Self-trapped states of electrons in dense fluids*

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(Received 1 July 1974)

The conditions which lead to electron self-trapping, in a material, are theoretically investigated. The theory is developed for the simple case of a dense fluid, composed of a single kind of atom, obeying the ideal gas equation of state, and interacting with an electron as a system of hard-sphere scatterers. Possible generalizations are noted. A static continuum approximation and statistical considerations define configurations in which atoms feel no net force, electron states are obtained for these configurations, and, then, stability is investigated. The theory developed is shown to reduce to the case first investigated by Toyozawa, in the limit of small distortions (from the average configuration in the absence of the electron). The material-electron coupling constant depends on the average density, and since the stiffness of the materials is shown to be the external pressure, both may be continuously and independently varied experimentally. The results, for arbitrary distortions, lead to stable self-trapping and metastable quasifree electrons for strong coupling, weak stiffness; stable quasifree electrons and unstable self-trapping for weak coupling, strong stiffness; and metastable self-trapping in a limited intermediate regime. The different regimes are delimited quantitatively. The theoretical importance of this work resides in the fact that the generally used adiabatic approximation can only be justified for system states near stable or metastable configurations. The experimental consequences of changes in the stability of configurations are dramatic changes in some properties. For example, the observed electron-drift-mobility plunge in fluid helium is shown to be strongly correlated with the predicted transition of self-trapped states to stability.

I. INTRODUCTION

The purpose of this paper is to investigate the conditions which will lead to electron self-trapping in materials. When these conditions are realized, electron transport characteristics and optical properties, for example, are strongly influenced. Dense fluids have been chosen as the materials of interest in this investigation. These materials are attractive experimentally since they can be well characterized and, as will be shown, the electron-material coupling and the stiffness of the material may be continuously and independently varied by control of the externally determined pressure and temperature.

It seems appropriate to begin by investigating "simple" cases and then systematically remove the simplicity to generalize the results. Therefore results will be presented for dense fluid helium at densities up to that of the liquid at atmospheric pressure, and for temperatures up to room temperature. Experimental results of low-field electron drift mobility are available. The theoretical simplicity offered by a material which is essentially an ideal gas, with a single type of atom, which scatters electrons with a spherically symmetric short-range potential, is ideal. Further, it may be generalized: by working in regimes where the equation of states has known modifications from that of an ideal gas; by studying multifluid mixtures; and by introducing species with more complicated angularly dependent electron-scattering characteristics. The flexibility available in experiments and theory offers systems which may well be prototypes of a wide class of technologically interesting materials, including structurally and compositionally inhomogeneous ones.

As might be expected for the simplest case, stable electron self-trapping occurs for large-coupling and low-stiffness materials. Metastable self-trapping is also found. The appropriate conditions can be established quantitatively. It is also found that unstable self-trapping is possible and, according to experiment, observable, as are conditions of nonthermal equilibrium. Possible generalization of the present work will be noted, throughout the paper, as appropriate. The details of the model, results, comparison with experiment, and discussion comprise the remainder of the paper. The work being reported is a modification and extension of previous work by the author (Ref. 9 below).

II. MODEL

The system consists of an excess electron and a collection of s-wave scatterers of a single kind. The scatterers are treated as a statistical continuum obeying the ideal-gas equation of state. According to the Born-Oppenheimer approximation,[1] the states available to the electron should be found with the atoms fixed in configurations where the net force on each atom vanishes.[2] Nearby configurations should also be examined to investigate stability; then atomic motion can be treated, as

usual, by perturbation theory. Allowing the atoms to move into configurations where the net force on each atom does not vanish is a study of fluctuations. The study of fluctuations far from equilibrium seems very difficult since, although the electron states for an arbitrary configuration may in principle be found, an assumption that the atomic motion may be treated perturbatively is strongly suspect and nonadiabatic processes are presumably important. It is therefore crucial to establish which configurations of the system are equilibrium ones.

Atomic configurations are to be specified by a position-dependent number density $\rho(r)$. The Schrödinger equation for the electron is to be solved, for a given $\rho(r)$, using the Wigner-Seitz (WS) potential

$$V_\infty\left(\frac{\rho(r)}{\rho_\infty}-1\right)\equiv -V_\infty\Delta(r)\ ,$$

where $\Delta(r)$ is the dilation and V_∞ is the potential[3] appropriate to the average density ρ_∞, which is obtained from the external pressure and temperature according to the fluid equation of state. The linear density dependence is known to be somewhat inconsistent with the WS potential, but this is of minor importance; the zero of energy has been taken as that for the uniform configuration $\rho(r)=\rho_\infty$. Finally, the polarizability of the fluid has been assumed small and neglected (which may not be reasonable for materials such as liquid neon, though it is appropriate for helium).

