-Seitz potential $V_{WS}\approx 4\pi\rho a(1+\frac{9}{5}(4\pi\rho a^3)^{1/3})$ is already higher than the right-hand side of (16).] At lower energies our whole approximation procedure breaks down; for $E=4\pi\rho a$, for example, the leading term in (14) is $E^{1/2}(\rho a^3)^{1/4}/8\pi^2$ in contradiction with (7), thus indicating an inconsistency in our procedure.

The reason for the failure of (7) at energies not satisfying (15) is most easily understood by considering a *very* low energy $E \ll \rho a$. In this case Eq. (6) contains one very small and one very large parameter, and any reasonable selection of the most important diagrams should consider both of them simultaneously. Furthermore, such a selection should not be based only in the powers of the two parameters, but also consider the coefficients $I_0(\mathcal{G})$ corresponding to each graph, and the fact that the number of topologically inequivalent graphs increases drastically with r and s. With all these difficulties, the problem becomes untreatable from a mathematical point of view. But it is possible instead to gain some insight into the problem from purely physical arguments.

D. Localized States and Failure of Expansion (7)

It is at present beyond any doubt that in any random potential there exist localized states[16,24,25] near the band edges, and that these states are associated with fluctuations in the potential. To see

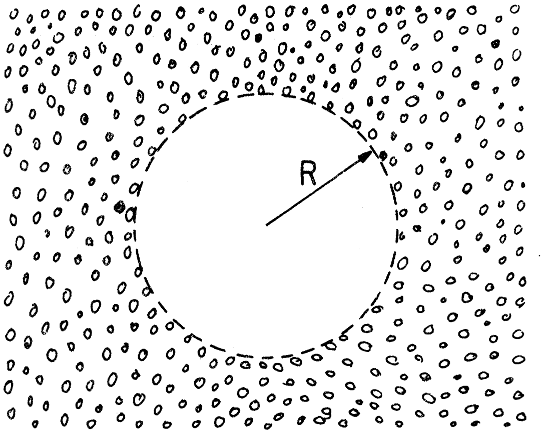

FIG. 5. Configuration of scatterers which can lead to a localized electron state.

what this means in the present problem, let us consider, for example, a configuration $\{\vec{x}_i\}$ like shown in Fig. 5[26] in which a spherical region of radius R has no scatterers, while outside their density is everywhere close to its average value. Such a configuration has a small but finite probability of occurring, of order $e^{-4\pi\rho R^3/3}$ per unit volume of the system.

It is possible to put an electron inside the empty region, which requires a localization energy of order $E \approx R^{-2}$, and by the Wigner-Seitz argument the repulsive interaction with the outside gas of scatterers can be replaced by a potential barrier of height $V_{WS} \approx 4\pi\rho a$. Clearly if $V_{WS} R^2 \gg \frac{1}{4}\pi^2$ we have a localized electron state (which incidentally is a simplified version of the bubble states in liquid He, considered by several authors[17,22,27]). It is now physically clear that the electron interacts most strongly with scatterers that are close to the "bubble," and the interaction becomes weaker and weaker as one considers more remote scatterers. It follows that a reasonable approximation procedure for $G(\vec{x}, \vec{x}' | E)$ at very low E should start by summing *all* diagrams linking scatterers in some vicinity of the points $\vec{x}$, $\vec{x}'$ of interest, say $|\vec{x} - \vec{x}_i| < A$, and successive approximations should let A increase to infinity. This is basically the procedure of Anderson[16] in his work on localization in tight-binding alloys.

So we know at least in principle how to obtain successive approximations for G. To carry out the actual calculation along these lines, however, and to justify rigorously each step, turns out to be a very difficult task. Anderson's paper has occasioned controversy for this very reason. Recent work has been done to simplify[28,29] Anderson's original derivation and to generalize his results[25] but the underlying mathematics is still complicated and not always very clear. We conclude from this discussion that the Green's-function approach is probably the most powerful method for a first-principle solution of our problem, but presents considerable practical difficulties as soon as one tries to do actual calculations. It seems therefore desirable to look for some alternative approach, in which a few physically reasonable assumptions are built in instead of being derived from the theory, if at this price considerable mathematical simplification of the problem is achieved. We will devote Sec. III to such an alternative approach.

E. Some Exact Results in One Dimension

It would be useful to have some exactly soluble problems at hand in order to check the validity of the assumptions of Sec. III. The only exact calculation done so far for a three-dimensional problem is the density of states found by Lloyd,[7] already mentioned in Sec. I. It refers to a very specific problem, and is of no help to us.

Among the soluble one-dimensional problems, the one that most closely resembles ours is the electron in a set of randomly located, repulsive, δ-function potentials. The Schrödinger equation is

$$-\frac{d^2\psi}{dx^2} + V_0 \sum_i \delta(x - x_i)\psi = E\psi \ . \tag{17}$$

Frisch and Lloyd[2] have shown that the solution of (17) can be reduced to the study of a one-dimensional, one-parameter, stochastic process. Combining their procedure with some results of Borland[30] it is possible to prove the following theorem[31]: Consider a chain of length L, and one fixed configuration $\{x_i\}$, $0 < x_1 < x_2 \cdots < x_N < L$. Call an interval (a, b) on the x axis empty if it does not contain any of the x_i. Call $M(l)$ the maximum number of disjoint empty intervals of length l which the chain can contain. Let $\mathfrak{N}(E)$ be the integrated density of states for the problem defined by Eq. (17) and the boundary conditions $\psi(0) = \psi(L) = 0$; then

$$M\left(\frac{\pi}{\sqrt{E}}\right) \leqslant \mathfrak{N}(E) \leqslant M\left(\frac{1}{\sqrt{E}} \operatorname{cotan}^{-1}\left(\frac{\sqrt{E}}{V_0} - \frac{4V_0}{\sqrt{E}}\right)\right), \tag{18}$$

where the branch taking values between 0 and π has to be taken for $\operatorname{cotan}^{-1}(x)$. The theorem is particularly useful for $E \to 0^+$. It then states that the number of states below E is approximately equal to the number of empty intervals of half a de Broglie wavelength, $l \approx \pi/\sqrt{E}$, thus suggesting that the lowest eigenstates are the one-dimensional analogs of the bubble, Sec. II D. It also gives the asymptotic form[31]

$$\langle \mathfrak{N}(E) \rangle = c\, e^{-\pi\rho E^{-1/2}} \tag{19}$$

(c slowly varying) for $E \to 0^+$. By analogy we expect

$$\langle \mathfrak{N}(E) \rangle \sim c\, e^{-\mathrm{const}\, E^{-3/2}} \tag{20}$$

for the three-dimensional problem.

