The integral is computed to an accuracy better than 1%. However, on account of the extremely strong cancelations within the curly brackets, numerical errors are magnified for small p. Better accuracy is attainable, but only at the expense of greatly increasing the required computer time. We therefore limit our attempt to a confirmation of the results at medium and high k calculated in the preceding paper. Both sets of results are shown in Fig. 5. The agreement is evident.

The procedure described in this section may be extended to any desired order in $r_s^{3/4}$, with multiplying algebraic complications. However, theoretical difficulties imposed upon the charged-Bose-gas problem by the simultaneous effects of the condensate and the long-range interaction have now become resolved.

In conclusion, we have given in this and the preceding paper two entirely different approaches to the theory of the charged Bose gas. We have demonstrated, in both approaches, that the perturbation theory is free of divergence to the order calculated.

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Properties of an Excess Electron in Liquid Helium: The Effect of Pressure on the Properties of the Negative Ion

B. E. Springett, Morrel H. Cohen, and Joshua Jortner
Departments of Physics and Chemistry and Institute for the Study of Metals,
The University of Chicago, Chicago, Illinois

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The Wigner-Seitz model formerly used to calculate the adiabatic barrier to electron penetration of liquid helium is applied to the study of the bubble model for a localized electron in liquid helium. Calculations of the pressure dependence of the radius of the negative ion agree with the experimental results to within an atomic radius in liquid helium. Comparison is made with other methods, and predictions regarding further properties of the negative ion are presented.

I. INTRODUCTION

THE bubble model for the negative ion in liquid helium has recently been the subject of continued experimental[1–7] and theoretical[5,6,8–14] interest. A localized state of an excess electron in a nonpolar dense fluid is expected to be stable provided that the electron-atom repulsion is sufficiently strong. That there exists a strong repulsion in liquid helium has been demonstrated by the adiabatic electron-injection experiments of Sommer[6] and of Woolf and Rayfield.[7] The electron-atom repulsion in this system is so large that a local fluid dilation leads to a localized state of the excess electron characterized by a lower free energy than the quasifree electron state. A stable configuration of the localized state is achieved by a balance between the electron-atom short-range repulsions, the increased kinetic energy of the electron, the contractible force on the bubble resulting from surface tension, and the pressure-volume work involved in the creation of the bubble. Until recently the only direct evidence for the formation of a localized negative ion was provided by the mobility measurements of Sanders and Levine.[3–5] The direct determination of the radius of the negative ion in liquid helium under varying conditions of pressure and temperature yields important information concerning the structure of the negative ion and, in particular,

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the nature of the electron-helium interaction and the configuration changes in the fluid. To date, several experimental methods have been proposed and used to determine the size of the negative ion in liquid helium:

(a) The mobility data[2,15] in normal He^4 (above the λ point) and in He^3 above 0.4°K can be adequately described in terms of classical hydrodynamics. This approach is quite reasonable, since the bubble size is considerably larger than the interatomic separations and the mean free paths of the elementary excitations, so that the bubble can be considered as a rigid sphere moving through the liquid. The bubble radius can then be estimated from the mobility using Stokes law, so that $R=e/d\eta\mu$, where R is the bubble radius, μ is the mobility, η is the fluid viscosity, and d is a numerical constant which for no slip conditions takes the conventional form $d=6\pi$, while if there is a perfect slip between the bubble and the surrounding fluid then $d=4\pi$.

(b) Mobility data in superfluid He^4 below about 1.7°K cannot be interpreted in terms of viscous hydrodynamics because the mean free path of the excitations is comparable to the ion size.[2] It was demonstrated by Meyer and Reif[2] that under these conditions roton scattering limits the ion-drift mobility above 1°K. Application of kinetic theory leads to the following expression for the mobility: $\mu=e/MvN_r\sigma$, where M is a reduced mass calculated taking into account the persistence of velocity, v is the relative velocity of ions and rotons, and σ is the ion-roton collision cross section. The roton density N_r can be calculated from the Landau model and σ is taken as $\pi(R+4)^2$ (Å^2), where the effective radius of a roton is taken to be 4 Å.[16,17] Because the effective mass which determines the momentum exchange in a collision is not known, this method is limited to the determination of relative changes of R at varying temperatures and pressures.[17]

TABLE I. Experimental and theoretical data for the size of the negative ion in liquid He^4 at the vapor pressure.

T (°K)	R (Å)	Method
4.2	14.0	a
3.0	12.7	a
1.7	15.96	b
1.7	14.5	c
1.9	13±4	d
4.2	20	e
0	12.5	f
0	12.5	g

[a] Mobility data in normal He^4 (Ref. 15) calculated for Stokes law with $d=4\pi$.

[b] Trapping lifetime for negative ions by vortex lines (Ref. 19).

[c] Trapping lifetime for negative ions corrected for the healing behavior of the superfluid on the edge of the exclusion region (Ref. 19).

[d] Effective-mass method (Ref. 18).

