

Self-consistent calculation of surface properties of electron-hole droplets*

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The surface energy of the electron-hole liquid in Ge is calculated using the density-functional formalism. The kinetic energy is included exactly within an uncoupled spherical band model. Corrections to order $|\nabla n|^2$ are included in the evaluation of the exchange and correlation energy and also in the evaluation of the effects of band coupling and anisotropy on the kinetic energy. We obtain a surface energy of 2.5×10^{-4} erg/cm² and an electrostatic dipole barrier $\Delta\Phi$ of 0.16 meV. The small value of $\Delta\Phi$ leads to the conclusion that the charge on the droplet is negative.

I. INTRODUCTION

Free excitons in Ge have been found to condense into metallic droplets at sufficiently low temperature and high density of excitons.¹⁻⁴ The surface properties of the electron-hole liquid droplet (EHD) are of considerable experimental and theoretical interest,⁵⁻¹³ primarily because the kinetics of EHD formation from the exciton gas depends on surface properties. The role of the surface is most clearly seen by considering the formation of EHD nuclei from density fluctuations during homogeneous nucleation.^{10, 13, 14} For small nuclei the surface energy supplies a relatively large positive contribution to the total free energy, and hence tends to inhibit droplet formation. For many situations this is the rate limiting factor. Besides being important in kinetic processes, the surface structure of the droplets determines in principle the normal modes of the surface. In practice we can use the surface tension to obtain an estimate of the low-frequency capillary modes of the droplet.⁵ Another question which has excited some experimental and theoretical work is the question of the charge on the drop at finite temperature.^{6, 7, 15} The surface charge will be important in how the droplet couples to electrical fields, and possibly in the dynamics of droplet motion through the lattice.

The surface properties of the EHD have been investigated by several authors.⁵⁻⁹ These papers established the order of magnitude of the surface energy. Results for the electrostatic dipole layer, and for the electron and hole work functions were considered to be speculative by these authors, and the need for more detailed calculation was generally indicated. In this paper we calculate the ground-state surface properties of the electron-hole liquid (EHL) in unstrained Ge at zero tem-

perature. The calculation was performed using the density-functional formalism.^{16, 17} Previous calculations have treated the kinetic energy by adding terms of the form $C(n)|\nabla n(r)|^2$ to the Thomas-Fermi kinetic-energy density.⁵⁻⁹ For simple metals this leads to errors of (15-20)% in the surface energy, compared to the method of Kohn and Sham¹⁷ which includes the kinetic-energy term correctly. Other surface properties such as the surface width and the electrostatic dipole layer are expected to depend quite sensitively on the exact treatment of the kinetic energy. Qualitatively, this results from the fact that any finite-order expansion of the kinetic energy in terms of a gradient expansion of the density cannot give the Friedel oscillations at the droplet surface.¹⁶ In the present calculation the energy minimization was carried out by means of the recently developed variation of potentials technique.¹⁸ This technique reformulates the variational problem into a simpler form, and gives answers which are fully equivalent to the self-consistent equation approach of Kohn and Sham.

In addition to treating the kinetic energy correctly, we have examined the contribution of the various interaction energy terms carefully. Previous studies divided the exchange and correlation energy evenly between the electrons and holes. Further, in the evaluation of the correlation energy, no account was taken of the fact that the electron and hole densities are not exactly equal everywhere. We have calculated the exchange and correlation energies in the local approximation in a manner which correctly apportions the energy between the bands, and takes into account the lack of local charge neutrality at the surface. We have included certain effects of multiple scattering¹⁹ in our local approximation to the exchange and correlation energy. Nonlocal corrections to the exchange

and correlation energy were roughly approximated in this paper by means of a gradient expansion in the density.^{20,21}

The structure of the paper is as follows. Section II describes the energy-functional approach to surfaces. Section III describes the evaluation of the exchange and correlation contribution to the surface energy. In Sec. IV we discuss the kinetic-energy terms. Sections V and VI give the results for the surface properties. Section VII provides a discussion of the results. Finally we give technical detail concerning the valence-band contribution to the EHL dielectric constant in the Appendix.

II. THEORY

The zero-temperature surface properties of an EHD are calculated in the density-functional formalism using the potential variation technique. The droplet is assumed to be sufficiently large that curvature effects are unimportant in determining the surface energy and the radial charge distribution. The surface is approximated by a planar EHL-vacuum interface at $x=0$, with the EHL density going to its bulk value as $x \rightarrow -\infty$, and to zero as $x \rightarrow +\infty$. Using this approximate model for the EHD surface, we can write the total energy of the system as a functional of the densities of the particles in the various electron and hole bands. It is convenient to divide this energy functional into a bulk and a surface contribution,

