figurational changes of the fluid. Indeed, the increase of the kinetic energy of the fluid atoms removed from the bubble region is not properly included in our analysis. This increase in kinetic energy will increase the energy required for bubble formation, leading to smaller values of R_0. The available mobility data, as well as the cross sections for the interaction of negative ions and quantized vortices in He II, all indicate that the cavity radius calculated herein is too large by about a factor of 2. A much more general treatment of the liquid configuration changes, as described in the following paper, leads to a smaller cavity radius, which is found to be in better agreement with the experimental data.

It would be extremely interesting to obtain direct spectroscopic evidence regarding the energy levels and charge distribution of the excess electron in liquid helium. The first optical transition of this center in liquid helium at 4.2°K and 1 atm should be located at about 0.1 eV (1000 cm^{-1}) and could be observed by application of the pulse radiolysis technique in conjunction with infrared spectroscopy to liquid helium. Another difficult but interesting experiment would be the study of the electron paramagnetic resonance spectrum of the excess electron in liquid helium. The resonance line corresponding to the localized electron in ^{4}He is expected to be extremely narrow, but will be broadened in ^{3}He by hyperfine interactions.

ACKNOWLEDGMENTS

We are grateful to Professor L. Onsager, Professor L. Meyer, Dr. M. Coopersmith, and Dr. J. Rosenshein for valuable discussions. This research was supported by the Directorate of Chemical Sciences, AFOSR and the U.S. PHS. We have also benefited from the use of facilities provided by ARPA for materials research at the University of Chicago.

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 43, NUMBER 8 15 OCTOBER 1965

Study of the Properties of an Excess Electron in Liquid Helium. II. A Refined Description of Configuration Changes in the Liquid

KAZUO HIROIKE,* NEIL R. KESTNER,† STUART A. RICE, AND JOSHUA JORTNER

Department of Chemistry and Institute for the Study of Metals, The University of Chicago, Chicago, Illinois

(Received 5 May 1965)

In this paper we present a study of the structural changes in liquid helium in the vicinity of an excess electron. We have used the formal similarity between the pair distribution function of an N-boson system, with the wavefunction expressed as the product of pair wavefunctions, and the pair distribution function of a classical fluid. The present model leads to an interfacial surface energy term which is in good agreement with the observed surface tension of liquid helium at 0°K. An important contribution to the bubble energy arises from the volume kinetic energy arising from the excess kinetic energy of the fluid atoms removed from the boundary layer. The bubble radius of 12.4 Å calculated herein is found to be in excellent agreement with the available experimental data.

I. INTRODUCTION

IN the preceding paper[1] a bubble model[2] as a representation of the localized state of an electron in liquid helium was examined. In that paper it was demonstrated, through the use of the pseudopotential formalism, that a stable liquid configuration is achieved by a balance between the short-range electron–atom repulsion (summed over all surrounding atoms) and the contractile force acting on the bubble and arising from the surface tension work and the pressure–volume work of bubble creation. When the experimental surface tension is employed in the calculations, the bubble radius is predicted to be of the order of 20 Å.

The analysis just described depends upon the use of very simple models for the change in liquid configuration accompanying the formation of a bubble. In particular, we have not assessed the role played by the transition region between bubble and bulk fluid, nor

* Present address: Department of Applied Science, Faculty of Technology, Tohoku University, Sendai, Japan.

† Present address: Department of Chemistry, Stanford University, Palo Alto, California.

[1] J. Jortner, N. R. Kestner, S. A. Rice, and M. H. Cohen, J. Chem. Phys. **43**, 2614 (1965).

[2] (a) R. A. Farrel, Phys. Rev. **108**, 167 (1957); (b) R. G. Kuper, *ibid.* **122**, 1007 (1961); (c) J. Levine and T. M. Sanders, Phys. Rev. Letters **8**, 159 (1962); (d) L. Onsager, *New Developments in Quantum Chemistry—Istanbul Lectures* (Academic Press Inc., New York, to be published); (e) J. Jortner, S. A. Rice, and N. R. Kestner, *ibid.*

examined the importance of the kinetic energy change arising from displacement of the atoms from the volume occupied by the bubble. The purpose of this paper is to explore a number of properties of the local structure of the liquid and to demonstrate that the conclusions reached in the preceding paper are reliable, and are not artifacts due to simplifications in the analysis. While we cannot solve the full N-body problem rigorously, it is possible to make a relatively general analysis which demonstrates the qualitative reliability of the simple model and confirms all that has already been deduced.

Abe[3] and Wu and Feenberg[4] have shown that the wavefunction describing the ground state of a boson system can be represented as a product of two particle (correlated) wavefunctions. In the following we exploit the formal similarity between the pair distribution function of an N-boson system with wavefunction written as the product of pair wavefunctions, and the pair distribution function of a classical fluid with atoms interacting through a pairwise additive potential.[5] When the excess electron is present, the analogous classical system is a fluid in an external field.