III. SEMICLASSICAL THEORY

A. Effective Potential and Density of States

We start by considering a situation which is completely opposite to the problem of Sec. II: an electron in a very smooth potential $V(\vec{x})$. It is well known that the density of states is approximately

$$n(E) \approx \frac{1}{(2\pi)^3} \int \cdots \int d^3\vec{x}\, d^3\vec{p}\, \delta[E - \vec{p}^2 - V(\vec{x})] \tag{21}$$

in this case. An elegant and general proof of this equation can be found, for example, in the paper by Gelfand and Yaglom,[32] who prove the equivalent equation

$$Z(\beta) = \int n(E) e^{-\beta E} dE \approx (4\pi\beta)^{-3/2} \int e^{-\beta V(\vec{x})}\, d\vec{x}\ . \tag{22}$$

We will now transform the hard-core problem into an approximately equivalent one in which the electron moves in a smooth effective potential, and then apply (21). The procedure is a slight reformulation of earlier work by Eggarter and Cohen.[18,19]

We note first that in the hard-core problem $\langle \vec{p}^2 \rangle = E$, since $\langle \psi | V | \psi \rangle = 0$ because of the boundary condition that ψ vanishes on the surface of each sphere. This, together with the uncertainty principle, gives a lower bound for the spatial extent of the wave functions of energy E:

$$\Delta x \geq 2\pi / (\Delta p_x) \approx 2\pi (3/E)^{1/2}\ . \tag{23}$$

If we restrict our attention to energies which are low enough to make $\Delta x \gg r_s$ [r_s defined by Eq. (11)] we see that the electron interacts with many scatterers simultaneously. It is thus natural to use the Wigner-Seitz argument locally to generate a smooth effective potential $\tilde{V}(\vec{x})$, related to the local density of scatterers $\tilde{\rho}(\vec{x})$ in the neighborhood of $\vec{x}$ by the Wigner-Seitz equations (11) and (12). We therefore assume

$$\tilde{V}(\vec{x}) = V_{WS}(\tilde{\rho}(\vec{x}))\ . \tag{24}$$

Clearly $\tilde{\rho}(\vec{x})$ must be constructed by sampling the density of hard spheres in the vicinity of $\vec{x}$, i.e., must have the form

$$\tilde{\rho}(\vec{x}) = \int \rho(\vec{x}\,') f(\vec{x} - \vec{x}\,')\, d\vec{x}\,'\ , \tag{25}$$

where $f(\vec{x})$ is a smooth positive weight function, whose integral over all space is 1, and which goes to zero over some characteristic distance L which has yet to be determined.

Two reasonable possibilities for the choice of L exist. These are $L \propto E^{-1/2}$, which is suggested by Eq. (23) and has been used by Eggarter and Cohen[18,19] and $L \propto |E - \overline{V}|^{-1/2}$, which follows from the variational calculation of Halperin and Lax[12] for electrons in a random Gaussian potential. Although we have not succeeded in finding a rigorous justification for either choice, we use $L \propto E^{-1/2}$ for the following reason: The spatial extent of the most localized wave functions, which is the smallest region the electron can sample, is essentially given by the uncertainty principle $\Delta x \approx 2\pi / \Delta p_x$. In the hard-core problem $\Delta p_x \approx (\frac{1}{3}\langle \vec{p}^2 \rangle)^{1/2} = (\frac{1}{3}E)^{1/2}$, hence $L \propto E^{-1/2}$. The situation is different in a Gaussian potential, where $\langle \vec{p}^2 \rangle = E - \langle \psi | V | \psi \rangle$. We believe that our choice is not in contradiction with the work of Halperin and Lax; the difference in sampling length is simply due to the fact that we deal with different problems. In our case the electron is always in a free space where $V = 0$; in their problem it moves in a potential that is close to $\overline{V}$.

Because of the energy dependence of L, the effective potential is also electron-energy dependent, $\tilde{V} = \tilde{V}(\vec{x}, E)$. This potential can be inserted in (21) to get an approximate density of states

$$n(E) \approx \frac{1}{4\pi^2} \int d\,\vec{x}\, [E - \tilde{V}(\vec{x}, E)]^{1/2}, \tag{26}$$

with the domain of integration consisting of all points which make the integrand real. If we want the ensemble average $\langle n(E) \rangle$ per unit volume we get the simpler form

$$\langle n(E) \rangle = (4\pi^2)^{-1} \langle [E - \tilde{V}(\vec{0}, E)]^{1/2} \rangle. \tag{27}$$

From the definition of $\tilde{\rho}$ and provided that within the range of f there is a huge number of scatterers (which will turn out to be the case in our problem), it follows that $\tilde{\rho}$ has a narrow Gaussian distribution, and the same is true for $\tilde{V}$. Let $\overline{\rho}$, $\overline{V}$ and σ_V, σ_ρ be their mean values and standard deviations, respectively. We can write (27) more explicitly as

$$\langle n(E) \rangle = \frac{1}{4\pi^2 (2\pi)^{1/2} \sigma_V} \int (E - V)^{1/2} e^{-(V - \overline{V})^2 / 2\sigma_V^2}\, dV \tag{28}$$

and after some elementary changes of variables

$$\langle n(E) \rangle = (4\pi^2)^{-1} \sigma_V^{1/2} F((E - \overline{V})/\sigma_v)\ , \tag{29}$$

where

$$F(x) = (2\pi)^{-1/2} \int_0^\infty z^{1/2} e^{-(x-z)^2/2}\, dz\ . \tag{30}$$

Everything is known in Eq. (29) except σ_V, which we could compute if we knew σ_ρ. This in turn requires the knowledge of the sampling function in Eq. (25) and we must content ourselves with an order of magnitude estimate since we have no way of determining $f(\vec{x})$ precisely. The approximation consists in replacing f by the characteristic function of a cubic box of side