[e] Theoretical calculation, variational method, and experimental surface tension (Ref. 11).

[f] Same as e. Statistical model for the fluid (Ref. 12).

[g] δ-function pseudopotential (Ref. 14).

(c) Measurements of momentum relaxation times of ions in superfluid He^4 by microwave techniques can be combined with the existing mobility data, leading to an evaluation of the effective mass of the ions.[18] The effective mass of the negative ion was reported to be $(110+100, -30)$ M_{He}. At temperatures near the λ point where the mean free path of the elementary excitations is small compared to the size of the negative ion, the contribution to the effective mass M^* of a sphere oscillating at the microwave frequency ω from viscous flow in the normal fluid can be related to the ionic radius.[18]

(d) Parks and Donnelly[19,20] have shown that ionic radii in He II can be accurately determined from the "lifetime edge" in the capture cross section for negative ions trapped by quantized vortex lines and rings. The lifetime of a negative ion trapped on a vortex line is determined by the exponential factor $\exp(\Delta i/kT)$, where Δi corresponds to the kinetic energy of the volume of the rotating superfluid excluded by the ion. Hence the lifetime is a sensitive function of the ion radius.

To summarize, we have displayed in Table I the available experimental data for the radius of the negative ion at the vapor pressure of liquid helium. These results are in semiquantitative agreement with some previous theoretical calculations.[9,11,12,14] Now, it should be noted that the bubble model implies that the negative ion should be characterized by a relatively high compressibility. If the negative ion consists of an electron localized in a region from which the helium atoms are essentially excluded, the radius of such a region should be sensitive to the hydrostatic pressure on the liquid. Unambiguous experimental evidence for the localized state of the negative ion is available; however, direct evidence for the bubble model of the localized state was only very recently obtained. Springett and Donnelly[17] determined the pressure dependence of the radius of the negative ion in He II between 1.1 and 1.6°K from measurements of trapping cross sections in quantized vortex lines. It was found that the negative ion radius changes from 15.96 Å at the vapor pressure to 10.22 Å at the pressure of 20 atm. In contrast, the pressure dependence of the radius of the positive ion in liquid helium was found to be negligible.[17]

In the present work we consider the predictions of the bubble model with respect to the pressure dependence of the radius of the negative ion. The Wigner-Seitz model, previously applied[11] in the calculation of the energy of the quasifree electron state in a helium lattice, is extended to deal with the localized state. These results are then compared with the treatment based on the variational method employed earlier.[11] It is found that a simple bubble structure for the

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negative ion is consistent with the experimental data, providing further theoretical evidence in support of this model.

II. THE BUBBLE

The bubble model for the negative ion rests on two basic assumptions implying the localization of the excess electron and the creation of a void in the fluid. Since the electron is in a localized state, it is required that its wave function tend to zero for large distance from the center of localization. We then consider the behavior of an electron in a region of the fluid characterized by the density distribution

$$\begin{aligned} &\rho=0, & r<R, \\ &\rho=\rho_0(P,T), & r>R, \end{aligned} \tag{1}$$

where $\rho_0(P,T)$ is the fluid number density at pressure P and temperature T, and R corresponds to the cavity radius. Although more complicated forms[11,12] of the density distribution were applied, it was demonstrated that for high densities (of the order of the liquid density) the thickness of the boundary layer is small and the description in terms of a simple step function is adequate. The total energy of the bubble may be written in the form

$$E_t=E_e+E_b, \tag{2}$$

where E_e is the ground-state electronic energy and E_b is the energy required to form a cavity in the liquid. This latter energy consists of a surface term $E_s=4\pi R^2\gamma$, γ being a surface tension, and a pressure-volume term $E_{PV}=(4\pi/3)PR^3$, so that

$$E_b=4\pi R^2\gamma+\tfrac{4}{3}\pi PR^3. \tag{3}$$

To find the equilibrium radius we set $\partial E_t/\partial R=0$. In the case when the electronic energy is determined variationally, we also require that the electronic energy is stable with respect to the variation of the parameters ξ_i determining the trial wave function, i.e., $\partial E_e/\partial\xi_i=0$.

III. THE WIGNER-SEITZ MODEL

The interaction energy of an excess electron with the unperturbed fluid cannot be adequately represented by an optical approximation for this does not account for the increase in the electronic kinetic energy associated with multiple scattering. The Wigner-Seitz model can be applied to an electron in a helium lattice leading to a reliable estimate of the energy barrier the liquid helium presents to the electron.[11] The lowest energy state V_0 of an excess electron in a helium lattice is given by

$$V_0=\hbar^2k_0^2/2m, \tag{4}$$

where the wave number k_0 is obtained from the relation

$$\tan k_0(r_s-\alpha)=k_0r_s. \tag{5}$$

Here r_s is the equivalent sphere size

$$r_s=(\tfrac{3}{4}\pi\rho_0(P,T))^{1/3} \tag{6}$$

and $a=1.13\hbar^2/me^2$ is the low-energy electron-helium atom scattering length, taking polarization of the He atom into account. To be completely consistent, the scattering length should be evaluated at the energy V_0, a correction of perhaps 10% in a which we have ignored. This correction is cancelled to a large extent by the long-range polarization of the medium by the quasifree electron.