II. GENERAL FORMULATION

The total energy of the system of N He atoms and one electron, E_t, may be decomposed into the sum of the electronic energy, E_e, and the energy required for bubble formation, E_b. The electronic energy, at constant fluid configuration, may be displayed in the form[1]

$$E_e(\zeta)=\left\langle \phi_\zeta \left| -\frac{\hbar^2}{2m}\nabla^2 \right| \phi_\zeta \right\rangle+\int v_\zeta(r)\rho(r)d^3r, \quad (1)$$

where v_ζ represents the diagonal matrix element of the pseudopotential and Eq. (1) simply represents the sum of kinetic and potential energies. As in previous work, the smooth wavefunction corresponding to the localized state is taken to be a $1s$ function, $\phi_\zeta=\exp(-\zeta r)$, and $\rho(r)$ is the atom density.

The bubble energy is conveniently expressed as the sum of the pressure–volume work, ϵ_{PV}, the surface kinetic energy, ϵ_{SK}, the surface potential energy, ϵ_{SP}, and the volume kinetic energy, ϵ_{VK}, arising from the removal of atoms from the cavity boundary to the bulk. Then

$$E_b=\epsilon_{PV}+\epsilon_{SK}+\epsilon_{SP}+\epsilon_{VK}, \quad (2)$$

where the pressure–volume work is

$$\epsilon_{PV}=p\int\left(1-\frac{\rho(r)}{\rho_0}\right)d^3r, \quad (3)$$

and ρ_0 is the normal fluid density. Note that ϵ_{VK} arises from the change in density attending bubble formation, and is not included in ϵ_{PV}. The atom density function is taken to have the form

$$\rho(r)=0; \quad r<R_0,$$
$$\rho(r)=\rho_0(1-\{1+\alpha(r-R_0)\}\exp[-\alpha(r-R_0)]); \quad r>R_0. \quad (4)$$

The bubble size and shape and the excess-electron charge distribution are now determined by the conditions that the total energy be stationary with respect to variation of the parameters ζ, α, and R_0.

In the preceding paper[1] we assumed that $\epsilon_{VK}=0$, and that $\epsilon_{SK}+\epsilon_{SP}=4\pi R_0^2\gamma$, where γ is the surface tension. In this paper we consider a more general expression for the bubble energy.

Let there be N helium atoms and one electron in the volume Ω and let the Hamiltonian operator of the system be

$$H=-\frac{\hbar^2}{2M}\sum_{k=1}^{N}\nabla_k^2-\frac{\hbar^2}{2m}\nabla_e^2+\sum_{j<k}u_{jk}(\mathbf{R}_{jk})+\sum_{k=1}^{N}v_k(\mathbf{R}_k), \quad (5)$$

where M and m are the mass of the helium atom and the electron mass, respectively, u_{jk} is the interaction potential between a pair of He atoms and v_k is the potential acting between a He atom and the electron. The electron–atom potential is represented in the pseudopotential formalism already mentioned. Now, in the limit $T\rightarrow 0$, the wavefunction of pure liquid He must be totally symmetric. We therefore take as a trial wavefunction for our system the form

$$\Psi=\exp[\tfrac{1}{2}\sum_{j<k}^{N}\omega_{jk}+\sum_{k=1}^{N}\chi(R_k)], \quad (6)$$

with the functions ω_{jk} and χ to be determined in terms of the radial distribution function of the liquid, etc. In terms of the singlet and doublet configuration space densities,

$$\rho^{(1)}(1)=N\int\Psi^2d\{N-1\}\Big/\int\Psi^2d\{N\}, \quad (7)$$

$$\rho^{(2)}(1,2)=N(N-1)\int\Psi^2d\{N-2\}\Big/\int\Psi^2d\{N\}; \quad (8)$$

the average kinetic energy and potential energy of the system are

$$\langle \mathrm{KE}\rangle_{\mathrm{He}}=\frac{\hbar^2}{8M}\int\nabla_1\rho^{(2)}(1,2)\nabla_1\omega(1,2)d(1)d(2)+\frac{\hbar^2}{8M}\int\nabla_1\rho^{(1)}(1)\nabla_1\chi(1)d(1), \quad (9)$$

$$\langle \mathrm{PE}\rangle=\frac{1}{2}\int\rho^{(2)}(1,2)u(1,2)d(1)d(2)+\int\rho^{(1)}(1)v(1)d(1). \quad (10)$$

[3] A. Abe, Progr. Theoret. Phys. (Kyoto) **19**, 57, 407 (1957).
[4] F. Y. Wu and E. Feenberg, Phys. Rev. **122**, 739 (1961).
[5] K. Hiroike, Progr. Theoret. Phys. (Japan) **27**, 342 (1962).

The reader should note that Eq. (9) does not contain the kinetic energy of the electron. It should also be noted that with the trial function (6) and the definitions (7) and (8), the system under investigation is isomorphous with a classical fluid characterized by the pair potential $kT\omega_{ij}$ and in an external field $kT\chi$. We may therefore immediately make use of a number of exact (and approximate) relationships from the classical theory of liquids.

We proceed by introducing, at this point, the further assumptions we find it convenient to use. These assumptions are:

(1) The bubble wherein the electron is localized is characterized by the density distribution (4).

(2) If $\rho^{(1)}(r)$ is the singlet density measured from an origin at the center of the bubble, then the limiting density ρ_∞ is

$$\lim_{|\mathbf{r}|\to\infty} \rho^{(1)}(\mathbf{r})=\rho_\infty$$

with ρ_∞ different from the normal liquid density, ρ_0, by a term of the order of Ω^{-1}.