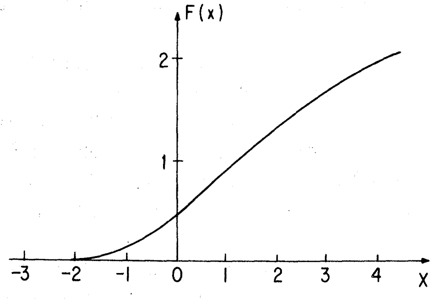

FIG. 6. Function $F(x)$, Eq. (30), which determines the shape of the density of states.

$$L \approx 2\pi(3/E)^{1/2} \tag{31}$$

centered at the origin. In order to correct somewhat this very crude approximation, we prefer to introduce an undetermined parameter c of order unity which can then be adjusted to fit the theory to experimental data. Thus we put

$$L = c\,2\pi(3/E)^{1/2}\,, \quad c \approx 1\,, \tag{32}$$

and

$$f(\vec{x}) = \begin{cases} L^{-3} & \text{inside a cubic box of side } L \text{ centered at the origin} \\ 0 & \text{everywhere else .} \end{cases} \tag{33}$$

It is now an easy matter to derive, assuming Poisson statistics for the number of scatterers in a cubic box, that

$$\sigma_\rho^2 = (2\sqrt{3}\,\pi c)^{-3/2}\rho E^{3/2} \tag{34}$$

and

$$\sigma_V^2 = \left(\frac{\partial V_{WS}}{\partial \rho}\right)^2 \sigma_\rho^2\,, \tag{35}$$

which completes the calculation of $\langle n(E)\rangle$, leaving only some arbitrariness in the choice of c.

The shape of $\langle n(E)\rangle$ is primarily determined by the function $F(x)$, Eq. (30), which is shown in Fig. 6. The asymptotic forms for $F(x)$ are readily obtained:

$$F(x) \sim x^{1/2}, \quad x \gg 1 \tag{36}$$

$$F(x) \sim |2x|^{-3/2}\, e^{-x^2/2}, \quad x \ll 1 \tag{37}$$

and so the density of states is given approximately by

$$\langle n(E)\rangle \sim (4\pi^2)^{-1}(E - \bar{V})^{1/2}\,, \quad (E - \bar{V})/\sigma_V \gg 1 \tag{38}$$

$$\langle n(E)\rangle \sim \frac{1}{4\pi^2}\,\frac{\sigma_v^2}{(2\,|E - \bar{V}|)^{3/2}}\; e^{-(E-\bar{V})^2/2\sigma_V^2}\,, \quad (E - \bar{V})/\sigma_V \ll -1\;. \tag{39}$$

The transition from the form (38) to the form (39) occurs over an energy range of order $\sigma_V(E = \bar{V})$. Assuming, for example, that ρ is low enough so that the optical approximation is valid, we have from Eqs. (34) and (35)

$$\sigma_V(E = \bar{V}) = (\rho a^3)^{1/4}(3\pi c^2)^{-3/4}\,\bar{V} \ll \bar{V}\,, \tag{40}$$

that is, the characteristic width of the tail of localized states is much smaller than the shift $\bar{V}$ of the band edge.

The asymptotic expression (38) is identical with (9), while the low-energy limit $E \to 0^+$, Eq. (39), is of the form (20) because $\sigma_V^2 \propto E^{-3/2}$, $E \to 0^+$. This strengthens our confidence in the semiclassical approximation made. It is also encouraging to see that the density of states, Eqs. (29) and (30), has the same functional form as the one found by Coopersmith[33] by a very sophisticated quantum-mechanical calculation. His result is $\langle n(E)\rangle = n_0^* g$, where n_0 is the free-electron density of states and g is a Gaussian centered at $\bar{V}$ and of width $W \propto \bar{V}(\rho a^3)^{1/4}$. Our result would agree exactly with Coopersmith's if (a) we made the simplifying assumption $\sigma_V(E) = \sigma_V(E = \bar{V})$ for all E (this was done in Ref. 18), and (b) we put $c = (3/2)^{5/6}(3\pi e)^{-1/2} \approx 0.3$. This choice of c, however, does not allow us to fit the experimental data of Sec. IV (they require $c = 1.4$). In addition, it is physically hard to believe that the electron should sample over less than half a de Broglie wavelength as $c \approx 0.3$ would indicate. We prefer to leave c as a parameter to be determined from experiment.

B. Percolation Theory and Nature of Electron States

Ziman[34] first pointed out that the transport properties of classical particles moving in a random potential constitute a problem closely related to percolation theory. We will now discuss the nature of electron states in the effective potential $\bar{V}(\vec{x}, E)$ defined by Eq. (24), starting from a similar classical point of view, and then investigate what changes the correct quantum-mechanical formulation of the problem would introduce in the discussion. The main ideas were already sketched by Eggarter and Cohen,[18] and further extended and clarified by Cohen[35] and by Economou *et al.*[13]

For each energy we will divide space into two regions, which we call allowed and prohibited, defined by the conditions $\bar{V}(\vec{x}, E) \le E$ and $\bar{V}(\vec{x}, E) > E$, respectively. The fraction of space which is allowed for a given energy E we denote as $c(E)$, and this quantity is clearly equal to the probability that a point chosen at random is allowed, i.e.,

$$c(E) = (2\pi)^{-1/2}\int_{-\infty}^{(E-\bar{V})/\sigma_V} e^{-t^2/2}\,dt\;. \tag{41}$$

For $E \to 0$ the upper limit goes to $-\infty$, and hence $c(E) \to 0$; for $E \to \infty$, $c(E) \to 1$. In addition $c(E)$ is a

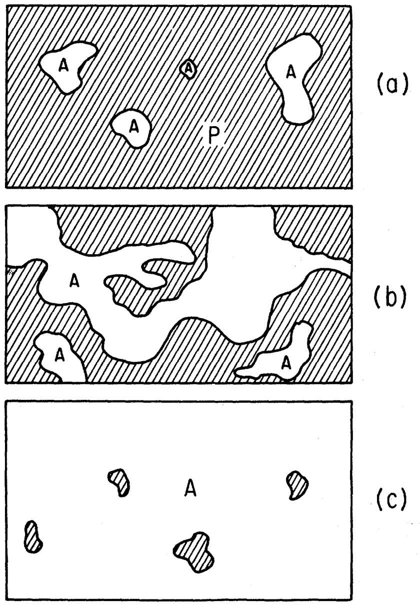

FIG. 7. Shaded region is in each case prohibited to a classical particle. In (a) we have $E < E_c$ and the allowed regions form isolated lakes; states are localized. In (b) E is slightly above E_c; allowed infinite channels coexist with allowed lakes, quantum mechanically all states are extended, but a fraction of them is resonant with high values of ψ only in one allowed lake. In (c) $E \gg E_c$, the particle can move almost freely with occasional scattering on prohibited islands; all states are extended.

monotonically increasing function of E; all this follows immediately from (41).