$$E[n_i(r)] = \bar{E} + A\Sigma[n_i]. \quad (1)$$

Here $n_i(r)$ is the density of particles in the i th band; \bar{E} is the bulk energy of a uniform EHL at the equilibrium bulk density; A is the surface area; and Σ is the surface energy per unit area. The ground-state properties are determined by minimizing E with respect to variations in the densities n_i . These variations are subject to the condition that the number of particles in each band remain a constant. From Eq. (1) it is clear that minimizing the surface energy Σ is equivalent to minimizing E . Hence from now on we will phrase the minimization problem in terms of Σ rather than E . Following the procedure used by Lang and Kohn²² for a single-component system, we can write an exact functional for Σ in terms of the densities $n_i(r)$:

$$\Sigma[n_i] = \sigma_s[n_i] + \sigma_{xc}[n_i] + \sigma_{es}[n_i]. \quad (2)$$

Here σ_s is the kinetic contribution to the surface energy for an EHL of noninteracting particles with densities $n_i(r)$; the exchange and correlation contribution to Σ is denoted by σ_{xc} ; while the third term on the right gives the electrostatic energy contribution

$$\sigma_{es} = \frac{1}{2} \int \frac{dr dr' \rho(r)\rho(r')}{|r-r'|}. \quad (3)$$

Here ρ is the net charge density. In Sec. III, we discuss the evaluation of σ_{xc} and in Sec. IV the evaluation of σ_s . Once functional forms for these quantities are obtained in terms of the variational potentials, we minimize Σ and obtain the ground-state surface properties. We stress at this point that using the variational potential technique is equivalent to solving the self-consistent Kohn-Sham equations for the same problem. The potential variation technique is straightforward to apply for the EHL, and avoids two difficulties associated with obtaining solutions to the self-consistent equations. The first problem is the divergent self-consistent potential obtained when a gradient term is included in the evaluation of σ_{xc} .²³ Second, since the variation of potentials technique is inherently stable numerically, it avoids the well-known numerical instabilities found when iterative schemes are used to solve the self-consistent equations for metallic surface problems.²²

III. EXCHANGE AND CORRELATION

The exchange and correlation contribution to the surface energy is approximated by a gradient expansion

$$\begin{aligned} \sigma_{xc}[n_i(r)] = & \int d^3r [e_{xc}(n_i(r)) - \bar{e}_{xc} \theta(x)] \\ & + \frac{1}{2} \sum_{ij} \int d^3r g_{ij}(n_i) |\nabla n_i(r)| |\nabla n_j(r)|. \end{aligned} \quad (4)$$

Here $e_{xc}(n_i)$ is the exchange and correlation energy per unit volume for a uniform EHL with densities n_i . The term \bar{e}_{xc} is the value of e_{xc} for the bulk equilibrium density of the uniform EHL. The first expansion coefficient in the gradient series is denoted by g_{ij} . In the rest of this section we evaluate the functions e_{xc} and g_{ij} .

The exchange energy for a uniform EHL has been obtained^{24,25}:

$$e_x(n_i) = -0.784 n_e^{4/3} - 1.048 n_h^{4/3} R^*. \quad (5)$$

Here n_e and n_h denote the total electron and hole densities. The evaluation of the correlation energy is complicated by the fact that the total electron and hole densities are not exactly equal in the surface region. We therefore first obtain the correlation energy e_c for a bulk uniform system, where $n_e = n_h$. If $n_e \simeq n_h$ (an approximation that we can verify after the fact), then we can expand e_c as

$$e_c(n_e, n_h) = e_c(n_e = n_h) + [\mu_e^c(n_e = n_h) - \mu_h^c(n_e = n_h)] \Delta n. \quad (6)$$

Here

$$\Delta n = \frac{1}{2} (n_e - n_h) \quad (7)$$

and

$$\mu_{e,h}^c(n_e = n_h) = \frac{\partial}{\partial n_{e,h}} e_c(n_e, n_h) \Big|_{n_e = n_h}. \quad (8)$$

The random-phase approximation (RPA) is used to evaluate e_c and $\mu_{e,h}^c$ within the model band structure used by Combescot and Nozières.²⁵ The electron bands are characterized by four ellipsoidal bands in the (1, 1, 1) directions. The two fluted valence bands are degenerate at $k=0$ and coupled by a matrix element of the density operator. Within the model band structure of Combescot and Nozières the valence bands are described by two spherical coupled bands which are characterized by a light-hole and a heavy-hole mass. For convenience we list all of our input parameters in Table I. Using this model band structure, we obtain an analytic expression for the imaginary part of the RPA dielectric constant. This formula, which is quite complicated because of the valence-band contribution, is included as the Appendix. The real part of $\epsilon(q, w)$ is then easily obtained as a one dimensional numerical integral by Kramers-Kronig inversion. Once $\epsilon(q, w)$ is known, $e_c^{\text{RPA}}(n_e = n_h)$ and $\mu_{e,h}^c$ are obtained by numerical integration. Results for $e_c^{\text{RPA}}(n_e = n_h)$ are shown in Fig. 1, and for $\mu_{e,h}^c$ in Fig. 2. The results for $e_c^{\text{RPA}}(n_e = n_h)$ are very close to those of Combescot and Nozières, being typically 2% more negative. The RPA values obtained for $\mu_{e,h}^c$ are used in the calculation of Σ . However, we further correct $e_c(n_e = n_h)$ to include the effects of multiple scattering, as follows.