In principle, solutions are to be sought for arbitrary $\rho(r)$ with the total energy (fixed atoms)[2] obtained by adding the electron contribution, $E_{el}(\rho(r))$, to the energy required to adiabatically construct the dilation $\Delta(r)$. Statistically, the energy to establish $\Delta(r)$ is given by the integral over all space of[4]

$$\rho(r)\left(kT\ln\frac{P(r)}{P_\infty}\right)-[P(r)-P_\infty]\ ,$$

where the pressure is

$$P(r)=\rho(r)kT\ .$$

An approximation to the Helmholtz free energy of the system, which neglects the entropy associated with the center of mass of the electron and the density distortion, is then obtained from

$$E_{TOT}(\Delta(r))=\rho_\infty kT\int\{\Delta(r)+[1-\Delta(r)]\ln[1-\Delta(r)]\}d^3r+E_{el}(\Delta(r))\ . \quad (1)$$

This equation can be verified to hold even if the equation of state is modified to include a small correction due to a nonzero second virial coefficient. The equation for the electron is

$$\left(-\frac{\hbar^2}{2m}\nabla^2-V_\infty\Delta(r)-E_{el}(\Delta(r))\right)\psi(r)=0\ . \quad (2)$$

The requirement that each atom feel no net force in the configuration $\Delta(r)$ is equivalent to requiring that $E_{TOT}(\Delta(r))$ be an extremum with respect to arbitrary small variations of $\Delta(r)$. Statistically, the requirement is of a constant chemical potential (electron interaction included):

$$kT\ln\left(\frac{P(r)}{P_\infty}\right)+\frac{V_\infty|\psi(r)|^2}{\rho_\infty}=0\ ,$$

which yields[5]

$$\ln[1-\Delta(r)]=-\frac{V_\infty|\psi(r)|^2}{\rho_\infty kT}\ . \quad (3)$$

Equation (3) would normally contain $\Delta(r)$-dependent atom-atom interactions, which vanish for an ideal gas. It is apparent throughout that V_∞ (which increases with ρ_∞) is the electron-material coupling constant, and $\rho_\infty kT$ (the external pressure) plays the role of the stiffness of the material. Thus by varying the pressure and temperature a continuous independent variation of coupling constant and stiffness may be achieved.

Toyozawa[6] treated the problem of self-trapping by a continuum in terms of a coupling constant and a material stiffness. Equation (2) is identical to the one he used. Further, if $\Delta(r)$ is assumed small ($\ll 1$) and Eqs. (1) and (3) are expanded to lowest nonvanishing order, his equations are obtained, with the given identifications for coupling constant and stiffness,

$$E_{TOT}=E_{el}+\rho_\infty kT\int\Delta(r)^2d^3r\ ,$$

$$\Delta(r)=\frac{V_\infty|\psi(r)|^2}{\rho_\infty kT}\ ,$$

but only in the limit of small dilation. This limit is indeed appropriate, in general, for the positive-energy solutions of Eq. (2), but may not be appropriate if Eqs. (2) and (3) yield bound electron states. The relationship of the present work to that of Toyozawa will be explored further below. In what follows, the general case is explored.

A. Quasifree states

A subset of solution to Eqs. (1)–(3) is given by

$$\psi(r)\simeq(\Omega)^{-1/2}e^{i\vec{k}\cdot\vec{r}};\quad \Delta(r)\simeq 0;$$

$$E_{TOT}\simeq\frac{\hbar^2k^2}{2m}\ .$$

That is, if the electron state is assumed diffuse (the normalization volume Ω large) then the right-hand side of Eq. (3) will be small and $\Delta(r)$ will also be small; Eq. (2) demonstrates that the diffuse electron is a self-consistent solution. With fixed atoms,[2] $\Delta(r)=0$ with $E_{TOT}=0$ is an energy minimum. Keeping $\Delta(r)=0$ and increasing E_{el} increases E_{TOT},

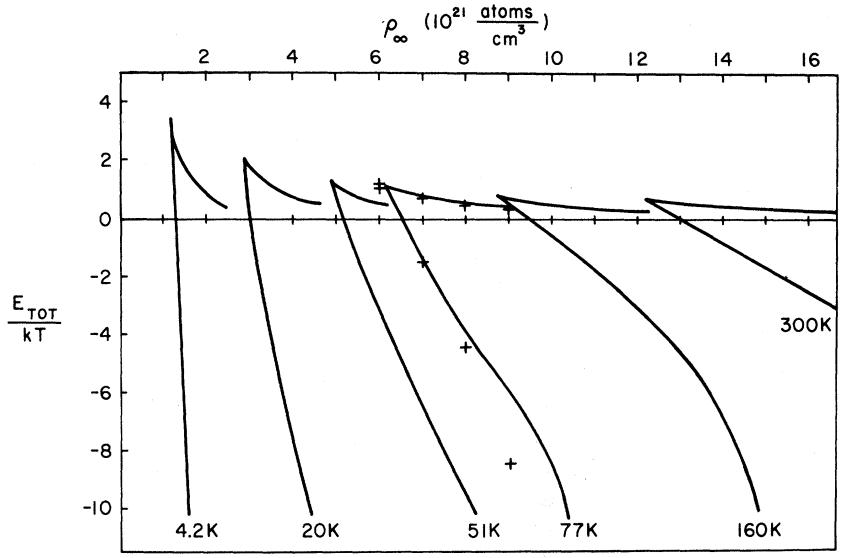

FIG. 1. Total energy in units of kT, for selected temperatures, of states satisfying Eqs. 1–3, as a function of number density for fluid helium. $E_{TOT}=0$ is also a solution. For any ρ_∞ and T the minimum energy state shown is an absolute minimum. Solutions are by the method of Appendix A, except those denoted by crosses, for 77 K, which are from the numerical method of Appendix B. See text for discussion.