Let us consider now a low energy $(E - \overline{V})/\sigma_V \ll -1$. Then $c(E) \ll 1$ and most of the space is prohibited. The allowed regions will form isolated "lakes"[36] in a "continent" of prohibited space, something like Fig. 7(a). A particle located initially in one of the lakes would remain there forever, at least, classically. In the other extreme case $(E - \overline{V})/\sigma_V \gg 1$, $c(E) \approx 1$, and most of the space is allowed. The situation is depicted in Fig. 7(c) with prohibited "islands" in an allowed "sea." A particle of energy E can now propagate freely, with occasional scattering on prohibited islands.

From continuity considerations it is clear that as energy increases the allowed lakes present at low energy grow in size, until, at some critical energy E_c, the first unbounded allowed channel will appear [Fig. 7(b)]. This represents the first possibility that a classical particle can diffuse away from its initial location.

The determination of E_c, or $c(E_c)$, is one of the central goals of percolation theory.[37,38] Another important quantity is the percolation probability $p(E)$ defined as the conditional probability that a point $\vec{x}$ belongs to an unbounded allowed channel *if* $\vec{x}$ is in allowed space; $p(E)$ is strictly zero for $E < E_c$ since there are no channels, and increases monotonically to 1 above E_c.

A classical dc mobility calculation should consider only the fraction $p(E)$ of the particles having energy E. In fact, particles with $E < E_c$ are bound to finite lakes and should not be counted, while particles with $E \geqslant E_c$ can drift steadily only if they are in infinite channels, which happens with probability $p(E)$.

When quantum effects are included, the possibility appears that electrons can tunnel across prohibited regions. However, one can convince oneself by putting numbers into the various equations that, for situations of practical interest, one can neglect processes involving tunnelings in a mobility calculation. The amplitude for tunneling across one prohibited region is considerably less than 1, and motion over any macroscopic distance requires the crossing of a huge number of prohibited regions. We conclude that $\mu(E) \propto p(E)$ is still a good approximation in a quantum-mechanical treatment of the problem.

Numerical work by Kirkpatrick[39] suggests that very close to the percolation threshold $\mu(E) \propto [c(E) - c(E_c)]^{8/5}$ would probably be a better assumption. Cohen[40] sees this as an indication that the width A and length l of the first percolation channel go as $A \propto [c(E) - c(E_c)]^{\alpha}$ and $l \propto [c(E) - c(E_c)]^{\beta}$, with $\alpha > 0$, $\beta < 0$, and $\alpha - \beta = \frac{8}{5}$. We have not attempted to include any of these corrections in our theory because they apply only when $c(E)$ is just a few percent above the critical concentration $c(E_c)$, and this energy range receives little weight in our computation of the mobility [Eq. (55) below]. This last statement is justified by the discussion at the end of Sec. IV A.

The question whether $\mu(E)$ is strictly zero or only very small for $E < E_c$ is irrelevant for our calculation, but has considerable importance from a conceptual point of view. The work of Anderson,[16] and especially the discussion of it given by Mott,[41] suggests the following: (i) For $E < E_c$ the exact eigenfunctions of the problem will be localized. The nonresonant character of tunneling from lake to lake makes it ineffective in causing delocalization. (ii) For $E \gtrsim E_c$ the states describing electrons in infinite channels form a continuum of extended states. The states describing electrons which were classically bound to lakes now become extended but resonant in character, with most of the wave amplitude in the original lake, and a small part of the wave function spilling over into nearby infinite channels. The fraction $1 - p(E)$ of resonant states goes rapidly to zero for increasing E, until (iii) at $E \gg E_c$ all states are extended, with considerable amplitude in the allowed sea, and small amplitude in prohibited islands.

The critical energy E_c separates localized from extended states, and is the "mobility edge" of the Mott-CFO[15] model of disordered materials.

We now turn our attention towards the determination of E_c. The percolation problem has so far been studied mainly on lattices by the use of Monte Carlo methods. Frisch, Hammersley, and Welsch[42] have determined in this way the percolation probability as a function of concentration of allowed sites for several Bravais lattices. We can convert our continuous problem into an approximately equivalent lattice problem if we simply imagine space divided into boxes of side L, the correlation length of the potential, and use accordingly the result for a cubic lattice, $c(E_c) = 0.3$, as an estimate for E_c. From the Gaussian character of $c(E)$ we then get the equation

$$E_c = \overline{V} - 0.52\sigma_V(E_c) \tag{42}$$

which in the very low-density limit becomes

$$E_c = \overline{V}\,[1 - 0.52(\rho a^3)^{1/4}(3\pi c^2)^{-3/4}]. \tag{43}$$

Our choice of the cubic geometry has been criticized by Zallen and Scher,[43] who claim that for percolation in a continuous potential the critical concentration is $c(E_c) = 0.15$ (instead of 0.30). Although their value has not been derived rigorously, we must admit that our choice of the cubic lattice is to a large extent arbitrary. Had we chosen a fcc lattice, for example, the result would have been $c(E_c) = 0.195$, while for a tetrahedral lattice $c(E_c) = 0.425$. Our $c(E_c)$ is therefore uncertain approximately by a factor of 2; but this is of no practical importance for our calculations: σ_V contains the parameter c anyway, and by adjusting it to fit the experiments we correct for all kinds of factors of order unity which have escaped the present elementary theory.