Bhattacharyya *et al.*²⁶ have used a self-consistent-field approximation (which they call the self-consistent particle-hole method) to calculate con-

TABLE I. Major parameters used in calculation (from Ref. 24).

Parameter	Value	Units
m_0	0.12	Electron mass
m_{dens}	0.22	Electron mass
m_h	0.347	Electron mass
m_e	0.042	Electron mass
a_B^* (Bohr radius)	177	Å
\mathcal{R}^* (Rydberg)	2.65	meV
\bar{n} (bulk density) ^a	2.25×10^{17}	cm ⁻³
r_s^a	0.58	

^aIntermediate result of this calculation.

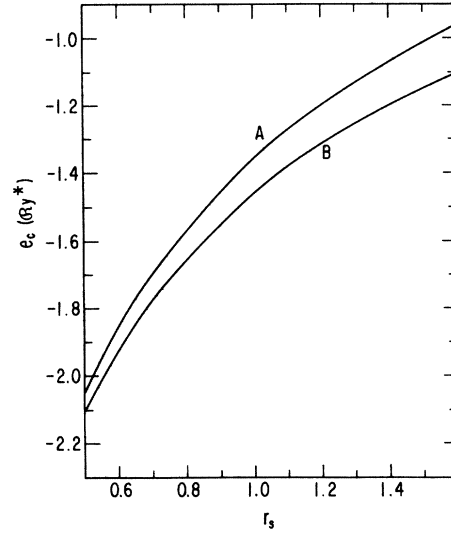


FIG. 1. (a) Correlation energy per pair from the exact RPA calculation. (b) Correlation energy with correction for multiple scattering included.

tributions to the correlation energy beyond the RPA. They use the full self-consistent particle-hole procedure for a simplified model band structure consisting of four spherical electron bands and two uncoupled spherical hole bands with the light- and heavy-hole masses. We extract our correction to the RPA result from their calculation. We first calculate the RPA correlation energy for this model band structure. Subtracting this RPA result from the self-consistent particle-hole result yields a correction Δe_c to our previous calculated RPA correlation energy which included valence-band coupling and electron-band anisotropy

$$e_c(n_e = n_h) = e_c^{\text{RPA}}(n_e = n_h) + \Delta e_c(n_e = n_h). \quad (9)$$

Figure 1 shows our final result for the correlation energy of the bulk EHL. Using these values

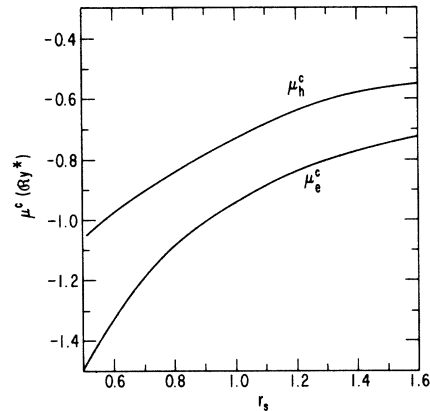


FIG. 2. Correlation contributions to the chemical potentials μ_e^c and μ_h^c .

for e_c , and the known values for the bulk kinetic and exchange energies, we can obtain the bulk equilibrium density and energy, $n_{\text{eq}} = 2.25 \times 10^{17} \text{ cm}^{-3}$; $E_B \simeq 29 \text{ }^\circ\text{K}$. The value for n_{eq} is in good agreement with other experimental and theoretical results.^{3,4,26} However the value for E_B is somewhat larger than recent experimental results⁴ 16–27 $^\circ\text{K}^4$ and¹⁰ 16–24 $^\circ\text{K}$. In view of the fact that the calculated value of E_B results from the sum of several large contributions of opposite sign, the lack of agreement is not too alarming. For example, a change in the correlation energy of 7% would lead to an E_B of 20 $^\circ\text{K}$. Still, the present calculation of e_c is the most complete known to us, including the effects of: the anisotropy of the electron bands, coupling between light- and heavy-hole bands within a spherical model, and multiple electron-hole scattering.

We should note that the expression for e_{xc} , obtained by adding Eqs. (9) and (5), is incorrect in the low-density limit $r_s \rightarrow \infty$, since $e_{\text{xc}} \rightarrow 0$. On physical grounds we expect the exchange and correlation energy per pair to go to the potential energy of the exciton in the limit of very low density. However, almost the entire integral for σ_{xc} in Eq. (4) is obtained from that region of the surface for which the density varies from the bulk density \bar{n} to about $0.05\bar{n}$. For this range in density, the metallic ground state is energetically favored over the corresponding exciton ground state. Hence we expect the evaluation of e_{xc} to be correct over the entire range of relevant surface densities.