and small changes in $\Delta(r)$ will be unable to bind the electron,[7] while costing energy to establish. Since the coordinate origin is arbitrary, the system has translational symmetry, but only statistically. In fact, if transport of the electron is established, wave-packet formation will result and what may be called a large polaron is obtained. The state $E_{TOT}=0$, calculated in the absence of motion, is either stable or metastable for all ρ_∞ and T. For electrons in such states, the usual low-field drift mobility is expected[8]:

$$\mu_{\text{SEMI-CL}} \simeq \frac{4e}{3}\,\frac{1}{(2\pi mkT)^{1/2}}\,\frac{1+B_v\rho_\infty}{4\pi a^2\rho_\infty}\,, \tag{4}$$

with m the mass, B_v the second virial coefficient, and a the low-energy s-wave length for the atom-electron scattering (0.62 Å for helium). The mean free path used results from an assumed random arrangement of scatterers.

B. Self-trapped states

The positive electron-energy solutions of Eq. (2) need not exhaust the spectrum of states which also satisfy Eq. (3)—negative-energy solutions can be sought. This has been done for helium (a = 0.62 Å which, given ρ_∞, defines V_∞), for T = 77 K and $\rho_\infty = (6, 7, 8, \text{ and } 9)\times 10^{21}$ atoms/cm^3 by a numerical scheme of iterating (by computer) Eqs. (2) and (3) to self-consistency. An additional (aside from $E_{TOT}=0$) two states were found for each ρ_∞. Both are configurations for a self-trapped electron; one has a minimum for E_{TOT} with respect to small variations of $\Delta(r)$, and the other is a saddle point for E_{TOT} in the space of spherically symmetric fluid configurations. The results obtained are essentially the same as the set previously obtained[9] by restricting

$$\Delta(r) = \frac{C}{\cosh^2 br}\,. \tag{5}$$

This two-parameter functional space may be used to define a semianalytic perturbation scheme in which the parameters C and b are chosen to satisfy a limited self-consistency and perturbations are carried out to improve it. The perturbation scheme is described in Appendix A; the numerical iteration scheme is described in Appendix B. The results of the two schemes are so close that the numerical one is a verification of the one [using Eq. (5)] which was used to obtain results for a large number of values of ρ_∞ and T. The electron is always kept in the ground state of Eq. (2).

Figure 1 gives the energy E_{TOT} of states satisfying Eqs. (2) and (3) as a function of ρ_∞ for selected temperatures. At sufficiently high ρ_∞, for all T, a solution is obtained with $E_{TOT}<0$. This is the stable self-trapped state; $E_{TOT}=0$ is a metastable solution, and there is an $E_{TOT}>0$ solution representing a self-trapped electron in a saddle-point configuration. As ρ_∞ is lowered the energy of the stable self-trapped state rises, eventually becoming positive. Then this state becomes metastable with $E_{TOT}=0$ achieving stability. For still lower ρ_∞ the energies of the metastable and saddle-point configurations approach. Using the method of Eq. (5) a degeneracy is finally found and no solutions are obtained (other than $E_{TOT}=0$) for lower ρ_∞. The numerical method shows a decreasing energy difference but, as degeneracy is approached, becomes so cumbersome that it must be abandoned. Physically, very weakly bound metastable states are essentially indistinguishable from moderately long-lived unstable ones which yield no extremum for E_{TOT} [i.e., which do not satisfy Eq. (3)].