A numerical solution of Eq. (5) for k_0 at the appropriate liquid density leads to the pressure dependence of the barrier to penetration of liquid helium by an electron.

We shall now apply these results for the calculation of the energy of a localized state. We write the wave function for the excess electron inside and outside the cavity in the form

$$\psi=f(r), \quad r<R, \tag{7a}$$

$$\psi=f(r)u(r), \quad r>R, \tag{7b}$$

where $f(r)$ is the wave function of the electron confined by a potential well and $u(r)$ is the ground-state wave function of an electron in the undisturbed liquid helium. The wave function satisfies the equation

$$(p^2/2m)f(r)=E_ef(r), \qquad r<R, \tag{8a}$$

$$(p^2/2m+V)f(r)u(r)=E_ef(r)u(r), \quad r>R, \tag{8b}$$

where V is the electron helium (repulsive) interaction potential and E_e is the electronic energy. Now $u(r)$ is taken to satisfy the equation

$$(p^2/2m+V)u(r)=V_0u(r), \tag{9}$$

with the normalization conditions chosen so that

$$(1/\Delta)\int_{\text{W.S. cell}} d^3r|u(r)|^2=1; \tag{10}$$

that is, $u(r)$ is the ground state in the absence of bubble formation and dynamical polaron-like distortions of the fluid. It follows that

$$(1/\Delta)\int_{\text{W.S. cell}} d^3ru^*(r)\mathbf{p}u(r)=0. \tag{11}$$

The integrations in (10) and (11) are performed over Wigner-Seitz cell, characterized by the volume

$$\Delta=(4\pi/3)r_s^3. \tag{12}$$

In order to simplify our eigenvalue equation, consider again Eq. (8b):

$$\begin{aligned} f(r)[p^2/2m+V]u(r)+(1/m)\mathbf{p}f(r)\cdot\mathbf{p}u(r)& \\ +u(r)(p^2/2m)f(r)=u(r)E_ef(r);\quad r>R.& \end{aligned} \tag{13}$$

Suppose now that $f(r)$ is slowly varying over the Wigner-Seitz cell. The term $(1/m)\mathbf{p}\cdot f(r)\mathbf{p}\cdot u(r)$ may then be considered a perturbation on the remaining terms in (13) which contributes first in second order because of (11). An effective-mass equation results in precisely the same way as for the effective-mass theory of impurity states in semiconductors,[21]

$$[p^2/2m^*+V_0]f(r)=E_ef(r)\,,\quad r>R. \tag{14}$$

We have calculated m^* for liquid He by an application of Bardeen's formula for the effective mass[22] appropriate to the present case where the effect of the electron-atom interaction on the wave function can be replaced by s- and p-wave scattering lengths with the result

$$m^*/m\approx 1.10. \tag{15}$$

On the other hand, we could have supposed that $f(r)$ varies extremely rapidly with r. In that case, $\mathbf{p}u(r)$ vanishes in the only region where $\mathbf{p}f(r)$ is appreciable, the outer regions of those Wigner-Seitz cells bordering the cavity, so that $f(r)$ satisfies

$$[p^2/2m+V_0]f(r)=E_ef(r)\,,\quad r>R. \tag{16}$$

The solution of (16) is proportional to $e^{-\kappa r}/r$ with $\hbar\kappa=(2m(V_0-E_e))^{1/2}$; that of (14) is the same except that m^* replaces m in κ. For liquid helium at the vapor pressure, we obtain $2m(V_0-E_e)/\hbar^2=0.48$ Å^{-2} and $1/r_s^2=0.24$ Å^{-2}. Thus, κr_s is 1.4, which puts us squarely in between both the slowly and rapidly varying limits. Because the equation satisfied by $f(r)$ is the same in both limits apart from an unimportant effective mass correction of 10%, we are justified in taking (16) as the equation actually satisfied by $f(r)$. The equation to be solved for the ground state now takes the simple form

$$\begin{aligned}(p^2/2m-E_e)f(r)&=0\,,\quad r<R,\\(p^2/2m+V_0-E_e)f(r)&=0\,,\quad r>R,\end{aligned} \tag{17}$$

which corresponds to the eigenvalue problem of a particle in a spherical well. The (unnormalized) solution is readily obtained in the form

$$\begin{aligned}f(r)&=(1/r)\sin kr\,,\quad r<R,\\f(r)&=(A/r)\exp(-\kappa r)\,,\quad r>R,\end{aligned} \tag{18}$$

where $k=(2mE_e/\hbar^2)^{1/2}$ and $\kappa=[2m(V_0-E_e)/\hbar^2]^{1/2}$.