The estimate of the gradient contribution to e_{xc} is made in the following way. Rasolt and Geldart²⁷ have calculated a gradient correction for the electron gas of the form

$$\Delta E_{\text{xc}}^{\text{grad}} = \int d^3r C(n) n^{-4/3} |\nabla n|^2. \quad (10)$$

For large n , the coefficient $C(n)$ goes to the value 2.6×10^{-3} obtained by Ma and Brueckner²⁰ and Sham.²¹ We use the following *ad hoc* expression to estimate the effects of the gradient correction for the EHL:

$$\Delta E_{\text{xc}}^{\text{grad}} = \int d^3r [C(n_e) n_e^{-4/3} |\nabla n_e|^2 + C(n_h) n_h^{-4/3} |\nabla n_h|^2]. \quad (11)$$

We do not place high reliability on the above expression but rather use it to obtain a rough estimate of the corrections to the local (zero-order) term.

IV. KINETIC ENERGY

The evaluation of σ_s proceeds in two steps. First, using the variational potential approach,

we calculate an exact contribution to σ_s using a simplified band structure consisting of four spherical electron bands and two spherical uncoupled hole bands. Later we shall describe a second contribution to σ_s which takes into account electron-band anisotropy and valence-band coupling.

The variational potential technique is easily extended to the calculation of the EHD surface properties. Assuming the simplified band structure, we define a variational potential $v_{\text{var}}^i(r)$ for each band. The strategy is then to use these potentials to determine the contribution to σ_s from each of the bands, and to determine the densities $n_i(r)$. Since the surface energy functional Σ , apart from σ_s , is constructed to be an explicit functional of the densities, we then minimize Σ by varying the potentials. Below we describe the form of the variational potentials used, and describe how to obtain $n_i(r)$ and σ_s in terms of them. Of course, σ_s and n_i only have physical significance for that set of potentials which minimize the surface energy.

Since nothing in our calculation depends on the y, z directions parallel to the surface, it is clear that the v_{var}^i depends only on the x coordinate perpendicular to the surface. Further v_{var}^i goes to a constant as $x \rightarrow \pm \infty$. Assuming that the particles are noninteracting, we then solve the single-particle Schrödinger equations for particles in the i th band moving in the potential v_{var}^i . From the single-particle wave functions $\psi_k^i(r)$ and eigenvalues e_k^i we can write

$$n_i(r) = \sum_{k=0}^{k_f^i} |\psi_k^i(r)|^2, \\ \sigma_s^i = \sum_i \left((2\pi^2 m_i)^{-1} \int_0^{k_f^i} dk k (k_f^i - k)^2 \left(\frac{1}{4} \pi - \gamma_k^i \right) - \int d^3r n_i(r) [v_{\text{var}}^i(r) - v_{\text{var}}^i(-\infty)] \right). \quad (12)$$

Here m_i and k_f^i denote the density-of-states mass and Fermi wave vector of the i th band. We use the symbol σ_s^i to denote the contribution to the surface kinetic energy from the simplified band-structure model. The phase shift of the k th wave function of the i th band is denoted by γ_k^i , i.e.,

$$\psi_k^i(r) = A \sin(kx + \gamma_k^i) e^{ik_y y} e^{ik_z z}, \quad x \rightarrow -\infty. \quad (13)$$

The expression in large parentheses on the right-hand side of Eq. (12) is the kinetic-energy contribution from a single spherical band of noninteracting electrons, as given by Lang and Kohn for the jellium surface.²²

The total kinetic-energy contribution to Σ can be written

$$\sigma_s[n_i(r)] = \sigma_s^s[n_i(r)] + \Delta\sigma_s[n_i(r)]. \quad (14)$$

The term $\Delta\sigma_s$ is included to account for the effects of valence-band coupling and electron-band anisotropy in the determination of σ_s . In order to obtain an approximate form for $\Delta\sigma_s$ we note that the kinetic-energy terms σ_s and σ_s^s can be approximated

$$\Delta\sigma_s[n_i(r)] = \int d^3r |\nabla n_h(r)|^2 \left(\frac{1+\gamma^{1/2}}{1+\gamma^{3/2}} \frac{1}{12m_h} - \frac{\gamma^{1/2}}{(1+\gamma^{1/2})(1+\gamma^{3/2})} \frac{1}{3m} \right) + \int d^3r \frac{|\nabla n_e(r)|^2}{n_e(r)} \left[\frac{1}{72} \left(\frac{1}{m_0} - \frac{1}{m_{\text{dens}}} \right) \right]. \quad (15)$$

Here $n_e(r)$ and $n_h(r)$ are the total electron and hole densities. The masses m_h , m_0 , and m_{dens} are, respectively, the heavy-hole mass, the electron optical mass, and the electron density-of-states masses; γ denotes the ratio of the light- to heavy-hole masses.