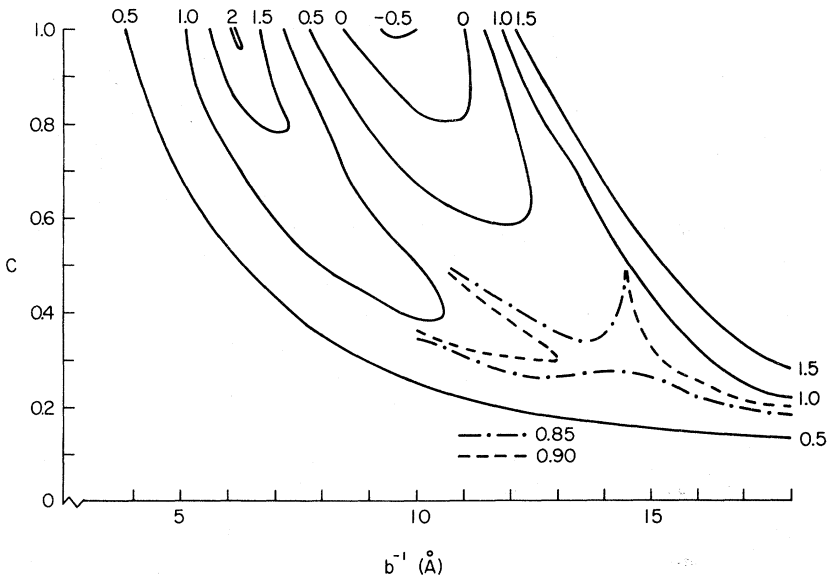

FIG. 2. Total energy contours in units of kT for $T=51$ K, $\rho_\infty=5.5\times10^{21}$ atoms/cm^3 (helium). The electron is in the lowest-energy state consistent with Eq. (2). The fluid density profile at each point is given by Eq. (5) so that C is the fractional density decrease at the origin and b^{-1} is the "radius" of the fluid distortion. Note the saddle-point and negative-energy configurations.

Insofar as V_∞ increases[3] with ρ_∞ and, for a given ρ_∞, the material stiffness ($\rho_\infty kT$) increases with T, Fig. 1 is a representation of the equilibrium-state energies as a function of coupling constant and stiffness. These results are quite similar to those given by Toyozawa[6] and Emin[10] in their calculations of self-trapping (or small polarons) in crystal models. In their work small polarons are restricted to dimensions of a single cell, while here these states overlap a substantial number of atoms (as will be shown) in agreement with the continuum approximation made to obtain them.

A clearer qualitative picture of the types of states shown in Fig. 1 (quasifree states, self-trapped states in stable or metastable configurations, and at the saddle point) is obtained, at a given ρ_∞ and T, by plotting the contours of E_{TOT} in the space of the dilation parameters: C and b^{-1} in Eq. (5), for example. Figure 2 shows such contours for helium at $\rho_\infty=5.5\times10^{21}$ atoms/cm^3 and $T=51$ K as a function of C (the dilation at the origin; $C=1$ means that the atoms are totally excluded at $r=0$) and b^{-1} (the "radius" or healing length of the dilation). There is a metastable state for $C=0$, a saddle point, at which $\int\rho_\infty\Delta(r)\times d^3r\sim50$ atoms, and a negative-energy region. Naturally an extremum in this figure need not represent one in the space of arbitrary $\Delta(r)$; for example, the saddle-point energy of Fig. 2 is close to but not quite the result in Fig. 1 for the same ρ_∞ and T, but perturbations can be carried out. The figure, however, suggests that a wave-packet conduction electron with $\rho(r)\simeq\rho_\infty$ (i.e., $C\sim0$, b^{-1} is approximately the size of packet) could collapse to the stable configuration (negative-energy well) by being thermally activated over the saddle point. It is probable that configuration tunnelling involving many atoms is a very slow process. These remarks are purely qualitative insofar as dynamical processes have not been investigated, though trends can be noticed: In the regime where self-trapped solutions have been obtained, the height of the saddle point decreases with ρ_∞, for example, which seems to imply that thermal activation from the quasifree states into the self-trapped minimum would be faster with increasing. ρ_∞.

For the regimes in which self-trapped states were found, it is a general result that the electron is more diffuse in the saddle-point configuration than in the stable or metastable one (for the same ρ_∞ and T). Further, at constant T, the electron diffuseness in the saddle-point configuration increases with ρ_∞; this trend is reversed for the stable or metastable configuration. For constant ρ_∞ the electron is more diffuse at lower temperatures for the saddle-point configuration; the trend is again reversed for the lower-energy configuration. The energy trends are shown in Fig. 1.

Figure 3 shows the density profile of the self-trapped low-energy configurations for $\rho_\infty=2.9$, 4.0, and 5.25 ($\times10^{21}$ atoms/cm^3), at $T=20$ K. Since the potential felt by the electron has been taken as linear with $\rho(r)$, this figure is also $V(r)$ versus r. The electron energy is shown so that the classical turning point can be seen. The configuration for the lowest ρ_∞ is metastable, the others stable. The radius of the mean sphere occupied by an atom (r_s), at ρ_∞, is shown. As can be seen (and this result is general), increasing ρ_∞ leads to an increased exclusion of atoms from the central region, a decreasing radius (classical