C. Semiclassical Mobility

In classical kinetic theory the mobility of an excess electron in a gas of heavy scatterers at temperature T is given by

$$\mu = Z^{-1} \int \mu(E) n(E)\, e^{-\beta E}\, dE , \tag{44}$$

$$Z = \int n(E)\, e^{-\beta E}\, dE , \tag{45}$$

where

$$\mu(E) = \tfrac{4}{3} e\, \tau(E) . \tag{46}$$

$\tau(E)$ is the mean collision time for electrons of energy E, i.e.,

$$\tau(E) \approx \lambda / v = (\sigma\rho\sqrt{E})^{-1} . \tag{47}$$

The preceding discussion, Sec. III B, suggests immediately how to change the various classical equations in order to apply them to our problem. First, Eq. (46) should contain a factor $p(E)$ to exclude localized (or resonant) states, i.e.,

$$\mu(E) = \tfrac{4}{3} e p(E) \tau(E) ; \tag{48}$$

second, the electrons cannot be considered as propagating in free space, but instead in the potential $\tilde{V}(\vec{x}, E)$, so that the velocity is

$$v = [E - \tilde{V}(\vec{x}, E)]^{1/2} ; \tag{49}$$

and third, the mean free path is reduced below its classical value $\lambda_c = (\sigma\rho)^{-1}$ by the presence of prohibited regions. We can get a simple estimate of the mean free path λ_p associated with scattering off prohibited islands. The correlation length of $\tilde{V}(\vec{x}, E)$ is L, Eq. (32). The probability of finding along a given path k correlation lengths of allowed space, a prohibited region occurring in the $(k+1)$th, is

$$p_k \approx c^k(E)\,[1 - c(E)] , \tag{50}$$

and so

$$\lambda_p \approx \textstyle\sum_k k L p_k = L c(E)\,[1 - c(E)]^{-1} \tag{51}$$

which combines with λ_c to give an energy-dependent mean free path

$$\lambda(E) = \frac{\lambda_c \lambda_p}{\lambda_c + \lambda_p} = \frac{L c(E)}{1 - c(E) + L\sigma\rho c(E)} . \tag{52}$$

The mean collision time can now be computed from this and the conditional average $\langle v^{-1}\rangle_a$ of the inverse velocity over allowed space:

$$\begin{aligned} \tau(E) &= \lambda(E)\,\langle v^{-1}\rangle_a \\ &= \frac{\lambda(E)}{(2\pi)^{1/2}\sigma_V c(E)} \int_{V<E} (E - V)^{-1/2} \\ &\qquad\times e^{-(V-\overline{V})^2/2\sigma_V^2}\, dV \\ &= 2\lambda(E)\, c^{-1}(E)\, \sigma_V^{-1/2} F'[(E - \overline{V})/\sigma_V] . \end{aligned} \tag{53}$$

In order to do numerical work with our equations we need in addition some explicit form for the percolation probability $p(E)$ given graphically by Frisch, Hammersley, and Welsh.[42] For our purposes

$$p(E) = \begin{cases} 0 , & c(E) \le 0.3 \\ 1 - e^{-25[c(E)-0.3]} , & c(E) > 0.3 \end{cases} \tag{54}$$

fits their numerical values (Fig. 6, simple cubic in Ref. 42) accurately enough. The approximation (54) fails for $c(E) \to (0.3)^+$, where $p(E) \propto [c(E) - 0.3]^{\alpha}$ with $\alpha \approx 0.6$ but the discrepancy is unimportant for our calculation for reasons given below at the end of Sec. IV A.

From Eqs. (48), (53), and (54) we find the energy-dependent mobility $\mu(E)$. The shape of this curve has the general form shown in Fig. 8. Below the mobility edge E_c, $\mu(E)$ vanishes because of the factor $p(E)$; for $E \gtrsim E_c$, $\mu(E)$ increases linearly [because this is the behavior we have chosen for our approximate $p(E)$, Eq. (54)] and for $E \gg \overline{V}$, $\mu(E)$ becomes free-electron-like, $\mu(E) \approx \frac{1}{3} e(\sigma\rho)^{-1}(E - \overline{V})^{-1/2}$,

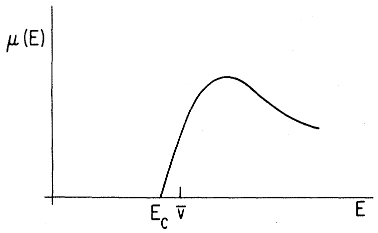

FIG. 8. Typical behavior of the mobility $\mu(E)$. At $E < E_c$ it vanishes because the percolation probability is zero; at $E \gtrsim E_c$ it increases roughly as $p(E)$; the decrease at higher energies occurs because the collision time $\tau(E)$ diminishes with increasing velocity.

differing from the classical expression only by a shift $\bar{V}$ in the zero of energy.

At this point we have all the necessary equations to compute the electron mobility $\mu(\rho, T)$ as a function of temperature and density of hard spheres:

$$\mu(\rho, T) = \frac{\int n(E)\,\mu(E)\,e^{-\beta E}\,dE}{\int n(E)\,e^{-\beta E}\,dE}\,. \tag{55}$$

A simplified version of this calculation was done by Eggarter and Cohen[19] and compared with an extremely complicated first-principle calculation of Neustadter and Coopersmith.[44] The comparison showed qualitative agreement: The mobility is close to the classical Langevin result

$$\mu_{\text{class}} = 4e/3\sigma\rho(2\pi mkT)^{1/2} \tag{56}$$

at low densities, and drops rather suddenly when the density of scatterers is increased beyond a critical value ρ_{crit}. The values of ρ_{crit}, however, turned out to be somewhat different in the works of Neustadter and Coopersmith and ours.

Since a mobility transition like the one described above has been observed experimentally for excess electrons in gaseous He, we devote Sec. IV to the study of this problem, as a test for the present theory.