The boundary conditions imposed on the solution of (18) are given in the conventional form

$$\begin{aligned}f|_{r\leq R}&=fu|_{r\geq R}\,,\\f'|_{r\leq R}&=(uf'+u'f)|_{r\geq R}\,,\end{aligned} \tag{19a}$$

for a point on the boundary. However, because of the microscopic structural details, the position of the boundary is not well defined relative to the Wigner-Seitz cells of the surrounding atoms. Though we may regard f as well defined (19a) if we maintain the fiction that the bubble has a sharp boundary at R, we must then regard u at R as a random variable which takes on the values it would have at all the points in the Wigner-Seitz cell with equal probability. We therefore replace (19a) by an averaged boundary condition obtained by multiplying each u or u' as it occurs in (19a) by u, averaging over the unit cell, and then taking the square root. The result is that

$$\begin{aligned}f|_{r\leq R}&=f|_{r\geq R}\,,\\f'|_{r\leq R}&=f'|_{r\geq R}\,,\end{aligned} \tag{19b}$$

as a consequence of (10) and (11), which is equivalent to the *average* boundary condition

$$(d\ln f/dr)_{r\leq R}=(d\ln f/dr)_{r\geq R}\,. \tag{20}$$

It will be convenient at this stage to define k in terms of the wave vector k_0 for the unperturbed fluid, setting $k=Xk_0$ and $\kappa=(1-X^2)^{1/2}k_0$. The boundary condition leads to the result

$$\cot Xk_0R=-(1-X^2)^{1/2}/X\,, \tag{21}$$

and the ground-state electronic energy is now obtained from the simple relation

$$E_e=X^2V_0. \tag{22}$$

The only acceptable solutions for Eq. (21) are $0\leqslant X\leqslant 1$, so that the electronic energy of the bound state is lower than the total energy of the quasifree state. Equation (21) can now be solved numerically for any fixed value of R.

One might question whether the leaking of the electron outside the bubble causes a local decrease in the fluid density through the electron-helium atom repulsion. To answer this, we note that the energy E_e depends only on k, Eq. (22), and that k depends on the condition of the surrounding fluid only through the entrance of the density at the surface of the bubble into (21). Hence E_e depends only on the density of the fluid just outside the bubble once the step-function approximation of Eq. (1) to the density is adopted. This in turn implies that there are no body forces acting on the fluid to cause density changes outside the bubble. Thus the step-function approximation, Eq. (1), is self-consistent, provided that the details of the surface energy are ignored.

It should be pointed out that the Wigner-Seitz method is also extremely useful for the calculation of the electronic energies of excited states. The general solutions are given by

$$\begin{aligned}f(r)&=j_l(kr)\,,\quad r<R,\\f(r)&=Ak_l(\kappa r)\,,\quad r>R,\end{aligned}$$

where j_l is the spherical Bessel function of the first kind and k_l is the modified spherical Bessel function of the third kind. l corresponds to the angular-momentum quantum number of the electron. The electronic energy is determined from the boundary conditions

$$\left(\frac{d\ln j_l(kr)}{dr}\right)_R=\left(\frac{d\ln k_l(\kappa r)}{dr}\right)_R.$$

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Turning our attention to the ground state of the system, the total bubble energy can now be written using Eqs. (2), (3), and (22):

$$E_t=\frac{\hbar^2k_0^2}{2m}X^2+4\pi R^2\gamma+\tfrac{4}{3}\pi R^3P. \tag{23}$$

The stable configuration is obtained from the relation

$$\frac{\partial E_t}{\partial R}=\frac{\hbar^2k_0^2}{m}X\frac{\partial X}{\partial R}+\frac{\partial E_s}{\partial R}+4\pi R^2P=0. \tag{24}$$

Application of Eq. (21) leads to the result

$$\frac{\partial X}{\partial R}=-\frac{k_0X(1-X^2)^{1/2}}{k_0R(1-X^2)^{1/2}+1}, \tag{25}$$

so that the stability criterion (23) can be written in the simple form

$$-\frac{\hbar^2k^2\kappa}{m(R\kappa+1)}+\frac{\partial E_s}{\partial R}+4\pi R^2P=0. \tag{26}$$

The ground-state energy of the system is then obtained from Eqs. (19b), (25), and (22). We have thus obtained a simple manageable approximation which will prove to be no worse than the variational methods previously applied.[11,12]