V. SURFACE ENERGY AND DIPOLE BARRIER

We report the calculated surface energy Σ , the surface width w defined as the distance between the 10 and 90% of bulk density positions and the electrostatic dipole barrier $\nabla\Phi$. We first give the results for our most complete model of the energy functional, and then report the results of two less complete calculations. In this way we hope to show the effects of various approximations in the calculation of the physical quantities. In the following we list the possible contributions to Σ : (a) σ_s^s [Eq. (12)], the exact kinetic-energy contribution described in Sec. IV for a simplified band structure which neglects electron-band anisotropy and valence-band coupling. (b) $\Delta\sigma_s$ [Eq. (15)], the correction to σ_s which accounts for electron-band anisotropy and valence-band coupling to order $|\nabla n_i|^2$. (c) As an alternative to (a) and (b), we can describe the entire kinetic-energy term by means of the gradient expansion of RY. This term is only correct to order $|\nabla n_i|^2$ and it misses higher-order contributions and cannot produce Friedel oscillations at the surface. (d) $e_{\text{xc}} = e_x + e_c$ [Eq. (4)], a local approximation for the exchange and correlation energy (this term includes the effects of unequal electron and hole densities). (e) $\Delta\sigma_{\text{xc}}$ [Eq. (11)], an estimate of the nonlocal contribution to the exchange and correlation energy to order $|\nabla n_i|^2$.

We constructed three model energy functionals from the contributions (a)–(e). Model A is our most complete calculation, and includes the exact kinetic energy for uncoupled spherical bands σ_s^s plus the band-structure corrections to order

in terms of a gradient expansion in the densities to order $|\nabla n_i|^2$. The expansion coefficient for a spherical band of noninteracting particles is well known; the equivalent expansion coefficients for the EHL have been determined by Reinecke and Ying (RY)⁸; these include the effects of valence-band coupling and electron-band anisotropy. Equating the coefficients to order $|\nabla n_i|^2$ yields

$|\nabla n_i|^2$. Model A also includes our best estimate of the local contribution to the exchange and correlation energy plus a nonlocal contribution to order $|\nabla n_i|^2$. Model B tests the effects of neglecting the nonlocal correction to the exchange and correlation energy. Model C tests the effects of approximating the kinetic energy by the gradient expansion of RY.

The variation of potentials technique requires a potential $v_{\text{var}}^i(r)$ for each band. By examining the self-consistent Kohn-Sham equations we find that at the minimum in energy each of the four electron bands has the same effective potential, while the two hole bands have a different effective potential. Hence in our variation procedure we introduce a single variational potential for the electrons and a second variational potential for the holes. Each potential is characterized by eight parameters which are varied to obtain the energy minimum. We constrain the total charge Q on the surface to be zero by adding a large penalty function to the surface energy of the form AQ^2 , where A is a large positive number. The minimization of Σ is carried out using a simplex search routine optimized for nonlinear minimization problems. In all cases the minimization can be performed without difficulty.

Model A

We include the terms (a), (b), (d), and (e) listed above. The minimization of the energy was carried out and we obtain

$$\Sigma = 2.45 \times 10^{-4} \text{ ergs/cm}^2,$$

$$w = 2.4 \times 10^{-8} \text{ cm}, \quad \Delta\Phi = 0.16 \text{ meV}.$$

Below we list the various contributions to σ in erg/cm²

$$\sigma_s^s = -5.58 \times 10^{-4}, \quad \Delta\sigma_s = 0.30 \times 10^{-4},$$

$$\sigma_{\text{xc}} = 7.24 \times 10^{-4}, \quad \Delta\sigma_{\text{xc}} = 0.48 \times 10^{-4},$$

$$\sigma_{\text{es}} = 0.016 \times 10^{-4}, \quad \Delta\sigma_c = 0.004 \times 10^{-4}.$$

The term $\Delta\sigma_c$ denotes the contribution to the correlation energy due to $n_e(x) \neq n_h(x)$ in the surface region; i.e., the second term of Eq. (6). The surface energy is the sum of relatively large canceling terms and is hence quite sensitive to the forms chosen for the various terms. Note also that the term σ_{es} that gives the electrostatic energy is small; to obtain accurate values for the dipole layer, the variation in energy must be carried out to very high accuracy. Since $\Delta\sigma_c$ is about 25% of the electrostatic energy, it plays a significant role in determining the size of the dipole barrier $\Delta\Phi$, which we see is quite small; i.e., about 10% of the binding energy per pair. In defining $\Delta\Phi$ we use the convention that $\Delta\Phi > 0$ indicates that the dipole barrier increases the binding of the holes.

Model B

Here we include terms (a), (b), and (d). This model is similar to model A except that we leave out the nonlocal contribution to the exchange and correlation energy given by (e). The results are

$$\Sigma = 1.98 \times 10^{-4} \text{ ergs/cm}^2,$$

$$w = 2.4 \times 10^{-6} \text{ cm}, \quad \Delta\Phi = 0.17 \text{ meV}.$$

An interesting result of this calculation is that the surface charge density is changed only slightly from the result obtained in A. The difference between the surface energy obtained here and that of model A is 0.47×10^{-4} ergs/cm². This is exactly the nonlocal contribution $\Delta\sigma_{xc}$ to the surface energy in model A. Thus the effect of the nonlocal term in σ_{xc} could have been obtained by simply evaluating the correction using the old self-consistent density without bothering to reminimize the energy. As expected, the size of the electrostatic dipole layer depends sensitively on the correction, but remains small.