IV. MOBILITY OF EXCESS ELECTRONS IN GASEOUS He

A. Consequences of He-He Interaction and of Thermal Motion of He Atoms

Before applying the theory of Sec. III to excess electrons in gaseous He, we must discuss some further properties of this system. First, at the temperatures $\approx 4\,^\circ\text{K}$ and densities $\approx 10^{20}$–10^{21} atoms/cm^3 we will be interested in, He shows considerable departures from ideal-gas behavior. Therefore the distribution of atoms in the "sampling box" defined by Eq. (33) will not follow a Poisson law. But the modification this introduces in the calculation is trivial; we simply must replace Eq. (34) by

$$\sigma_\rho^2 = (2\sqrt{3}\,\pi c)^{-3/2}\rho E^{3/2}\;k_B T\left(\frac{\partial\rho}{\partial P}\right)_T\,, \tag{57}$$

since, as is well known, the fluctuation in the number of particles for a gas in the grand canonical ensemble is

$$\langle\Delta N^2\rangle = \langle\Delta N^2\rangle_{\text{ideal gas}}\;k_B T\left(\frac{\partial\rho}{\partial P}\right)_T\,. \tag{58}$$

To calculate $(\partial\rho/\partial P)_T$ we use the equation of state

$$P = \rho k_B T\,[1 + \rho B(T)] \tag{59}$$

and the experimental values[45] of the first virial coefficient $B(T)$.

Second, we have the fact that He atoms are not fixed in space. This has a very important consequence: The mobility of "localized" electrons becomes nonzero. To discuss this point, let us consider specifically a situation like that shown in Fig. 9, in which a very low-energy electron is trapped in a region of low gas density. If an electric field is applied the electron can drift steadily simply by pushing out of the way some He atoms. This motion would be very complicated to follow in detail, since the He atoms are in thermal agitation, and the local density $\tilde{\rho}(\vec{x})$ around the electron would fluctuate in time. The only thing we can say about it is that the number of He atoms that are pushed away must be sufficient to keep the local density $\tilde{\rho}(\vec{x})$ at values that are compatible with the electron energy, i.e., we have the constraint

$$V_{WS}[\tilde{\rho}(\vec{x})] < E \quad \text{at all times.} \tag{60}$$

The object "trapped electron + low-gas-density region" will be called a "pseudobubble" because of its similarity with the "bubble" state in liquid He.[17,22,27]

If for the time being we consider only low energies $|E - E_c| \gg kT$ we conclude also that pseudobubbles are rather stable. Jumps to an extended state would require an increase in electron energy much bigger than the average thermal fluctuations in this quantity, and are therefore rare events. If furthermore we restrict ourselves to a zero-field mobility calculation, the pseudobubble stability is not destroyed by its drift motion.

The above arguments are not valid for electron states below but close to the mobility edge: $|E - E_c| \approx kT$. But these states are not important in the evaluation of $\mu(\rho, T)$, Eq. (55), as long as their mobility is much lower than that of free electrons. The reason is the following: If the peak in $n(E)e^{-\beta E}$ is deep in the tail of localized states, then the region $E \lesssim E_c$ is practically depopulated. If the peak in $n(E)e^{-\beta E}$ is close to or above E_c, then a nonnegligible fraction of the electrons is in extended states, and these dominate the mobility, so again $E \lesssim E_c$ is not an important region. We therefore do not need a detailed discussion of these states.

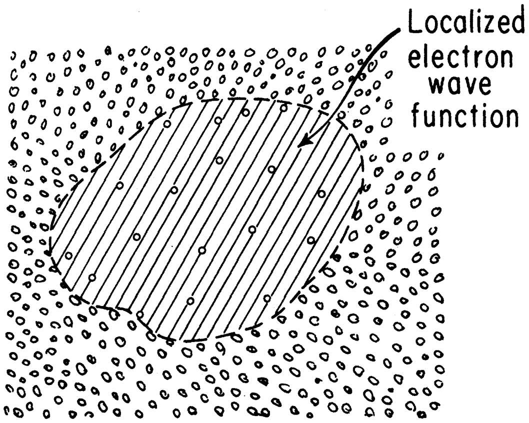

FIG. 9. Region of lower than average gas density contains a trapped electron. We call this object a pseudobubble.

B. Qualitative Discussion of μ-vs-ρ Curves

Levine and Sanders[17] have measured the mobility of excess electrons injected in gaseous He at $T \approx 4$ °K and pressures up to the saturated vapor. Similar measurements at higher temperatures were done by Harrison.[46] The curves μ vs ρ, at constant temperature, look in all cases like those shown in Fig. 10.

We can understand this shape in a very intuitive manner by using the ideas developed so far. It is easy to verify that the function $n(E)e^{-\beta E}$ has one maximum, say at $E_{\max}$, and is rather sharply peaked. For low density $\rho < \rho_1$, Fig. 10, this maximum occurs above $\overline{V}$, the electron spends most of the time in extended states, and the classical Langevin mobility is approximately correct. The reason why $\mu < \mu_{\text{class}}$ is that the mean free path for any energy is smaller than the classical value $\lambda_{\text{class}} = (\sigma\rho)^{-1}$ because of the presence of prohibited "islands."

As the density is increased, the average potential $\overline{V}$ and the mobility edge E_c shift to the right with respect to $E_{\max}$. In the density range $\rho_1 < \rho < \rho_2$ the peak in $n(E)e^{-\beta E}$ moves from the right to the left of E_c, and the mobility decreases drastically because so does the fraction of electrons in extended states. For $\rho > \rho_2$, finally, practically all electrons are well below E_c, in pseudobubble states, and the mobility curves saturate at a value characteristic for these objects.

Our next task will be to put the above argument in numerical form.

C. Parameters Characterizing Pseudobubbles

As stated in Sec. IV A, a detailed study of the motion of an electron in a pseudobubble state would be extremely complicated. It is nevertheless possible to make an approximation which reduces the problem to an almost trivial form, and still retains enough of the physics to give reasonable numerical estimates of pseudobubble sizes, mobilities, etc.

We start by defining, for each pseudobubble, an equivalent hard sphere of radius R_{eq} which has the same mobility as the pseudobubble. It is clear that this can always be done, no matter what the mobility of the pseudobubble in question is.