IV. THE PRESSURE DEPENDENCE OF THE BUBBLE RADIUS

To determine the pressure dependence of V_0 from Eqs. (4) and (5), use has been made of the density measurements of Keesom and Keesom.[23] These results, collected in Table II, are in good agreement (at $P=0$) with the calculation of Burdick[13] and the experimental data of Sommer[6] and of Woolf and Rayfield.[7] Now, to determine the bubble radius, the surface tension has to be specified. Two difficulties immediately arise: The experimental surface tension along the liquid-vapor interface provides only a lower limit for the estimate of the surface work expended on the formation of a microscopic cavity in the liquid because the electron-atom repulsion tightens the surface, increasing the kinetic-energy contribution, and the pressure dependence of the surface tension is not known. The calculation of Reiss *et al.*[24] of the energy expended on the introduction of a spherical cavity in a classical rigid-sphere fluid is not applicable for liquid helium below the boiling point because it predicts that the surface energy is proportional to T. Hiroike *et al.*[10] provided a calculation of the surface tension determining the energy for bubble formation in liquid helium by making use of the formal similarity between the pair distribution function of a boson system with the wave function expressed as a product of pair wave functions and the pair distribution function of a classical fluid. The calculated surface tension was $\gamma_H=0.53$ dyn/cm at $T=0°\text{K}$ and the surface energy was found to be linear in R^2 for the range $R=5$–50 Å. The surface tension was found to vary approximately as ρ_0^2, provided that the radial distribution function was not affected by the increase of pressure. Another source of information for the pressure dependence of the surface tension is provided from the computations of Amit and Gross[25] for the surface tension at a plane surface using a δ function pseudopotential for helium-helium interaction within the Hartree approximation. The free-surface tension was expressed in the form

$$\gamma_{\text{AG}}=0.7\hbar C\rho_0, \tag{27}$$

where C is the velocity of first sound. This result is valid at $T=0°\text{K}$. The sound measurements of Atkins and Stasior[26] have been used to compute γ_{AG}.

TABLE II. The pressure dependence of the interaction energy of an excess electron with the unperturbed fluid.

P (atm)	ρ_0 (g/cm^3)	r_s (Å)	k_0 (Å^{-1})	V_0 (eV)
0	0.1452	2.219	0.540	1.111
4	0.1508	2.191	0.553	1.165
8	0.1562	2.166	0.564	1.212
12	0.1607	2.145	0.575	1.259
16	0.1648	2.128	0.583	1.295
20	0.1685	2.112	0.592	1.335

In view of these ambiguities in the determination of the surface tension, an attempt was first made to combine the experimental results of Springett and Donnelly[17] on the pressure dependence of R with the predictions of the Wigner-Seitz model to derive a set of pressure-dependent values for the surface tension. From Eq. (24) we get the values of $\partial E_s/\partial R$ as a function of the pressure (Table III). Assuming that all the variation of E_s arises from structural changes on the surface of the bubble, and that the surface tension is independent of the bubble radius, we get $\partial E_s/\partial R=8\pi\gamma R$. The pressure dependence of the surface tension thus obtained is displayed in Table III. The value at $P=0$ is in agreement with the model of Hiroike *et al.* The effective surface tension of the bubble increases by about a factor of 3 in the pressure range of 0–20 atm. These results show the same trend as the estimate based on the Amit-Gross theory[25] of the free surface, which predicts a factor of 2. An alternative theoretical estimate based on the Wigner-Seitz model was carried out for the pressure dependence of R. Here the surface tension at the vapor pressure was fitted to give the experimental R value and γ was varied with pressure according to the Amit-Gross formula. The energy curves thus obtained are presented in Fig. 1. As it is apparent from Fig. 2, the agreement with the

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TABLE III. Estimated values of the pressure dependence by the Wigner-Seitz method.

P (atm)	R_0[a] (expt)	$\partial E_s/\partial R$	γ (dyn/cm)	$\gamma_{AG}=0.7$ (dyn/cm)	γ_H (dyn/cm)
0	15.96	2.3×10^{-6}	0.57[b]	0.38	0.53
4	13.30 ± 0.5	2.8×10^{-6}	0.85 ± 0.04	0.44	
8	12.15 ± 0.5	3.2×10^{-6}	1.06 ± 0.11	0.50	
12	11.39 ± 0.5	3.6×10^{-6}	1.27 ± 0.19	0.55	
16	10.77 ± 0.5	4.2×10^{-6}	1.56 ± 0.13	0.60	
20	10.22 ± 0.5	5.1×10^{-6}	1.97 ± 0.39	0.65	

[a] Experimental values from Ref. 17.

[b] The error in this value is quite small. Springett and Donnelly (Ref. 17) take the radius at $P=0$ as known independently of their calculation of the pressure dependence of R. The other errors quoted arise from the experimental uncertainty in the R values.

experimental data is satisfactory, the discrepancy being of the order of the radius of the helium atom.

Some variational calculations were also performed applying the variational method.[11,12] Using the value of $\gamma=0.53$ dyn/cm obtained by Hiroike *et al.*[12] for $P=0$, the surface tension at different pressures was scaled again according to the Amit-Gross formula. The results for the pressure dependence of R are of the same quality as obtained by the Wigner-Seitz model. For the sake of comparison we have also performed a calculation for the primitive model of a particle in a box using the same scaling procedure for the surface tension. These results are presented in Fig. 2, while in Fig. 3 we present the pressure dependence of the electronic ground-state energy calculated by the different techniques. Finally, we have also performed a calculation using Clark's model[14] based on a δ function pseudopotential for the helium-electron and helium-helium interactions. This treatment leads to the result $R=15(8\pi a\rho_0)^{-1/2}$. This equation does not predict the proper pressure dependence of R.