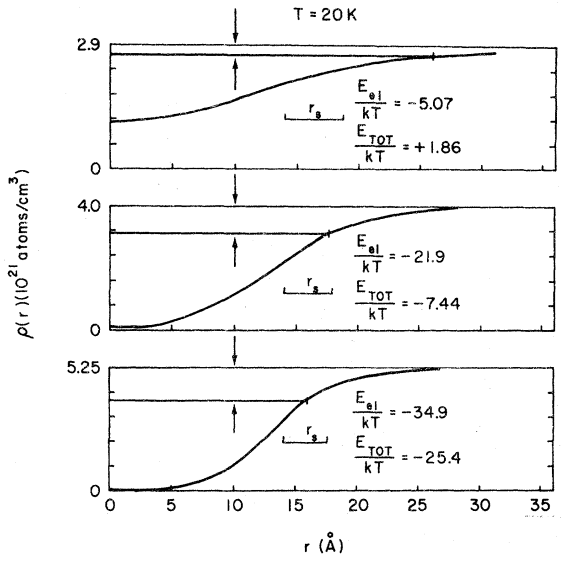

FIG. 3. Density profile $\rho(r)$ [also $V(r)$] for lowest-energy self-trapped states in helium at 20 K, for three values of ρ_∞ as noted. Electron energy is noted to show the classical turning point of the electron. Electron and total energies are indicated, as well as r_s, the radius of the mean sphere occupied by an atom for a density of ρ_∞.

turning point), and a sharpening of the density profile. The square-well model often used for liquid helium is a limiting case which is well justified by the trend of the present results.

Figure 4 shows the locus, in $\rho_\infty - T$ space, of the transition from metastability to stability of the low-energy self-trapped configuration in helium.[11] A line is also shown at which the low-energy self-trapped state has $E_{TOT} = -2kT$. There are stable self-trapped states for higher ρ_∞ and/or lower T than the line denoting the transition. The dashed line gives the density of helium at its saturated vapor pressure and the temperature in question; the (gas-liquid) critical point is noted.[12] Since self-trapped electrons should have much lower drift mobilities than conduction-band electrons, one expects that isothermal measurements of mobility would show a drop for densities in the neighborhood of that at which stable self-trapped states exist. This has been observed[13] and measurements are noted in the figure by showing the density at which the observed mobility is 10^{-1} or 10^{-2} of the semiclassical value expected for a conduction electron [Eq. (4)]. Clearly, the observed mobility drop correlates well with the predicted transition of self-trapped states to stability.

III. DISCUSSION

The states of the system, with the atoms at rest,[2] have been found for configurations in which the net force on each atom vanishes statistically. Atomic motion can be treated perturbatively to deal with configurations adjacent to the ones calculated. It should be realized that the apparent translational symmetry ($r = 0$, not defined) of the system disappears on allowing atomic motion, though it is still present statistically. One might worry that the disorder which appears when atomic motion is allowed may void some of the results obtained. This should not be the case for the stable self-trapped states obtained, since the distance over which disorder-induced incoherent scattering takes place

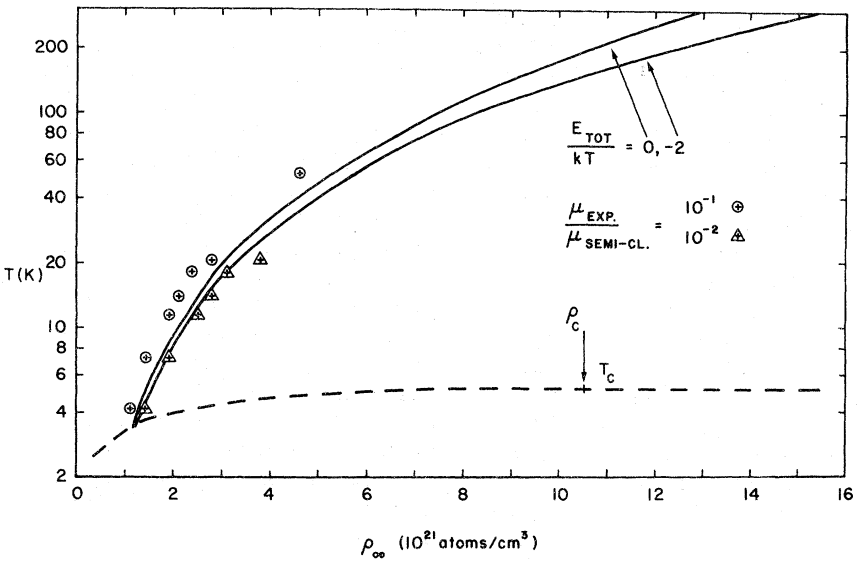

FIG. 4. Locus in density and temperature space for the transition from metastability to stability of electron self-trapped states in fluid helium ($E_{TOT} = 0$). Conditions for which $E_{TOT} = -2kT$, i.e., the stable self-trapped state has energy $2kT$ below the configuration with $\rho(r) = \rho_\infty$ and a conduction band ($k = 0$) electron, are also shown. The experimental points denote isothermal measurements (Ref. 13) of mobilities of 10^{-1} and 10^{-2} of the semiclassical value [Eq. (4)]. Dashed line gives the density of helium at its saturated vapor pressure (the gas-liquid critical point is shown); see Ref. 12.