(3) The pair trial function ω_{jk} depends only on the distance between the molecules j and k,

$$\omega(\mathbf{R}_j,\mathbf{R}_k)=\omega(|\mathbf{R}_j-\mathbf{R}_k|). \tag{11}$$

(4) The pair correlation function $g^{(2)}(\mathbf{R}_j,\mathbf{R}_k)$, defined by $\rho^{(2)}(\mathbf{R}_j,\mathbf{R}_k)=\rho^{(1)}(\mathbf{R}_j)\rho^{(1)}(\mathbf{R}_k)g^{(2)}(\mathbf{R}_j,\mathbf{R}_k)$ depends only on the separation of the molecules j and k

$$g^{(2)}(\mathbf{R}_j,\mathbf{R}_k)=g^{(2)}(|\mathbf{R}_j-\mathbf{R}_k|). \tag{12}$$

(5) The functions ω and $g^{(2)}$ are related to each other by the same functional relation as when the system is uniform, i.e., when the term $\sum\chi(R_k)$ does not exist.

(6) The relation between ω and $g^{(2)}$ is approximated by the hypernetted chain relation[5]

$$\omega(|\mathbf{R}-\mathbf{R}'|)=\ln g^{(2)}(|\mathbf{R}-\mathbf{R}'|)-g^{(2)}(|\mathbf{R}-\mathbf{R}'|)+(\rho_\infty\Omega)^{-1}\sum_{\mathbf{K}}\{1-[S(\mathbf{K})]^{-1}\}\exp[i\mathbf{K}\cdot(\mathbf{R}-\mathbf{R}')], \tag{13}$$

where

$$S(\mathbf{K})=1+\rho_\infty\int(g^{(2)}-1)\exp(-i\mathbf{K}\cdot\mathbf{R})d^3R.$$

(7) The function $g^{(2)}$ is, to an adequate approximation, the radial distribution function of pure helium at the density ρ_∞.

The average kinetic energy of the He atoms can now be rewritten in the form:

$$\begin{aligned}\langle\mathrm{KE}\rangle_{\mathrm{He}}=\rho_\infty\Omega\frac{\hbar^2}{8M}\left\{\rho_\infty\int\frac{(\nabla_Rg^{(2)})^2}{g^{(2)}(R)}\rho^3R-\frac{1}{\rho_\infty\Omega}\sum_{\mathbf{K}}\frac{[S(\mathbf{K})-1]^3}{S(\mathbf{K})}K^2\right\}-\frac{\hbar^2}{4M}\left\{\rho_\infty\int\frac{(\nabla_Rg^{(2)})^2}{g^{(2)}(R)}d^3R\right.\\ \left.-\frac{1}{\rho_\infty\Omega}\sum_{\mathbf{K}}\frac{[S(\mathbf{K})-1]^3}{S(\mathbf{K})}K^2\right\}\int\Delta\rho(\mathbf{R})d^3R+\frac{\hbar^2}{8M}\int\Delta\rho(\mathbf{R})\Delta\rho(\mathbf{R}')\left[\frac{(\nabla_Rg^{(2)})^2}{g^{(2)}(|\mathbf{R}-\mathbf{R}'|)}\right.\\ \left.-\frac{1}{(\rho_\infty\Omega)^2}\sum_{\mathbf{K}}\sum_{\mathbf{K}'}\frac{[S(\mathbf{K})-1]^2[S(\mathbf{K}')-1]}{S(\mathbf{K})}(i\mathbf{K})(i\mathbf{K}')\exp[i(\mathbf{K}+\mathbf{K}')\cdot(\mathbf{R}-\mathbf{R}')]\right]d^3Rd^3R'+\frac{\hbar^2}{8M}\int\frac{[\nabla_R\rho^{(1)}(\mathbf{R})]^2}{\rho^{(1)}(\mathbf{R})}d^3R,\end{aligned} \tag{14}$$

where we have used the substitution

$$\Delta\rho(\mathbf{R})=\rho_\infty-\rho^{(1)}(\mathbf{R}). \tag{15}$$

Similarly, the potential energy [Eq. (10)] may be represented in the form

$$\begin{aligned}\langle\mathrm{PE}\rangle=\tfrac{1}{2}\rho_\infty^2\Omega\int u(\mathbf{R})g^{(2)}(\mathbf{R})d^3R-\rho_\infty\left[\int u(\mathbf{R})g^{(2)}(\mathbf{R})d^3R\right]\int\Delta\rho(\mathbf{R})d^3R\\ +\frac{1}{2}\int\Delta\rho(\mathbf{R})\Delta\rho(\mathbf{R}')u(|\mathbf{R}-\mathbf{R}'|)g^{(2)}(|\mathbf{R}-\mathbf{R}'|)d^3Rd^3R'+\int v(\mathbf{R})\rho^{(1)}(\mathbf{R})d^3R.\end{aligned} \tag{16}$$