From these results we conclude that somewhat more sophisticated models than that of the particle in the box, which take into account properly the bubble energy, give a reasonable account of the pressure dependence of the size of the negative ion in liquid helium.

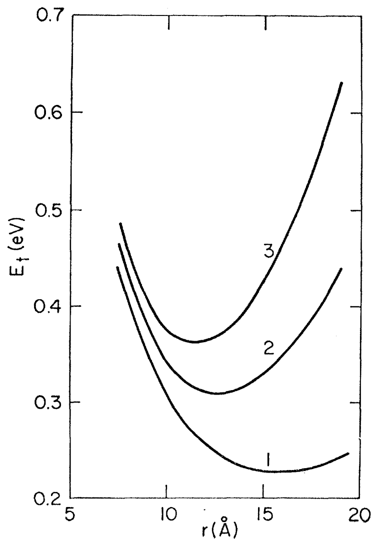

FIG. 1. The pressure dependence of the ground-state potential curves for the negative ion calculated by the Wigner-Seitz model: (1) $P=0$ atm; (2) $P=10$ atm; (3) $P=20$ atm.

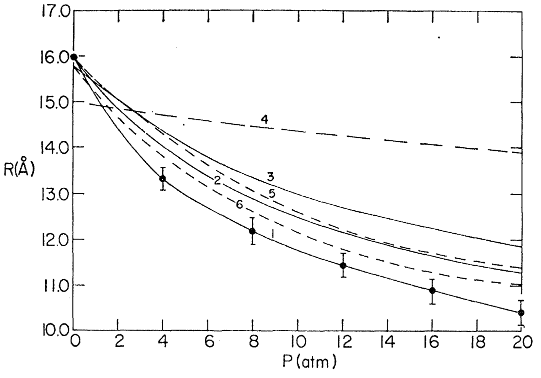

FIG. 2. The pressure dependence of the radius of the negative ion: (1) Experimental data (Ref. 17); (2) the Wigner-Seitz model with the surface tension fitted ($\gamma=0.57$ dyn/cm) at $P=0$ and scaled by $C\rho_0$; (3) the particle in the box model fitted and scaled as in 2. (4) Clark's formula (Ref. 14); (5) the variational method with the surface tension, $\gamma=0.53$ dyn/cm at $P=0$ and γ scaled according to ρ_0^2 at higher pressures. (6) the variational method with $\gamma=0.53$ dyn/cm at $P=0$ and scaled by $C\rho_0$ at higher pressures.

V. DISCUSSION

We have presented a treatment based on the Wigner-Seitz model of the localized state of an excess electron in a nonpolar dense fluid characterized by a positive scattering length. The predictions of this model regarding the radius of the negative ion in liquid helium and its pressure dependence are similar to the results of the more elaborate calculations based on the variational method. From these results we conclude that:

(a) The remarkable compressibility of the negative ion in liquid helium arises from the pressure dependence of the bubble energy E_b. The pressure-volume term

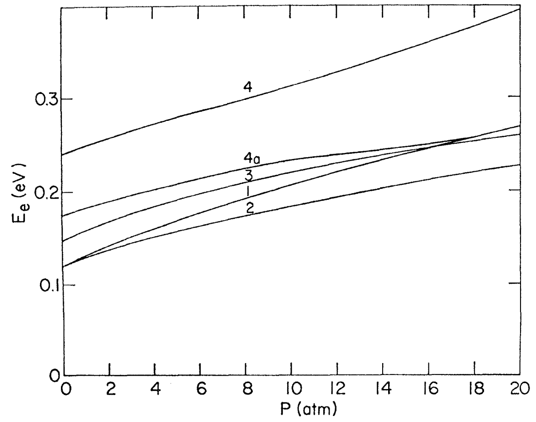

FIG. 3. The pressure dependence of the electronic energy of the negative ion: (1) Fitting of experimental data; (2) Wigner-Seitz model with the surface tension fitted ($\gamma=0.57$ dyn/cm) at $P=0$ and scaled by $C\rho_0$; (3) the particle in box model fitted as in 2; (4a) kinetic energy for the variational method fitted as in 2; (4) **total electronic energy for the variational method fitted as in 2.**

and the surface term each contributes about equally to the pressure dependence of R.

(b) The pressure dependence of the surface tension required to account for the change in the radius of the negative ion amounts to an increase of the surface tension by a factor of 2–3 over the pressure range of 0–20 atm, and is roughly consistent with the theory of Amit and Gross.

(c) Once the bubble model for electron localization in liquid helium is accepted, the details of the electron-helium interaction potential are not very important in accounting for the pressure dependence of the bubble radius.