[approximately the mean free path for momentum-exchange scattering, equal to $p4\pi\rho_\infty a^2)^{-1}$] is large as compared to the typical size of the stable self-trapped states obtained. Further, nonadiabatic processes due to atomic motion about equilibrium configurations are not expected to be severe: In the first place, the configurations are stable; also, the electron ground state is well separated from excited states. The above arguments are not appropriate for configurations which are unstable and far from equilibrium, and/or for electron states which are extended over dimensions larger or of the order of the disorder-induced incoherent-scattering mean free path. The first case violates the assumptions inherent in the adiabatic approximation,[14,15] and the last case loses sight of part of the existing disorder.[15-17]

The conditions for stable self-trapping have been established by the results presented, and are not surprising—strong coupling and weak stiffness. One may speculate, in a more general case, that weak stiffness is not really necessary, but rather that weak barriers between different atomic configurations (lattice metastabilities) are sufficient—such might be the case of amorphous solids.

The present result, giving the energies of the states of the system, is not sufficient to predict or explain experimental observations in detail. Configurational entropies are needed to calculate a density of states for the system and, if transport is to be investigated, the dynamical process in question must be calculated. If thermodynamic equilibrium is not assumed, then lifetimes of the states are also necessary. At this time these concerns will not be pursued in detail; some qualitative observations, however, deserve mention.

For the type of fluid under investigation, the general features of electron behavior, with pressure and temperature, are clear. At high density, especially at low temperature, the stable self-trapped state is so overwhelmingly favored by energy considerations, and the barrier for populating it is so low, that it will have the predominant population. At low density, especially for high temperature, the free-electron-like conduction band is favored; only unstable self-trapped states exist and large dilations are necessary for trapping, so that such configurations are at high energies.[18] For intermediate conditions, even though self-trapped states may not be favored energetically they do have an entropy advantage, which has been neglected in the present treatment, insofar as they may be considered free particles of possibly large effective mass (m^*),

$$\Delta S = \tfrac{3}{2} k \ln(m^*/m) ,$$

relative to the quasifree-electron states. An effective mass of the order of the atomic one would make the entropy factor substantial (in the hydrodynamic limit,[13] m^* is one-half of the mass of the atoms displaced by the dilation). These considerations can only be qualitative since there is no known formula for m^*, except in a hydrodynamic limit.

The bulk of experiments on excess electrons in fluids are measurements of low-field drift mobility.[13,19,20] The expected mobility for quasifree electrons has already been mentioned, and the influence of self-trapping will be to substantially reduce the observed mobility, as noted in Fig. 4. Mobilities of self-trapped species are expected to be given by[13]

$$\mu \simeq \frac{e}{6\pi\eta R}\left(1+\frac{9\pi\eta}{4\rho_\infty R(2\pi MkT)^{1/2}}\right),$$

where η is the viscosity of the fluid, R the effective radius, and M the reduced mass between m^* and the atomic mass. In the limit of a strongly bound self-trapped state the dilation is essentially a square well, with R being its radius. The effective mass will be large (hydrodynamic limit) so that M is approximately the atomic mass. For weak, though stable, binding the region of the dilation can be quite penetrable by host atoms [as the results and Eq. (4) show] so R can be small and ill defined. m^* is not well known either, so that the above formula is not very helpful.

Since some experiments[19-21] have indicated the observability of nonthermal-equilibrium conditions, some qualitative comments regarding state lifetimes may be helpful. The trends of Fig. 1 imply that the stable self-trapped states should have a lifetime which increases with ρ_∞ (fixed T) and decreases with T (fixed ρ_∞), against release to a quasifree-electron state. The time for self-trapping, from a quasifree state, should decrease with ρ_∞ (fixed T) and increase slightly with T (fixed ρ_∞), judging from the height of the saddle-point configuration. A somewhat speculative extrapolation of the calculated trends to unstable self-trapped states, for conditions where self-trapping has no stable or metastable configurations, can be made. Trapping times, to such states, should decrease with ρ_∞ (fixed T) since they can be found at lower energies. The lifetimes of unstable states against electron release to a quasifree state should become longer and more sharply defined as ρ_∞ is increased and stability is approached. This extrapolation is partially prompted by recent experiments,[19,20] and will be further discussed elsewhere with the experimental results.

IV. SUMMARY

The conditions which lead to electron self-trapping in simple fluids have been calculated and the stability of such states discussed. It has been shown that the present work is formally related to

previous work on self-trapping, or small-polaron formation, by Toyozawa and Emin. The comparison with previous work exhibits the similarity of the results and emphasizes the flexibility of the materials considered, in that coupling constant and material stiffness may be continuously and independently varied experimentally. The calculations have been shown to be capable of adequately interpreting observations of low-field electron drift mobility in a semiquantitative manner.

ACKNOWLEDGMENTS

The author would like to thank Dr. K. S. Dy and Dr. M. Silver for comments in the course of the investigation, and Dr. L. Staunton for aid in optimizing some of the computer programs. The interaction with Dr. J. Jahnke led to fruitful dialog between theoretical ideas and his experimental expertise and results. Many of the ideas which originally led to this work are due to Drs. Levine and Sanders.