From the normalization condition we find that

$$N=\int\rho^{(1)}(\mathbf{R})d^3R=\rho_\infty\Omega-\int\Delta\rho(\mathbf{R})d^3R, \tag{17}$$

$$\rho_\infty=\rho_0+\Omega^{-1}\int\Delta\rho(\mathbf{R})d^3R, \tag{18}$$

so that, as asserted, ρ_∞ differs from $\rho_0=N/\Omega$ by a term of the order of Ω^{-1}. Although the first terms in Eqs. (14) and (16) are of order Ω and the other terms of the order of 1, the difference between ρ_∞ and ρ_0 cannot be neglected, since the addition of the excess electron to the liquid makes an energy change of the order of 1. The sum of the first terms in Eqs. (14) and (16) is the energy of the liquid helium at the uniform density ρ_∞, i.e.,

$$\frac{E(\rho_\infty)}{\Omega}=\rho_\infty^2\frac{\hbar^2}{8M}\left\{\int\frac{(\nabla_R g^{(2)})^2}{g^{(2)}(R)}d^3R-\frac{1}{\rho_\infty^2\Omega}\sum_{\mathbf{K}}\frac{[S(\mathbf{K})-1]^3}{S(\mathbf{K})}K^2\right\}+\tfrac{1}{2}\rho_\infty^2\int u(R)g^{(2)}(R)d^3R. \tag{19}$$

Since ρ_∞ and ρ_0 differ only by terms of the order of $1/\Omega$, $E(\rho_\infty)$ may be expanded about ρ_0 in the Taylor expansion

$$\frac{E(\rho_\infty)}{\Omega}=\frac{E(\rho_0)}{\Omega}+(\rho_\infty-\rho_0)\frac{\partial}{\partial\rho_0}\left(\frac{E(\rho_0)}{\Omega}\right)+\cdots, \tag{20}$$

and only the first two terms in the expansion need to be retained. It should be noted at this point that $S(\mathbf{K})$ and $g^{(2)}(R)$ in Eq. (19) are taken for the density ρ_∞. Using the thermodynamic definition of pressure, Eq. (20) is transformed into the form

$$E(\rho_\infty)=E(\rho_0)+\left(\frac{p_0}{\rho_0}+\frac{E(\rho_0)}{\rho_0\Omega}\right)\int\Delta\rho(\mathbf{R})d^3R+O(\Omega)^{-1}, \tag{21}$$

with p_0 the equilibrium pressure at the density ρ_0.

To proceed, we note that the second term in the expression for $\langle\text{KE}\rangle$ and $\langle\text{PE}\rangle$ is just $-2E(\rho_0)/\rho_0\Omega$, when we replace ρ_∞ by ρ_0. Since these terms are of the order of 1 the error made by the substitution $\rho_0\to\rho_\infty$ is of the order of $1/\Omega$, and hence negligible.

With the definition

$$\Delta E=\langle\text{KE}\rangle+\langle\text{PE}\rangle-E(\rho_0) \tag{22}$$

we obtain

$$\Delta E=\left[\frac{p_0}{\rho_0}-\frac{E(\rho_0)}{\rho_0\Omega}\right]\int\Delta\rho(\mathbf{R})d^3R+\frac{\hbar^2}{8M}\int\Delta\rho(\mathbf{R})\Delta\rho(\mathbf{R}')\left\{\frac{(\nabla_R g^{(2)})^2}{g^{(2)}(|\mathbf{R}-\mathbf{R}'|)}\right.$$
$$\left.+\frac{1}{(\rho_0\Omega)^2}\sum_{\mathbf{K}}\sum_{\mathbf{K}'}\frac{[S(\mathbf{K})-1]^2[S(\mathbf{K}')-1]}{S(\mathbf{K})}\mathbf{K}\cdot\mathbf{K}'\exp[i(\mathbf{K}+\mathbf{K}')\cdot(\mathbf{R}-\mathbf{R}')]\right\}d^3Rd^3R'$$
$$+\frac{1}{2}\int\Delta\rho(\mathbf{R})\Delta\rho(\mathbf{R}')u(|\mathbf{R}-\mathbf{R}'|)g^{(2)}(|\mathbf{R}-\mathbf{R}'|)d^3Rd^3R'+\frac{\hbar^2}{8M}\int\frac{[\nabla_R\rho^{(1)}(\mathbf{R})]^2}{\rho^{(1)}(\mathbf{R})}d^3R+\int v(\mathbf{R})\rho^{(1)}(\mathbf{R})d^3R. \tag{23}$$

The definition (22) implies that ΔE is the increase of the energy of the fluid due to the presence of the bubble and of the excess electron. It should be noted that we have not yet included the kinetic energy of the electron in the energy expression. Upon addition of the kinetic energy of the electron, a representation of the total energy of the system is obtained.