(d) The energy of the quasifree electron state in unperturbed liquid helium increases by about 20% in the pressure range of 0–20 atm. On the other hand, the energy of the localized electron state increases by about 50% in this pressure range. However, even at higher pressures the energy of the localized state is still lower than the free-state energy, and the bubble is the energetically stable configuration. This conclusion is consistent with previous calculations[11] based on the variational method which indicate that the pressure necessary to induce a transition from the localized to the delocalized state in liquid helium is higher than the melting pressure of the liquid.

We shall now turn our attention to a detailed comparison of the Wigner–Seitz and the variational methods which were used to account for the electron–liquid-helium interactions. It should be pointed out that the variational method does not lead to a reliable description of the electron-helium interactions in the limit $R \rightarrow 0$, so that this treatment does not account properly for the energy of a quasifree electron state in the unperturbed fluid. In this case, the variational method leads to an electronic energy which can be expressed in the form[11] $(V_0)_{\text{var}} = 4\pi\rho_0 \int (V+V_R) r^2 dr$ corresponding to the product of the number density and the Fourier transform of the electron-helium atom pseudopotential, evaluated at $\mathbf{k}=0$. This result, in effect, inserts the Born approximation, which is not applicable for the strongly interacting electron-helium atom system and therefore leads to an overestimate of the interaction energy, into the optical model, which does not account for multiple-scattering effects and thus underestimates the interaction energy. Although the result obtained by the pseudopotential method $(V_0)_{\text{var}} = 1.32$ eV for liquid He^4 at 1°K is in reasonable agreement with the energy calculated by the Wigner–Seitz model $V_0 = 1.11$ eV and with the experimental result[7] $(V_0)_{\text{exp}} = 1.02 \pm 0.08$ eV, it should be noted that the agreement is a consequence of the mutual cancellation of somewhat serious errors. Besides, the variational method predicts a wrong density dependence of V_0 at high densities, while the Wigner–Seitz model predicts the same linear dependence of V_0 on ρ_0 (of the form $V_0 = (\hbar^2/m) 2\pi\rho_0\alpha$) at low densities and a superlinear increase of V_0 with ρ_0 at densities comparable to that of the liquid. As far as the localized state of an excess electron in liquid helium is concerned, the variational method leads to somewhat higher electronic energy than the Wigner–Seitz model. A direct experimental determination of the ground-state electronic energy will involve the observation of the threshold for photo-ionization of the electron from the ground state in the cavity to the continuum quasifree state, as in the experiment of Northby and Sanders.[27] Since the continuum state is located at 1.04 eV, while the ground-electronic state (at $P=0$) is located either at 0.12 eV (according to the Wigner–Seitz model) or at 0.24 eV (according to the variational treatment), the photo-ionization thresholds predicted by the two models are 0.92 eV (Wigner–Seitz) and 0.80 eV (variational). A direct experimental determination of the photo-ionization threshold will therefore be of considerable interest.[27]

Regarding the relative merits of the two methods, it should be pointed out that in view of the simplicity of the Wigner–Seitz model it will prove to be extremely useful for the treatment of bound and free excited electronic states of an excess electron in a dense nonpolar fluid. In this case, the variational method will be fraught with difficulties in view of the orthogonality restrictions imposed on the pseudo-wave function for the excited state which has to be orthogonal to all the lower unoccupied states. The simple mathematical structure of the equations derived by the Wigner–Seitz method makes it also possible[28] to derive some general stability conditions for a localized state of an excess electron in a nonpolar fluid characterized by a positive scattering length. We are also hopeful that the Wigner–Seitz method can be made to yield an improvement over existing models,[29] of solvated electrons in polar fluids.

We now turn our attention to some predictions of the model employed in the present work which will help to provide further information concerning the properties of the free and bound electrons in liquid helium.

(a) The barrier of liquid He^4 to adiabatic penetration by an electron is expected to increase by about 20% in the pressure range 0–20 atm at 1°K. This effect is amenable to experimental observation. In this context it is also interesting to point out that the energy barrier of He^3 for electron injection should be considerably lower, because of the lower density of this fluid. The calculated energy of the free-electron state in liquid He^3 is $V_0 = 0.59$ eV at 3°K and $V_0 = 0.74$ eV at 1°K. An experimental observation of this lower barrier for electron injection into He^3 will be of considerable interest.

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[27] J. A. Northby and T. M. Sanders, Bull. Am. Phys. Soc. **11**, 361 (1966).

[28] B. E. Springett, J. Jortner, and M. H. Cohen, Bull. Am. Phys. Soc. II, 12, 97 (1967)

[29] J. Jortner, J. Chem. Phys. **30**, 839 (1959).

(b) It has been already mentioned that the photoionization experiments of negative ions in liquid helium of Northby and Sanders[27] are of considerable interest in determining the ground-state energy of the negative ion.