APPENDIX A

Solutions to Eqs. (1)–(3) in the text are desired. Define

$$F = 1 - (C/\cosh^2 br) \ , \tag{A1}$$

where C and b are constants which will be chosen in such a way as to construct a perturbation series (λ, which is later set to unity, will denote the order of perturbation). Expand ψ, E_{e1}, $\rho(r)/\rho_\infty$, and E_{TOT} in a power series in λ, using

$$\lambda G(r) \equiv -F + \exp\left(-\frac{V_\infty |\psi_0(r)|^2}{\rho_\infty kT}\right) , \tag{A2}$$

where ψ_0, the zero-order term in ψ, and a choice of C and b define $G(r)$ in such a way that, hopefully, it is "small." Inserting the expansion and definitions into Eqs. (1)–(3) and equating powers of λ in Eq. (2) yields

$$[T + V_\infty(F-1) - E_{e1}^{(0)}]\psi_0 = 0 \ , \tag{A3}$$

$$[T + V_\infty(F-1) - E_{e1}^{(0)}]\psi_1 + V_\infty\left(G - 2\frac{V_\infty}{\rho_\infty kT}F\psi_0\psi_1 - E_{e1}^{(1)}\right)\psi_0 = 0 \ , \tag{A4}$$

etc., and also

$$\frac{\rho(r)}{\rho_\infty} = \left(1 - \lambda\frac{2V_\infty}{\rho_\infty kT}\psi_0\psi_1 + O(\lambda^2)\right)\exp\left(-\frac{V_\infty}{\rho_\infty kT}|\psi_0|^2\right) , \tag{A5}$$

$$E_{TOT} = \rho_\infty kT\int d\vec{r}\left[1 - \exp\left(-\frac{V_\infty}{\rho_\infty kT}|\psi_0|^2\right) - \frac{V_\infty|\psi_0|^2}{\rho_\infty kT}\exp\left(-\frac{V_\infty}{\rho_\infty kT}|\psi_0|^2\right)\right] + E_{e1}^0 + \lambda V_\infty\int G|\psi_0|^2 d\vec{r} + O(\lambda^2) \ . \tag{A6}$$

Note that terms of $O(\lambda)$ containing ψ_1 in (A6) cancel so that (A4) need not be solved for results correct to order λ. Equation (A3) can be solved for any C and b exactly.[8] In this work, the "smallness" of (A2) is achieved by choosing C and b such that $G(0) = G(b^{-1}) = 0$. Alternative choices are possible. It is then found that $G(r)$ is indeed small [compared to $F(0)$ or to kT, for example] for all r. One may judge the appropriateness of the method by comparing E_{TOT} correct to $O(\lambda)$, in (A6), to

$$E_{TOT}^{(0)} = \rho_\infty kT\int d\vec{r}(1 - F + F\ln F) + E_{e1}^{(0)} \ . \tag{A7}$$

The method gives quite good results and is further verified by comparing the results with those of the numerical scheme described in Appendix B. It is not as good for E_{TOT}/kT large and negative, where a better choice of F might be

$$F = 1 - \Theta(R - r) \ , \tag{A8}$$

i.e., a square well of radius R. An electronic calculator and computations by hand are quite adequate throughout this technique.

APPENDIX B

A numerical (computer-based) scheme of iteration to self-consistency was developed to solve Eqs. (1)–(3) given ρ_∞, T, and the material (which determines V_∞). The scheme followed was to expand ψ in a basis of the s states of a spherically symmetric harmonic oscillator. The frequency of the oscillator was used to optimize convergence. The restriction to spherically symmetric states was made to minimize energies. The method starts with a trial function of the ground state only of a harmonic oscillator of arbitrary frequency. Total energy extrema were sought, in the first pass, as a function of the oscillator frequency. The frequencies at which extrema were found (there were two) were then chosen as the oscillators to provide the basis sets. After setting the trial potential by restricting occupation to the oscillator ground state, approximations to solutions of that Schrödinger equation were sought by diagonalizing that Hamiltonian in an $N\times N$ basis. $N = 2$–10 were examined until expanding the basis led to no appreciable changes in ψ or E_{e1}. In continuing, it was found that calculating the potential with only three terms of the expansion and then diagonalizing 10×10 matrices led to iterations which converged very well after only three or four passes. Coefficients in the expansion of the wave function become small very quickly. All integrals were done analytically as certain power series, with Γ functions, and the computer was used to sum series and diagonalize real symmetric matrices.

For a chosen ρ_∞, T, and V_∞, approximately five runs of 10–15 sec each on a 360/75 were required to obtain the two solutions. Two runs were made

to search oscillator frequencies, and the next three runs were iterations; basis-set expansions were done within each run. It seems quite reasonable that there are only two solutions if the electron is restricted to the ground state of the potential it determines and only spherically symmetric states are sought. The method becomes cumbersome when the two solutions obtained are quite similar, i.e., when they are nearly degenerate in total energy. Results are discussed in the text and Fig. 1.