In the following discussion the simple distribution (4) is used, so that

$$\Delta\rho(R)=\rho_0;\qquad R<R_0,$$
$$\Delta\rho(R)=\rho_0[1+\alpha(R-R_0)]\exp[-\alpha(R-R_0)];\qquad R>R_0. \tag{24}$$

The resultant expression for the total energy change of the system (including the excess-electron energy) is obtained, after rather long and cumbersome computations, in the form

$$E_t=\tfrac{1}{2}\zeta^2+4\pi\rho_0\int_{R_0}^\infty v_\zeta(R)\{1-[1+\alpha(R-R_0)]\exp[-\alpha(R-R_0)]\}R^2dR+\frac{4\pi p_0}{\alpha^3}[8+6\alpha R_0+2\alpha^2R_0^2+\tfrac{1}{3}\alpha^3R_0^3]$$
$$+\frac{\pi}{2M}\rho_0\alpha^4\int_0^\infty(R_0+R)^2\frac{R^2\exp(-2\alpha R)dR}{1-(1+\alpha R)\exp(-\alpha R)}+\frac{4\pi^2\rho_0^2}{\alpha^4}\left[\int_0^\infty Ru(R)g^{(2)}(R)F(R)dR\right.$$
$$\left.-\int_0^\infty Ru(R)g^{(2)}(R)2\alpha R(8+6\alpha R_0+2\alpha^2R_0^2+\tfrac{1}{3}\alpha^3R_0^3)dR\right]$$
$$+\frac{1}{4\pi^2M\alpha^4}\left[\int_0^\infty RG(R)F(R)dR-\int_0^\infty RG(R)2\alpha R(8+6\alpha R_0+2\alpha^2R_0^2+\tfrac{1}{3}\alpha^3R_0^3)dR\right]. \tag{25}$$

In Eq. (25) the energy is expressed in atomic units.

The functions $F(R)$ and $G(R)$ are defined by

$$F(R)=(-21-12\alpha R_0-2\alpha^2R_0^2)+(16+12\alpha R_0+4\alpha^2R_0^2+\tfrac{2}{3}\alpha^3R_0^3)(\alpha R)+(-3-2\alpha R_0-\tfrac{1}{2}\alpha^2R_0^2)(\alpha R)^2+\tfrac{1}{24}(\alpha R)^4$$
$$+[(21+12\alpha R_0+2\alpha^2R_0^2)+(\tfrac{17}{2}+\tfrac{9}{2}\alpha R_0+\tfrac{1}{2}\alpha^2R_0^2)(\alpha R)+(1+\tfrac{1}{2}\alpha R_0)(\alpha R)^2]\exp(-\alpha R) \quad (26a)$$

for $0<R<2R_0$, and

$$F(R)=[(-21+20\alpha R_0+10\alpha^2R_0^2)+(-5+20\alpha R_0+6\alpha^2R_0^2)\alpha(R-2R_0)+(\tfrac{5}{2}+8\alpha R_0+\tfrac{3}{2}\alpha^2R_0^2)\alpha^2(R-2R_0)^2$$
$$+(\tfrac{3}{2}+\tfrac{5}{3}\alpha R_0+\tfrac{1}{6}\alpha^2R_0^2)\alpha^3(R-2R_0)^3+(\tfrac{1}{3}+\tfrac{1}{6}\alpha R_0)\alpha^4(R-2R_0)^4+\tfrac{1}{30}\alpha^5(R-R_0)^5]\exp[-\alpha(R-2R_0)]$$
$$+[(21+12\alpha R_0+2\alpha^2R_0^2)+(\tfrac{17}{2}+\tfrac{9}{2}\alpha R_0+\tfrac{1}{2}\alpha^2R_0^2)(\alpha R)+(1+\tfrac{1}{2}\alpha R_0)(\alpha R)^2]\exp(-\alpha R), \quad (26b)$$

$$G(R)=4\pi^4\rho_0^2\frac{1}{g(R)}\left(\frac{dg}{dR}\right)^2-\left\{\int_0^\infty dKK^3\frac{[S(K)-1]^2}{S(K)}[(K^2R^2)^{-1}\sin KR-(KR)^{-1}\cos KR]\right\}$$
$$\times\left\{\int_0^\infty dKK^3[S(K)-1][(K^2R^2)^{-1}\sin KR-(KR)^{-1}\cos KR]\right\} \quad (27)$$

for $R>2R_0$.

It is now pertinent to examine the nature of the several terms in the energy expression (25). The first two terms represent the electronic energy of the excess electron (using the simple 1s-type trial wavefunction[1]), the third term,

$$\epsilon_{\rm PV}=(4\pi p/\alpha^3)\{8+6\alpha R_0+2\alpha^2R_0^2+\tfrac{1}{3}\alpha^3R_0^3\}, \quad (28)$$

represents the pressure–volume work, and the change in kinetic energy due to removal of atoms from the boundary region is

$$\epsilon_{\rm VK}=\frac{\pi}{2M}\rho_0\alpha^4\int_0^\infty(R_0+R)^2\frac{R^2\exp(-2\alpha R)dR}{1+(1+\alpha R)\exp(-\alpha R)}. \quad (29)$$

$\epsilon_{\rm VK}$ tends to zero in the limit $\alpha\rightarrow\infty$, i.e., for the case of an infinitely sharp bubble. However, for finite values of α (of the order of unity), (29) is of considerable importance. Finally, the surface kinetic and potential energy terms may be displayed in the form

$$\epsilon_{\rm SK}=\frac{1}{4\pi^2M\alpha^4}\int_0^\infty dRRG(R)[F(R)-(16\alpha R+12\alpha^2RR_0+4\alpha^3R_0^2R+\tfrac{2}{3}\alpha^4R_0^3R)],$$

$$\epsilon_{\rm SP}=\frac{4\pi^2\rho_0^2}{\alpha^4}\int_0^\infty dRRu(R)g(R)[F(R)-(16\alpha R+12\alpha^2R_0R+4\alpha^3R_0^2R+\tfrac{2}{3}\alpha^4R_0^3R)]. \quad (30)$$