(c) The effective inertial mass of the negative ion in liquid helium can be obtained by microwave measurements of momentum relaxation times.[18] The inertial mass M^* of a sphere oscillating at frequency ω due to viscous flow in the normal fluid just below the λ point can be estimated as

$$M^*=\tfrac{2}{3}\pi\rho_0R^3(1+\tfrac{9}{2}(\rho_n\delta/\rho_0R)), \qquad (28)$$

where ρ_n is the normal fluid density [so that at $T\lesssim T_\lambda$, $(\rho_n/\rho_0)\sim1$], η is the normal fluid viscosity, and $\delta=(2\pi\eta/\omega\rho_n)^{1/2}$ is the penetration depth. Since M^* is approximately proportional to R^3, our results imply that the internal effective mass should decrease by about a factor of 2 in the pressure range 0–20 atm.

(d) The vibration frequency for the symmetric stretching mode of the negative ion can be determined from Fig. 1 in the form $\nu=(1/2\pi)(f/M)^{1/2}$, where the force constant f is given by $f=\tfrac{1}{2}(\partial^2E_t/\partial r^2)_{r=R}$. Taking the oscillator mass to be equal to the experimental inertial mass $M=M^*=(110+100,\ -30)M_{\mathrm{He}}$ the symmetric vibration frequency is found to be surprisingly low: $\nu=4\times10^{10}$ sec^{-1} at $p=0$ and $\nu=10^{11}$ sec^{-1} at $p=20$ atm. Because other (asymmetric) vibration modes of the negative ion should be characterized by comparable frequencies, microwave absorption measurements (in the frequency range of 10 GHz) on negative ions in liquid helium will determine these low-frequency modes. These low-vibration frequencies of the negative ion are probably not related to the periodic discontinuities in the mobilities of ions in liquid He II observed by Careri *et al.*,[30,31] since the same effect is also experimentally observed in the case of the positive ion.

ACKNOWLEDGMENTS

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[30] G. Careri, S. Cunsolo, and P. Mazzoldi, Phys. Rev. **A136**, 303 (1964).

[31] J. A. Cope and P. W. F. Gribbon, Phys. Letters **16**, 128 (1965); *Superfluid Helium*, edited by J. F. Allen (Academic Press Inc., New York, 1966), p. 83. These authors have come to the opposite conclusion.

Errata

Relativistic Self-Consistent-Field Theory for Closed-Shell Atoms, Yong-Ki Kim [Phys. Rev. **154**, 17 (1967)]. The right-hand side of Eq. (128) should be multiplied by $\frac{1}{2}$. The "experimental" energy of the He atom in the Concluding Remarks should be $E_{\mathrm{expt}}=-2.903387$ $(\pm1.1\times10^{-6})$ atomic units. Also in the same section, the relativistic correction calculated by Pekeris (Ref. 36) corresponding to ours should be $-E_j-2\alpha^2$.

Hyperfine Splittings and g_F Values of Metastable H_2, Lue Yung-Chow Chiu [Phys. Rev. **145**, 1 (1966)]. A phase factor $(-1)^{J+J'}$ has been neglected in evaluating the matrix element for the term H_1(hfs). The right-hand side of the first two equations in the right column of p. 3 should be multiplied by a factor $(-1)^{J+J'}$. So whenever $J'-J=\pm1$, a negative sign will appear before the coupling constant a. Consequently a in Eqs. (2.8a), (2.8b), (3.4) (for both P and $\bar{P}$), and (3.8) should be replaced by $-a$. K_1 and K_2 which are obtained through Eq. (3.8) should now read

$$K_1=1097.70 \text{ Mc/sec}, \qquad K_2=1053.42 \text{ Mc/sec}. \qquad (4.2)$$

Owing to the same phase-factor error, the quantity (g_S+g_N) in Eq. (3.6) should be replaced by (g_S-g_N), and the right-hand sides of all of the six equations denoted by Eq. (3.9) should be multiplied by a factor $\frac{3}{5}$ [which is the ratio $(g_S-g_N)/(g_S+g_N)$]. The $g_F^{(1)}$'s (and consequently the g_F's), which were obtained through Eq. (3.9) and which were listed in Table I should be replaced by a set of new values. The new values are given in the following Table I and they show better agreement with the experimental values.

TABLE I. Calculated $g_F^{(1)}$ and g_F $(=g_F^{(0)}+g_F^{(1)})$ values for $N=1$ rotational level of the $c^3\pi_u$ state of ortho-H_2.

J	F	$g_F^{(0)}$	$g_F^{(1)}$	g_F
0	1	−0.003	−0.211	−0.214
1	0	···	···	···
1	1	+0.624	+0.257	+0.881
1	2	+0.624	+0.028	+0.652
2	1	+1.878	−0.046	+1.832
2	2	+1.042	−0.028	+1.014
2	3	+0.833	0	+0.833

The author wishes to thank Dr. A. N. Jette for calling her attention to a sign error which led to the above corrections.