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*Work supported by the Materials Research Center, UNC, under Grant No. GH-33632 from the National Science Foundation.

[1]See, for example, M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon, Oxford, 1959), Chap. 4.

[2]From now on, when it is assumed that the atoms are fixed, what is not allowed is atomic motion which yields density changes. The continuum approach to be used treats atomic motion which does not vary the density statistically, as the source of a pressure which provides a stiffness for the fluid. Then so-called atomic motion will yield density variations which are controlled by the stiffness and interactions with the excess electron.

[3]$V_\infty = \hbar^2 k^2/2m$, where $\tan k(r_s - a) = kr_s$, a is the s-wave scattering length of the atoms, and r_s is the radius of the mean sphere occupied by an atom at the density in question (ρ_∞). The scattering length specifies the atoms under consideration. V_∞ increases with density, linearly for low densities.

[4]The electron-material interaction energy is being taken into account within the electron contribution. The Helmhotz energy to establish $\Delta(r)$ is given by a chemical potential and a pressure contribution as $\int (\mu - \mu_\infty)\, dN - (P - P_\infty)\, dV$. For an ideal gas, $\mu - \mu_\infty = kT \ln P/P_\infty$. See, for example; H. B. Callen, *Thermodynamics* (Wiley New York, 1960), p. 327. Thus the equation in the text results.

[5]The expression is the Boltzmann distribution for the atomic density, and for an ideal gas the only interactions are with the electron.

[6]Y. Toyozawa, Prog. Theor. Phys. 26, 29 (1961).

[7]It is well known that for a finite-range (R) potential in three dimensions VR^2 must be sufficiently large to produce bound states.

[8]See, for example, J. Lekner, Phys. Rev. 158, 130 (1967).

[9]J. P. Hernandez, Phys. Rev. A 7, 1755 (1973). In that paper some results were presented; however, in a somewhat too ambitious attempt to deal with fluctuations, ρ_∞ was thought to be the density far from the electron, which is not well defined for an arbitrary configuration or for one with fluctuations. As is discussed later on in the text, extreme care must be taken in dealing with fluctuations so that the assumptions of the adiabatic approximation are not violated, and to have some assurance that statistical averaging procedures do not neglect important features of the disorder.

[10]D. Emin, in *Electronic and Structural Properties of Amorphous Semiconductors*, edited by P. G. LeComber and J. Mort (Academic, New York, 1973), Chap. 7.

[11]The "limit lines" discussed in Ref. 9 are the locus of the degeneracy points in Fig. 1 and thus did not have constant E_{TOT}.

[12]See, for example, W. H. Keesom, *Helium* (Elsevier, Amsterdam, 1942).

[13]The measurements are those of J. L. Levine and T. M. Sanders, Jr. [Phys. Rev. 154, 138 (1967)]; H. R. Harrison and B. E. Springett [Phys. Lett. 35, 73 (1971)]; H. R. Harrison [thesis (University of Michigan, 1971) (unpublished)]; for 20 and 53 K, those of Ref. 20 below.

[14]This criticism, at conditions for which self-trapped stability has been demonstrated, is applicable to the work in Ref. 15. They neglect the commutator of the atomic kinetic-energy operator with the electron-atom interaction, which has the hidden assumption that the adiabatic approximation is valid. This assumption fails when the stable configuration is not the one they assumed [$\Delta(r) = 0$].

[15]T. P. Eggarter, Phys. Rev. A 5, 2496 (1972), and references therein to preliminary results published with M. Cohen.

[16]Part of the argument in J. P. Hernandez and J. M. Ziman [J. Phys. C 6, L251 (1973)] in criticism of the approach of Ref. 15 is being repeated here. In considering only the disorder in a system, a statistical approach is clearly necessary and averages will be taken. In a random arrangement of spheres of radius a, the mean interaction length with the disorder is $(4\pi\rho a^2)^{-1}$. It seems inconsistent to attempt to treat the disorder by assuming order, equivalent to averaging over space, for distances greater than $(4\pi\rho a^2)^{-1}$. The Wigner-Seitz potential (Ref. 3) if assumed constant over some dimension (L) is indeed an assumption of over this dimension. The fact that a statistical distribution of the constant, from one region to another, is used does not restore the disorder within the regions themselves.

[17]For a reply to Ref. 16, see T. P. Eggarter and M. H. Cohen, J. Phys. C 7, L103 (1974).

[18]Perhaps a method for dealing with such unstable states might use a time-dependent $\rho(r, t)$ in which statistical considerations are incorporated, since the adiabatic treatment cannot be justified.

[19]J. A. Jahnke and M. Silver, Chem. Phys. Lett. 19, 231 (1973).

[20]J. A. Jahnke, M. Silver, and J. P. Hernandez, Phys. Rev. B (to be published).

[21]H. R. Harrison and B. E. Springett, Chem. Phys. Lett. 10, 418 (1971), as interpreted in Ref. 19.