It is interesting to consider the limiting behavior of the surface terms for the case $\alpha\rightarrow\infty$. The surface tension term

$$4\pi R_0^2\gamma_0=\lim_{\alpha\to\infty}(\epsilon_{\rm SK}+\epsilon_{\rm SP}) \quad (31)$$

represents the reversible work expended in the introduction of a spherical cavity of radius R_0 into the fluid, accompanied by the introduction of a hollow rigid sphere. The interfacial tension γ_0 between the fluid and a perfect rigid wall differs from the interfacial tension between the liquid and its vapor, but should be of the same order of magnitude.

In the limit $\alpha\rightarrow\infty$ we find

$$F(R)=\alpha^4(-\tfrac{1}{2}R_0^2R^2+\tfrac{2}{3}R_0^3R+\tfrac{1}{24}R^4); \qquad R<2R_0$$
$$F(R)=0; \qquad R>2R_0 \quad (32)$$

so that

$$\lim_{\alpha\to\infty}\epsilon_{SK}=\frac{1}{4\pi^2M}\left[\frac{1}{24}\int_0^{2R_0}R^5G(R)dR-\frac{R_0^2}{2}\int_0^{2R_0}R^3G(R)dR\right], \tag{33}$$

$$\lim_{\alpha\to\infty}\epsilon_{SP}=4\pi^2\rho_0^2\left[\frac{1}{24}\int_0^{2R_0}u(R)g(R)R^5dR-\frac{R_0^2}{2}\int_0^{2R_0}u(R)g(R)dR\right]. \tag{34}$$

Numerical estimates show that the first terms in Eqs. (33) and (34) are small compared with the terms depending on R_0^2. Thus for the limit of zero temperature the interfacial tension γ_0 can be displayed in the form

$$\gamma_0=-\left[\frac{1}{32\pi^3M}\int_0^{2R_0}R^3G(R)dR+\frac{\pi\rho^2}{2}\int_0^{2R_0}R^3u(R)g(R)dR\right]. \tag{35}$$

III. NUMERICAL CALCULATIONS

Calculations of the electronic energy have already been described. In Table I we display the values of E_e calculated for liquid helium over the ζ, α, and R_0 range of interest. The bubble energy is expressed in terms of the radial distribution function, its first derivative and the interaction potential between a pair of helium atoms. The radial distribution function can be expressed in terms of the liquid-structure factor $S(K)$,

$$g(R)=1+\frac{1}{2\pi^2\rho}\int_0^\infty K[S(K)-1]\sin KRdK, \tag{36}$$

whereupon

$$\frac{dg}{dR}=\frac{1}{2\pi\rho}\left[\int_0^\infty K\{S(K)-1\}\left(\frac{K}{R}\cos KR-\frac{1}{R^2}\sin KR\right)dK\right]. \tag{37}$$

The experimental values of $S(K)$ for the ground state of ^{4}He were taken from x-ray diffraction data. The results of Goldstein and Reekie[6] were modified by applying the normalization suggested by Feynman and Cohen,[7] i.e., multiplication by a numerical factor of 0.97 throughout the whole region and use of a linear extrapolation near the origin to the limit $S(0)=0$. The calculation of $g(R)$ and $[dg(R)/dR]$ was performed using Eqs. (36) and (37). Because of the limitations of the experimental data, we set $S(K)=1$ for $K>6A^{-1}$. The computed function $g(R)$ becomes positive at $R=2.36$ Å. For $R<2.36$ Å we set $g(R)=0$. The pair interaction potential was chosen in the form of a Lennard-Jones potential:

$$u(R)=4\epsilon[(\sigma/R)^{12}-(\sigma/R)^6],$$

with $\sigma=5.613a_0$ and $\epsilon=0.00003719$ a.u. These parameters, combined with the radial distribution function, lead to a good value for the energy per atom in the fluid.[4]

The integrals in Eq. (25) were evaluated by numerical integration on an IBM 7094. The results of the calculations of the bubble energy are displayed in Table II. The stationary values for the energy (for each value of R_0) are presented in Table III. The ground-state energy of the excess electron is obtained from Fig. 1. The parameters characterizing the bubble size and shape are $R_0=23.5$ a.u. and $\alpha=1.5$ a.u., while the excess-electron charge distribution is characterized by $\zeta=0.13$ a.u., leading to a ground-state energy of the system of $\Delta E=2\times10^{-2}$ a.u.

In order to obtain further insight into the nature of the various contributions to the bubble energy, we now consider the surface terms $\epsilon_{SP}+\epsilon_{SK}$ and the volume kinetic energy. In the limiting case $\alpha\to\infty$, the interfacial surface tension is obtained from Eq. (31). In Table IV we display the calculated values of γ_0 for a relatively large value of α ($\alpha=3$ a.u.). The surface energy is linear in R_0^2, and the calculated values of γ_0 show only a 2% variation in the region $R_0=10-90$ a.u.