Model C

In this model we test the effects of replacing the kinetic energy σ_s with the gradient expansion of RY. The energy is then minimized in the standard way for the gradient technique by varying the densities. We find that

$$\Sigma = 1.80 \times 10^{-4} \text{ ergs/cm}^2,$$

$$w = 1.60 \times 10^{-6} \text{ cm}, \quad \Delta\Phi = 0.53 \text{ meV}.$$

Model C differs from model B only in the treatment of the kinetic energy. We see that this results in a change in the energy of only 10%; however, the surface width is decreased by about 33%, and the electrostatic dipole barrier is larger by a factor of 3. From this calculation it seems reasonable to conclude that the surface energy of

the EHD may be adequately treated by the gradient technique. However, those properties which depend sensitively on the energy such as the surface density profile and the dipole barrier must be calculated in the more complete formalism of Kohn and Sham. The value of the dipole layer in this calculation is similar to that reported in the gradient calculation of RY.

VI. SIGN OF DROPLET CHARGE

The sign of the charge on the EHD depends on the relative values of the electron and hole work functions. At a finite temperature, the component with the largest work function evaporates less readily, and hence gives the sign of the droplet charge. The work function $\Phi_{e,h}$ for a given component depends both on that component's bulk chemical potential $\mu_{e,h}$ and on the electrostatic dipole barrier $\Delta\Phi$ at the surface:

$$\Phi_{e,h} = \mu_{e,h} \pm \Delta\Phi, \quad (16)$$

where

$$\mu_{e,h} = \frac{\partial e}{\partial n_{e,h}}. \quad (17)$$

Here e is the energy per unit volume for a uniform EHL. The evaluation of Eq. (17) involves the quantities $\mu_{e,h}^c = \partial e_c / \partial n_{e,h}$, which were discussed in Sec. III. At the bulk density we find

$$\mu_e = -4.09 \text{ meV}, \quad (18)$$

$$\mu_h = -2.53 \text{ meV}. \quad (19)$$

Previous theoretical estimates of μ_e and μ_h were obtained^{6,7} by dividing the exchange and correlation energy equally between electrons and holes. Were we to use this procedure we would obtain $\mu_e = -3.99$ meV and $\mu_h = -2.63$ meV; thus the previous approximation used to obtain μ_e and μ_h is in fact quite good.

Using the value for $\Delta\Phi$ found in model A, we obtain $\Phi_e - \Phi_h = -1.24$ meV. This leads to the conclusion that the charge on the EHD is negative. Since the dipole barrier $\Delta\Phi \approx 0.2$ meV, we see that the sign of the charge is determined by the bulk chemical potentials. The fact that $\Delta\Phi$ is small for all of our self-consistent calculations leads us to have confidence in the calculated sign of $\Phi_e - \Phi_h$.

VII. RESULTS AND CONCLUSIONS

Our best result for the surface tension is $\sigma = 2.4(5) \times 10^{-4}$ ergs/cm². We also conclude that the EHD should be negatively charged. Recently, several groups have obtained experimental estimates of σ by fitting the experimental data to various models of droplet nucleation and kinetics.

Experimental values obtained for σ are 1.0×10^{-4} ,¹¹ 1.8×10^{-4} ,¹² and $(2.4 - 2.8) \times 10^{-4}$ ergs/cm².²⁸ The scatter in the reported results makes comparison with experiment difficult. However, Westerwelt¹⁰ and Westerwelt *et al.*²⁸ who claim to have a reliable measurement of $\sigma = (2.4 - 2.8) \times 10^{-4}$ ergs/cm² at a temperature of 2°K.²⁹ Our result of 2.4(5) ergs/cm² is in good agreement. Pokrovskii and Svistunova have experimentally determined that the charge on the EHD is negative,¹⁵ which is also in agreement with the result we obtained.

The major features of our calculation are summarized below. The use of the self-consistent procedure is necessary to obtain accurate values for the electrostatic dipole layer. However, the self-consistent procedure does not significantly alter the value of σ from the result obtained in the gradient approximation. An accurate evaluation of the correlation energy is necessary, and the inclusion of multiple scattering effects changed σ significantly. The inclusion of a term in the correlation energy which takes account of the lack of local charge neutrality at the surface does not contribute significantly to σ but does affect the value of the electrostatic dipole barrier. Important contributions to σ came from gradient corrections to both kinetic energy and the exchange and correlation energy. The *ad hoc* nature of our gradient correction for the nonlocal exchange and correlation energy leads us to suggest that this is the most obvious place to further improve our calculation. Owing to the small absolute size of the correction, we would expect it to change the value of σ by no more than 15%.