Next, we want to estimate R_{eq}. Here we make the approximation[19] that the mobility of an object in the gas is primarily determined by the number ΔN of He atoms that this object has to displace during its motion; hence

$$\tfrac{4}{3}\pi R_{\text{eq}}^3 \rho \approx \Delta N . \qquad (61)$$

The problem of estimating R_{eq} now reduces to find ΔN. We stated before that the density of He atoms in the vicinity of the electron may fluctuate in time, but has an upper bound imposed by Eq. (60). This equation can be inverted numerically to give an inequality of the form

$$\tilde{\rho}(\vec{x}) < \rho_{\max}(E) . \qquad (62)$$

But $\tilde{\rho}(\vec{x})$ is essentially the density of atoms in a volume $L^3(E)$, hence the deficiency of He atoms is $\Delta N \approx L^3(E)[\overline{\rho} - \tilde{\rho}(\vec{x})]$. The local density $\tilde{\rho}(\vec{x})$ fluctuates in time but is constrained by the inequality (62) to remain deep in the tail of a Gaussian probability distribution. Since this distribution goes rapidly to zero for decreasing $\tilde{\rho}(\vec{x})$ we can conclude that $\tilde{\rho}(\vec{x}) \approx \rho_{\max}(E)$ most of the time, so finally,

$$\Delta N \approx L^3(E)\,[\overline{\rho} - \rho_{\max}(E)] . \qquad (63)$$

Equations (61) and (63) determine $R_{\text{eq}}(E)$. Since very rough approximations were made we introduce a second adjustable parameter of order unity, and replace (61) by

$$R_{\text{eq}} = c'(3\Delta N/4\pi\rho)^{1/3}. \qquad (64)$$

It turns out that $c' = 0.4$ gives the best fit to the ex-

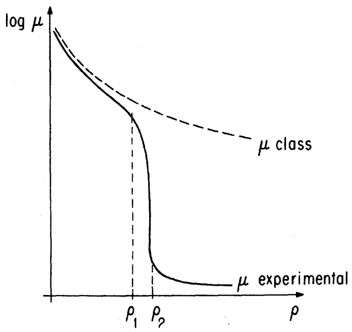

FIG. 10. Typical constant-temperature mobility curve for an excess electron in gaseous He. The dotted line is the prediction of classical kinetic theory.

perimental data.

The mobility of a pseudobubble, which is by definition the same as the mobility of a hard sphere of radius $R_{eq}(E)$, can now be computed from the interpolation formula[47]

$$\mu_{pb}(E) = \frac{e}{6\pi\eta R_{eq}} \left(1 + \frac{9\eta\pi}{4\rho R_{eq}(2\pi M_{He} k_B T)^{1/2}}\right). \quad (65)$$

Although the foregoing discussion is justified only for $|E - E_c| \gg kT$, we use the set of equations defining the pseudobubble mobility $\mu_{pb}(E)$ for all values of E up to E_c. That this can be done follows from the discussion at the end of Sec. IV A. This concludes the work needed to compare the theory with the experimental data. The mobility at any temperature and density can now be calculated numerically using Eq. (55) with

$$\mu(E) = [1 - p(E)]\,\mu_{pb}(E) + \tfrac{4}{3} e p(E) \tau(E) . \quad (66)$$

The first term in the right-hand side describes pseudobubbles, i.e., electrons in localized states, while the second term is the mobility associated with extended states, defined in Sec. III, Eqs. (48)-(54).

D. Numerical Work and Comparison with Experiments

A calculation of the μ-vs-ρ curves for electrons in He at various temperatures, using the above set of equations, was done by Eggarter and Cohen in Ref. 19. The scattering length was taken as 0.62 Å.[48] The data were displayed as $\ln\mu$-vs-P/P_s curves for $T = 3.65$, 3.9, and 4.19 °K. P/P_s is the ratio of the gas pressure to the saturated vapor pressure at each temperature. Results are shown as Fig. 3 in Ref. 19. The reason for choosing $\ln\mu$ and P/P_s as variables is that the experimental data of Levine and Sanders were presented in this way. All calculations were carried out with ρ and T as independent variables, and at the end P/P_s was computed from the known properties of He.[45] With the choice of parameters $c = 1.7$ and $c' = 0.3$

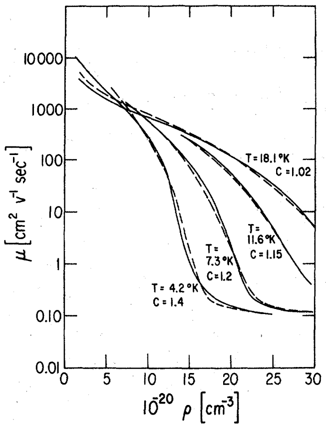

FIG. 12. Mobilities as measured by Harrison (full lines) and as calculated with the present theory. The parameter c had to be changed slightly with temperature to get a good fit.

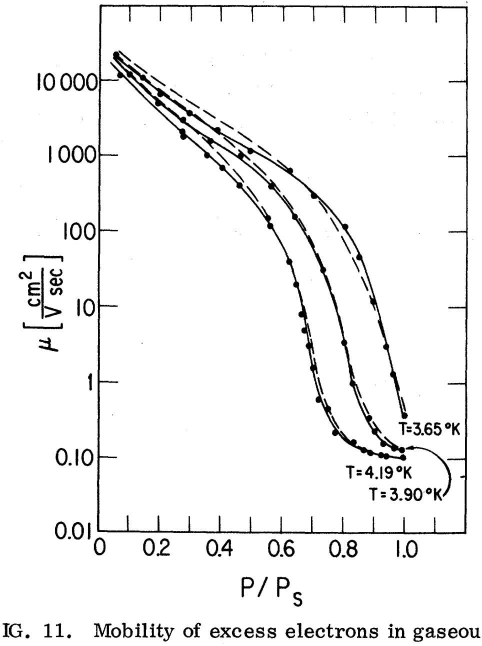

FIG. 11. Mobility of excess electrons in gaseous He. The circles are the results of measurements by Levine and Sanders; the dotted lines are the predictions of the present theory. The full lines have no theoretical significance.