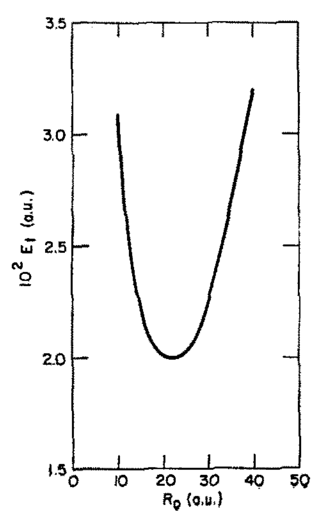

FIG. 1. The ground-state energy of an excess electron in liquid helium.

[6] L. Goldstein and J. Reekie, Phys. Rev. **98**, 857 (1955).
[7] R. P. Feymman and M. Cohen, Phys. Rev. **102**, 1189 (1958).

TABLE I. The electronic energy for a localized excess electron in liquid helium.

R_0 (a.u.)	α (a.u.)	ζ (a.u.)	10^2E_e (a.u.)
10	1.0	0.02	4.0607
		0.03	6.2578
		0.05	5.4987
		0.07	4.7147
		0.10	3.8740
		0.15	3.1058
	1.5	0.02	4.0820
		0.03	6.2970
		0.05	5.5921
		0.07	4.8567
		0.10	4.0709
20	1.0	0.02	4.1100
		0.03	6.2906
		0.05	4.6945
		0.07	3.4174
		0.10	2.3510
		0.15	2.1084
	1.5	0.02	4.0872
		0.03	5.9539
		0.05	4.4020
		0.07	3.1352
		0.10	2.0440
		0.15	1.7488
	2.0	0.02	4.1213
		0.03	6.0013
		0.05	4.4719
		0.07	3.2119
		0.10	2.1095
		0.15	1.7873
	3.0	0.02	4.1534
		0.03	6.0457
		0.05	4.5378
		0.07	3.2851
		0.10	2.1728
		0.15	1.8251
30	1.0	0.03	5.8541
		0.05	3.7814
		0.07	2.5917
		0.10	2.0033
		0.15	2.3220
	1.5	0.03	5.4836
		0.05	3.4265
		0.07	2.2192
		0.10	1.5965
		0.15	1.8928
	2.0	0.03	5.6178
		0.05	3.5692
		0.07	2.3538
		0.10	1.7140
		0.15	1.9987
	3.0	0.03	5.6457
		0.05	3.6056
		0.07	2.3827
		0.10	1.7270
		0.15	2.0006
40	1.0	0.03	6.4153
		0.05	4.2864
		0.07	3.4288
		0.10	3.2859
		0.15	3.8363
	1.5	0.03	5.0857
		0.05	2.9471
		0.07	2.0638
		0.10	1.8987
		0.15	2.4415
	2.0	0.03	5.2844
		0.05	3.1419
		0.07	2.2460
		0.10	2.0696
		0.15	2.6083
	3.0	0.03	5.4383
		0.05	3.2926
		0.07	2.3850
		0.10	2.1978
		0.15	2.7325
50	1.0	0.03	8.2139
		0.05	6.3579
		0.07	5.8673
		0.10	5.9793
		0.15	6.5901
	1.5	0.03	5.0959
		0.05	3.2144
		0.07	2.7121
		0.10	2.8039
		0.15	3.4133
	2.0	0.03	5.1279
		0.05	3.2342
		0.07	2.7209
		0.10	2.8076
		0.15	3.4162
	3.0	0.03	5.3778
		0.05	3.4729
		0.07	2.9491
		0.10	3.0309
		0.15	3.6388
60	1.0	0.03	13.9038
		0.05	12.4653
		0.07	12.2616
		0.10	12.4648
		0.15	13.0740
	1.5	0.03	5.6987
		0.05	4.2318
		0.07	4.0144
		0.10	4.2140
		0.15	4.8363
	2.0	0.03	5.7216
		0.05	4.2408
		0.07	4.0165
		0.10	4.2142
		0.15	4.8363
	3.0	0.03	5.6741
		0.05	4.1803
		0.07	3.9493
		0.10	4.1452
		0.15	4.7671

The calculated interfacial surface tension is $\gamma_0=0.52$ dyn/cm, in fairly good agreement with the experimental surface tension,[8] $\gamma=0.356$ dyn/cm at $T\rightarrow 0°$K.

IV. DISCUSSION

In the present paper we have presented a study of the structural changes in liquid helium in the vicinity of an excess electron. When we compare the results obtained herein with the predictions of the simple

[8] G. A. Cook, *Argon, Helium and the Rare Gases* (Interscience Publishers, Inc., New York, 1964).

TABLE II. Contribution to the energy of bubble formation in liquid helium (all energies in units of 10^{-2} a.u.).