APPENDIX

We give an analytic formula for the valence-band contribution to the imaginary part of the RPA

$$N_{ij}(q, \omega) = -\frac{1}{4m_i\omega} \left[\left(\frac{1}{2}q^2 - m_i\omega\right)^2 \ln\left(\frac{k_2^2}{k_1^2}\right) - \left(\frac{1}{2}q^2 + m_j\omega\right)^2 \ln\left(\frac{k_2^2 + 2m_j\omega}{k_i^2 + 2m_j\omega}\right) \right] - \frac{(m_i - m_j)^2}{8m_i m_j} (k_2^2 - k_1^2). \quad (A4)$$

Here k_1 and k_2 are functionals of q and ω . The explicit functional forms of k_1 and k_2 are given below for the various cases.

For the intraband case we define the following supplementary functions:

$$k_1^A = (k_{F,i}^2 - 2m_i\omega)^{1/2}, \quad (A5)$$

$$k_1^B = (1/q)(m_i\omega - \frac{1}{2}q^2), \quad (A6)$$

$$\omega_1 = (q/m_i)(k_{F,i} - \frac{1}{2}q), \quad (A7)$$

$$\omega_2 = (q/m_i)(k_{F,i} + \frac{1}{2}q). \quad (A8)$$

dielectric constant $\text{Im}\epsilon(\vec{q}, \omega)$. The evaluation of $\text{Im}\epsilon(\vec{q}, \omega)$ is carried out within the model band structure of Ref. 25 and includes valence-band coupling in a spherical approximation. The contribution of the ellipsoidal electron bands to $\text{Im}\epsilon(\vec{q}, \omega)$ is well known and easily calculated. Once the expression for $\text{Im}\epsilon(\vec{q}, \omega)$ is known, then $\text{Re}\epsilon(\vec{q}, \omega)$ can be straightforwardly obtained by a numerical evaluation of the Kramers-Kronig relation. Alternatively the expression for $\text{Re}\epsilon(\vec{q}, \omega)$ can be obtained directly in the form of a one-dimensional numerical integral.

We give results for the noninteracting density-density response function $\text{Im}\chi_{ij}^0$, which is related to $\text{Im}\epsilon(\vec{q}, \omega)$ by

$$\text{Im}\epsilon(\vec{q}, \omega) = \frac{-4\pi}{q^2} \sum_{ij} [\text{Im}\chi_{ij}^0(\vec{q}, \omega)]. \quad (A1)$$

The indices run over all the bands and the term χ_{ij}^0 indicates the density response of the i th band to a potential which couples to the density of the j th band. There are four spherically symmetric ($q = |\vec{q}|$) contributions from the valence bands to $\text{Im}\chi_{ij}^0$: an intraband contribution from each band; and two terms involving interband transitions from the light- to the heavy-hole band and vice versa. The intraband terms are given by

$$\text{Im}\chi_{ii}^0(q, \omega) = \chi_{\text{Lind}}^0(q, \omega) - (3m_i/8\pi q)N_{ii}(q, \omega). \quad (A2)$$

The interband terms are

$$\text{Im}\chi_{ij}^0(q, \omega) = (3m_i/8\pi q)N_{ij}(q, \omega). \quad (A3)$$

Here m_i denotes the mass of the i th band and the term $\chi_{\text{Lind}}^0(q, \omega)$ is the Lindhard response function for a spherical band of noninteracting electrons. The function N_{ij} is given by

Here $k_{F,i}$ denotes the Fermi wave vector of the i th band, i.e., the light- or heavy-hole band. The functions k_1 and k_2 for the intraband case are

$$k_1 = k_1^A \Theta(2k_{F,i} - q) \Theta(\omega_1 - \omega), \quad (A9)$$

$$k_1 = k_1^B \Theta(q - 2k_{F,i}) \Theta(\omega_2 - \omega) \Theta(\omega + \omega_1), \quad (A10)$$

$$k_1 = k_1^B \Theta(2k_{F,i} - q) \Theta(\omega_2 - \omega) \Theta(\omega - \omega_1), \quad (A11)$$

$$k_2 = k_{F,i} \text{ for all } q \text{ and } \omega. \quad (A12)$$

The first interband case we consider is for transitions from the heavy- to the light-hole band. We

again list several supplementary functions and then k_1 and k_2 :

$$R = \left(\frac{q^2 m_l m_h}{(m_h - m_l)^2} + \frac{2m_l m_h}{m_h - m_l} \omega \right)^{1/2}, \quad (\text{A13})$$

$$k_z^0 = [m_h / (m_h - m_l)] q, \quad (\text{A14})$$

$$k_1^A = [2m_h (\epsilon_F - \omega)]^{1/2}, \quad (\text{A15})$$

$$k_1^B = |R - k_z^0|, \quad (\text{A16})$$

$$k_2^A = |R + k_z^0|, \quad (\text{A17})$$

$$\omega_1 = \epsilon_F - (1/2m_h)(k_{F,l} + q)^2, \quad (\text{A18})$$

$$\omega_2 = \epsilon_F - (1/2m_h)(k_{F,l} - q)^2, \quad (\text{A19})$$

$$\omega_3 = (1/2m_l)(k_{F,h} + q)^2 - e_F, \quad (\text{A20})$$

$$\omega_4 = (1/2m_l)(k_{F,h} - q)^2 - e_F. \quad (\text{A21})$$

Here the subscripts l and h refer, respectively, to the light- and heavy-hole band. The hole band Fermi energy is given by e_F .