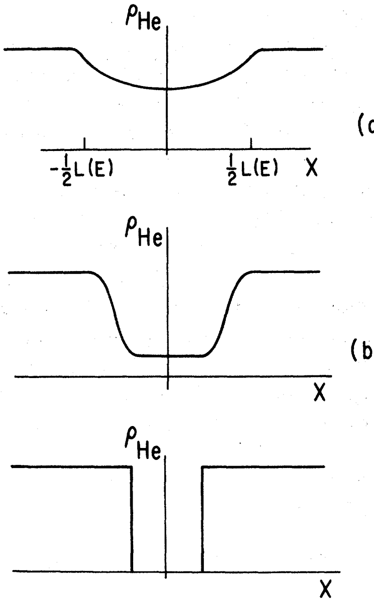

FIG. 13. Density of He gas in the vicinity of a trapped electron in (a) gas at low pressure, (b) gas at high pressure, and (c) liquid He.

a good fit to the experimental data was achieved.

Unfortunately, a small numerical error in the computation of P/P_s occurred in that work; we are very grateful to Dr. J. Hernandez for discovering it and bringing it to our attention. The correct value for P/P_s is

$$(P/P_s)_{\text{correct}} = 1.1298(P/P_s)_{\text{Ref.19}} \;. \tag{67}$$

To bring the theory again into agreement with experiment after this correction is made, the parameters c and c' had to be redetermined. It turns out that $c = 1.4$, $c' = 0.4$ give the best fit to the measured mobilities. The new curves are shown in Fig. 11.

The mobilities vary over five orders of magnitude, and nowhere is our theory off by more than a factor of 1.5. Considering that the present is only an order-of-magnitude calculation, the agreement is very good.

The main errors occur in the low-density region $P/P_s \lesssim 0.5$ where our mobility is below but close to the classical result Eq. (56) while the experimental data are somewhat lower. As is discussed in Ref. 19 this is due to the fact that Eq. (52) overestimates the mean free paths above but close to the average potential. (This energy is the most populated at the densities in question.) A quantum-mechanical particle will scatter on potential fluctuations even if these are not high enough to reflect a classical particle; thus our classical calculation overestimates the mobility.

Electron mobility measurements at higher temperatures, up to $T \approx 20\,^\circ\text{K}$ were recently done by Harrison.[46] Hernandez checked the present theory against these new data, and found that again a good fit could be obtained, provided the parameter c was slightly decreased with increasing temperature.[49] He kindly sent us his results, which are shown in Fig. 12.

E. Some Further Discussion of Pseudobubbles

The idea of pseudobubble states was crucial in explaining the "saturation" of the mobility curves at high density ($\rho \gtrsim \rho_2$ in Fig. 10). It would be interesting to have a good physical feeling for what these pseudobubbles look like, and what their relation to the bubble state in liquid He is. The present theory is not detailed enough to carry out such a study, but it is nevertheless possible to draw some conclusion from purely physical arguments.

We are considering a situation in which an electron is surrounded by He atoms. These atoms are in thermal motion, and interact with the electron via a repulsive potential. The electron-He interaction clearly tends to keep the atoms away from the electron, while the thermal motion tends to produce a distribution of atoms which is on the average homogeneous in space. As a result of these opposing tendencies, some kind of equilibrium situation must be reached, in which the density of He atoms inside the pseudobubble looks like that in Fig. 13(a). The typical distance over which a deficiency of He atoms exists is of order $\frac{1}{2}L(E)$, something like 50 Å at $T \approx 4\,^\circ\text{K}$, while the equivalent radius of the pseudobubble, defined as the radius of the hard sphere that deplaces the same number of atoms as the pseudobubble, is given by Eqs. (63) and (64). Typical values are around 14 Å, close to the bubble radii reported for the liquid state of similar temperatures $T \approx 4\,^\circ\text{K}$.[17, 46] At given temperature and pressure, pseudobubbles of different equivalent radii coexist; R_{eq} is a function of energy: $R_{\text{eq}} = R_{\text{eq}}(E)$, and since there is a probability distribution $Z^{-1}n(E)\,e^{-\beta E}$ for the electron energy, this implies a probability distribution for R_{eq}. It is certain that also the shape of pseudobubbles, i.e., the curve $\rho(x)$ shown in Fig. 13(a), is not well defined; this curve should be interpreted as describing some vague kind of average shape.

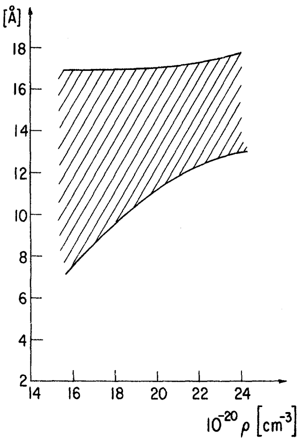

FIG. 14. At each density 99% of all pseudobubbles have equivalent radii in the shaded region. It can be seen that fluctuations in pseudobubble sizes decrease as the density becomes higher.

Let us accept these ideas and discuss what happens when the density is increased at constant temperature. The main change will be a relative gain of importance of the electron-He interaction with respect to the thermal motion. Also as the interatomic separation decreases, the He-He interaction, not mentioned so far, will start to play a significant role. As seen from Eq. (58) and the fact that $k_B\, T(\partial\rho/\partial P)_T > 1$ this interaction produces an increase in $\langle \Delta N^2 \rangle$ with respect to the ideal gas, indicating a tendency of the atoms to cluster together. As a result of all this one would expect pseudobubbles to look more and more like square wells [say as in Fig. 13(b)] as the density of the gas is increased. In Fig. 14 we have plotted in a (ρ, R_{eq}) plane a shaded area which, for each density, contains the equivalent radii of 99% of all pseudobubbles (it corresponds to $T = 4.19\,^\circ\mathrm{K}$). We can see that for increasing density the fluctuations in R_{eq} become smaller, and it is reasonable to assume that also fluctuations in shape will diminish as ρ increases.

We believe therefore that our pseudobubbles and the bubbles in liquid He [which can be idealized by a He density like that shown in Fig. 13(c)] are physically the same thing, and that the quantitative differences between the two can be fully explained by the different He densities. Pseudobubbles become better and better defined, with increasing ρ until eventually at the density of liquid He the minimum in free energy corresponds to a bubble like Fig. 13(c), and this minimum is so peaked that fluctuations in shape and size are insignificant.

It is interesting to note that Harrison[46] reaches exactly the same conclusions from a self-consistent calculation of the most-probable bubble configuration, combined with an analysis of the experimental data.

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