α (a.u.)	R_0 (a.u.)	ϵ_{VK}	ϵ_{PV}	ϵ_{SK}	ϵ_{SP}
1.0	10	0.0101	0.0026	−0.0013	0.0766
	20	0.0373	0.0156	0.1162	0.2354
	30	0.0814	0.0476	0.6230	0.1451
	40	0.1421	0.1073	1.9349	0.5222
	50	0.2190	0.2033	4.6125	0.4303
	60	0.3116	0.3444	9.3609	0.01945
	70	0.4198	0.5391	17.030	−1.0184
	80	0.5431	0.7961	28.6141	−2.7904
	90	0.6813	1.1242	45.2525	−5.5923
1.5	10	0.0144	0.0021	−0.0156	0.0683
	20	0.0543	0.0141	−0.0392	0.2493
	30	0.1190	0.0445	−0.0322	0.5389
	40	0.2078	0.1020	0.0671	0.9341
	50	0.3197	0.1953	0.3424	1.4309
	60	0.4542	0.3331	0.8997	2.0243
	70	0.6103	0.5239	1.8675	2.7081
	80	0.7774	0.7765	3.3965	3.4752
	90	0.9848	1.0995	5.6600	4.3172
2.0	10	0.0187	0.0019	−0.0158	0.0630
	20	0.0711	0.0134	−0.0558	0.2390
	30	0.1558	0.0430	−0.1148	0.5252
	40	0.2716	0.0995	−0.1845	0.9218
	50	0.4169	0.1915	−0.2536	1.4292
	60	0.5906	0.3276	−0.3075	2.0480
	70	0.7912	0.5165	−0.3289	2.7787
	80	1.0175	0.7668	−0.2970	3.6220
	90	1.2682	1.0873	−0.1881	4.5789
3.0	10	0.0271	0.0018	−0.0146	0.0582
	20	0.1039	0.0128	−0.0552	0.2289
	30	0.2271	0.0416	−0.1217	0.5082
	40	0.3937	0.0971	−0.2138	0.8966
	50	0.6008	0.1877	−0.3315	1.3938
	60	0.8455	0.3222	−0.4744	2.0000
	70	1.1249	0.5092	−0.6423	2.7150
	80	1.4364	0.7573	−0.8349	3.5391
	90	1.7774	1.0753	−1.0517	4.4721

phenomenological model previously used, it becomes apparent that the present model of the configuration changes in the fluid leads to a smaller cavity radius and a somewhat higher energy for the localized state. It should be noted that the interfacial surface tension obtained from the present theory is in fairly good agreement with the observed surface tension of liquid helium at 0°K. It should also be noted that the surface energy terms calculated herein are not the source of the change in the cavity size. The dependence of the bubble radius on the surface tension was examined in the preceding paper[1] and found to be fairly small (R_0 varying approximately as $\gamma^{\frac{1}{4}}$ for the particle in a box model). Indeed, earlier calculation in which E_b was approximated by the surface energy term lead to a cavity radius of 36 a.u. for $\gamma=0.36$ dyn/cm (corresponding to zero temperature). It is the inclusion of the volume kinetic energy term, arising from the excess kinetic energy of the fluid atoms removed from the boundary layer, which leads to a substantial decrease of the bubble size.

TABLE III. Dependence of the ground-state energy of a localized electron in liquid helium on the bubble size.

R_0 (a.u.)	α (a.u.)	ζ (a.u.)	10^2E_t (a.u.)
10	0.8	0.17	3.080
20	1.3	0.15	2.020
30	1.5	0.10	2.260
40	1.5	0.10	3.208
50	1.7	0.08	4.980

The available experimental data[9] are in agreement with the results of our analysis. The Stokes law of mobility for a bubble of radius 23.5 a.u. is $\mu_-=0.0235$ cm^2/V·sec, in (fortuitously) good agreement with the experimental value $\mu_-=0.020$ cm^2/V·sec for a negative ion liquid helium at 4.2°K and at 1 atm. (Note that we have neglected here the temperature dependence of the bubble size.) In a recent study[10] of the interactions of ions and quantized vortices in rotating He II, Donnelly has shown that the cross sections for the negative ion–vortex interaction are strongly dependent on the size of the negative ion. The experimental results can be adequately interpreted by assuming that the negative ion is characterized by a radius of 12.1 Å, again in good agreement with the bubble radius of 12.4 Å calculated by us.

TABLE IV. Surface potential and kinetic energy terms for $\alpha=3$ a.u.

R_0 (a.u.)	Total volume work $\epsilon_{SK}+\epsilon_{SP}$ (a.u.)	$(1/R^2)(\epsilon_{SK}+\epsilon_{SP})$ (a.u.)	γ_0 (dyn cm^{-1})
10	0.0436×10^{-2}	4.36×10^{-6}	0.540
20	0.1737	4.343	0.5380
30	0.3865	4.294	0.5319
40	0.6828	4.268	0.5287
50	1.0623	4.249	0.5264
60	1.5256	4.238	0.5250
70	2.0727	4.230	0.5240
80	2.7042	4.225	0.5234
90	3.420	4.223	0.5231

ACKNOWLEDGMENTS

This research was supported by the Directorate of Chemical Sciences of the U.S. Air Force Office of Scientific Research and the U.S. Public Health Service. We have also benefited from facilities provided by the Advanced Research Projects Agency for materials research at the University of Chicago.

[9] L. Meyer, H. T. Davis, S. A. Rice, and R. J. Donnelly, Phys. Rev. **126**, 1927 (1962).
[10] R. J. Donnelly, Phys. Rev. Letters **14**, 39 (1965).