The functions k_1 and k_2 are the following: If

$$q < k_{F,l} + k_{F,h},$$

$$k_1 = k_1^A \Theta(\omega_2 - \omega) \Theta(\omega - \omega_1), \quad (\text{A22})$$

$$k_1 = k_1^B \Theta(\omega - \omega_2) \Theta(\omega_3 - \omega), \quad (\text{A23})$$

$$k_2 = k_2^A \Theta(\omega - \omega_1) \Theta(\omega_4 - \omega), \quad (\text{A24})$$

$$k_2 = k_{F,h} \Theta(\omega - \omega_4) \Theta(\omega_3 - \omega). \quad (\text{A25})$$

If $q > k_{F,l} + k_{F,h}$,

$$k_1 = k_1^B \Theta(\omega_3 - \omega) \Theta(\omega - \omega_4), \quad (\text{A26})$$

$$k_2 = k_{F,h} \Theta(\omega - \omega_4) \Theta(\omega_3 - \omega). \quad (\text{A27})$$

The final case covers interband transitions from the light- to heavy-hole bands. We define the supplementary functions

$$S = \left(\frac{q^2 m_l m_h}{(m_h - m_l)^2} - \frac{2m_l m_h}{m_h - m_l} \omega \right)^{1/2}, \quad (\text{A28})$$

$$k_z^1 = [m_l / (m_h - m_l)] q, \quad (\text{A29})$$

$$k_1^A = [2m_l (e_F - \omega)]^{1/2}, \quad (\text{A30})$$

$$k_1^B = |S - k_z^1|, \quad (\text{A31})$$

$$k_2^A = |S + k_z^1|, \quad (\text{A32})$$

$$\omega_1 = e_F - (1/2m_l)(k_{F,h} - q)^2, \quad (\text{A33})$$

$$\omega_2 = (1/2m_h)(k_{F,l} + q)^2 - e_F, \quad (\text{A34})$$

$$\omega_3 = [2(m_h - m_l)]^{-1} q^2, \quad (\text{A35})$$

$$\omega_4 = (1/2m_h)(k_{F,l} - q)^2 - e_F. \quad (\text{A36})$$

The functions k_1 and k_2 are defined below. We note that if $q < k_{F,h} - k_{F,l}$, then $N_{i,l}(q, \omega) = 0$. If

$$k_{F,h} - k_{F,l} < q < [(m_h - m_l)/m_h] k_{F,h},$$

$$k_1 = k_1^A \Theta(\omega_1 - \omega) \Theta(\omega), \quad (\text{A37})$$

$$k_2 = k_{F,l} \Theta(\omega_2 - \omega) \Theta(\omega), \quad (\text{A38})$$

$$k_2 = k_2^A \Theta(\omega - \omega_2) \Theta(\omega_1 - \omega). \quad (\text{A39})$$

If

$$[(m_h - m_l)/m_h] k_{F,h} < q < k_{F,l} + k_{F,h},$$

$$k_1 = k_1^A \Theta(\omega_1 - \omega) \Theta(\omega), \quad (\text{A40})$$

$$k_1 = k_1^B \Theta(\omega - \omega_1) \Theta(\omega_3 - \omega), \quad (\text{A41})$$

$$k_2 = k_{F,l} \Theta(\omega_2 - \omega) \Theta(\omega), \quad (\text{A42})$$

$$k_2 = k_2^A \Theta(\omega - \omega_2) \Theta(\omega_3 - \omega). \quad (\text{A43})$$

If

$$k_{F,l} + k_{F,h} < q < [(m_h - m_l)/m_h] k_{F,l},$$

$$k_1 = k_1^B \Theta(\omega - \omega_4) \Theta(\omega_3 - \omega), \quad (\text{A44})$$

$$k_2 = k_{F,l} \Theta(\omega - \omega_4) \Theta(\omega_2 - \omega), \quad (\text{A45})$$

$$k_2 = k_2^A \Theta(\omega - \omega_2) \Theta(\omega_3 - \omega). \quad (\text{A46})$$

If

$$q > [(m_h - m_l)/m_l] k_{F,l},$$

$$k_1 = k_1^B \Theta(\omega - \omega_4) \Theta(\omega_2 - \omega), \quad (\text{A47})$$

$$k_2 = k_{F,l} \Theta(\omega - \omega_4) \Theta(\omega_2 - \omega). \quad (\text{A48})$$

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