

## Free surface of He II and the electron bubble\*

Timothy C. Padmore<sup>†</sup>*Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850*

Milton W. Cole

*Department of Physics, University of Washington, Seattle, Washington 98105*

(Received 28 June 1973)

A simple phenomenological model of the structure of an inhomogeneous quantum fluid is proposed. As examples of the application of the model the structure of the free surface of He II and the structure of the negative-ion bubble in He II are investigated. The free-surface structure compares well with the results of a more elaborate microscopic calculation. Questions concerning the effect of surface curvature and "tightening" of the bubble surface are examined.

## I. INTRODUCTION

The structure of the free surface of helium has not been measured directly, but is of theoretical interest and is of importance in interpreting the behavior of films and other structures such as the electron bubble. As a tool for the quantitative investigation of such surface effects, we propose in this paper a simple phenomenological model for the structure of an inhomogeneous quantum fluid. We apply the model to calculate the free surface of He II and the structure of the electron bubble. The results on the free surface are in good agreement with the results of a recent microscopic calculation<sup>1</sup> of the surface. The predicted bubble structure is also in substantial agreement with the experimental evidence.<sup>2-7</sup> Perhaps of greater importance, the model is sufficiently transparent to allow a simple physical interpretation of its consequences. In particular, we find that the effect of curvature of the bubble surface is very slight and that the effect of the "tightening" of the bubble surface which has been proposed to occur<sup>8,9</sup> is small. We also find an asymmetrical healing behavior of the density near a free surface.

## II. THE MODEL

The basic method we employ is to write the free energy of the system as a functional  $F[n]$  of the fluid density  $n(\vec{r})$ , a procedure discussed previously by Widom for Bose fluids and by Hohenberg and Kohn for Fermi fluids.<sup>10</sup> The equation determining  $n$  will then be

$$\frac{\delta F}{\delta n} = 0, \quad (1)$$

where  $n$  is subject to the constraint

$$\int n(\vec{r}) d\vec{r} = (\text{const}) \quad (2)$$

and to appropriate boundary conditions.

We will now attempt to guess a reasonably useful and accurate form for the functional  $F$ . The analysis will be confined to  $T=0$ .

We now write down the first term in  $F$ , which includes the local effects of the interparticle interactions and is determined by the properties of a hypothetical homogeneous system:

$$F_{\text{pot}}^{(a)} = mc^2 n_0 \int f(n/n_0) d\vec{r}. \quad (3)$$

Here  $m$  is the mass of an atom,  $c$  is the sound velocity, and  $n_0$  is the number density of the fluid. The function  $f$ , which is proportional to free energy per unit volume, is chosen to fit known thermodynamic properties of the homogeneous bulk.

Writing  $f = (n/n_0)\mathcal{F}$  defines a free energy per particle  $\mathcal{F}$ . Despite the fact that we have  $T=0$ , it is not quite all right to replace the free energy  $\mathcal{F}$  by the internal energy  $\mathcal{E}$ . This is because the entropy per particle of the vapor phase<sup>11</sup> is singular, like  $T^{-1}$ , for  $T \rightarrow 0$ . The singularity occurs because the equilibrium density of the vapor becomes exponentially small [as  $\exp(-\epsilon_B/kT)$ , where  $\epsilon_B$  is the binding energy per particle] for  $T \rightarrow 0$ . Thus, at a nonzero (but small) temperature,  $\mathcal{F}$  will have the form indicated in Fig. 1 by the dotted curve. A Maxwell construction yields the small vapor density  $n_v$  and a corresponding small pressure. As  $T \rightarrow 0$  the dotted curve approaches more and more closely the solid one, *except* at  $n=0$ , where  $\mathcal{F}(0) \neq \mathcal{F}(1)$ . With this understanding we can therefore use the solid curve, which represents the internal energy, for  $\mathcal{F}$ .

We choose  $\mathcal{F}$  in the form<sup>12</sup>

$$\mathcal{F}(x) = A + Bx^2 + Cx^3 + Dx^4. \quad (4)$$

We use our freedom to choose  $\mathcal{F}(1) = 0$ . The requirement of zero pressure at  $n = n_0$  implies  $\mathcal{F}'(1) = 0$ , and the correct compressibility at  $n = n_0$  is

guaranteed by  $\mathcal{F}''(1)=1$ .  $\mathcal{F}(0)$  is fixed by requiring that  $mc^2\mathcal{F}(0)$  be the experimental binding energy per particle (7.14°K). For helium at  $T=0$  one finds

$$A=0.260, \quad B=-1.06, \quad C=1.08, \quad D=-0.28. \quad (5)$$

This  $\mathcal{F}$  is plotted as the solid curve in Fig. 1.

Taking  $F_{\text{pot}}^{(a)}$  alone leads to a sharp boundary at a free surface:

$$n(\vec{r}) = \begin{cases} n_0, & \vec{r} \text{ in liquid} \\ 0, & \text{otherwise,} \end{cases} \quad (6)$$

which is unphysical. It is necessary to include nonlocal terms. An obvious contribution to include is a quantum kinetic-energy term

$$F_{\text{kin}} = \frac{-\hbar^2}{2m} \int \sqrt{n} \nabla^2(\sqrt{n}) d\vec{r}. \quad (7)$$

This term is exactly right for a noninteracting Bose system or a system with weak point interactions.<sup>10, 13</sup>

Inclusion of (7) and (3) is sufficient, indeed, to smooth the free surface, and this sort of functional has been investigated previously. In particular the choice<sup>13</sup>  $f(x) = \frac{1}{2}(x-1)^2$  describes the weakly interacting Bose gas (WIBG).<sup>14</sup> The latter function is the dashed curve in Fig. 1. Unfortunately, the WIBG leads to conceptual as well as quantitative difficulties since it is, after all, a gas, and there is no zero-pressure state and no low-density ("vapor") phase.

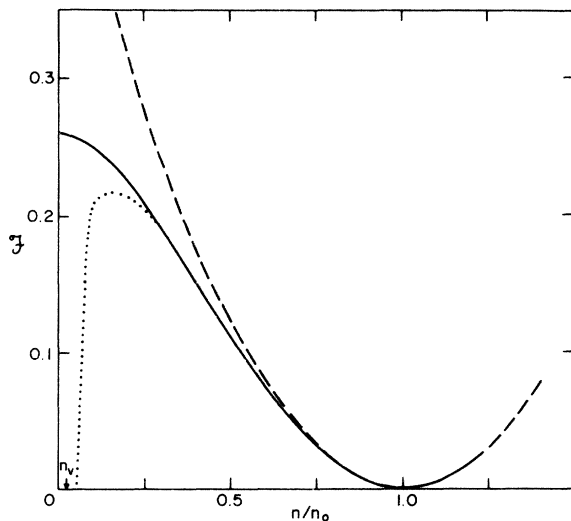


FIG. 1. The "bulk" free-energy density  $\mathcal{F}$ . The solid line is the  $T=0$  result, Eqs. (4) and (5). The dotted line is the qualitative form for  $T$  near 0 with an equilibrium vapor density  $n_v$ . The dashed line is  $f(x)$  for the WIBG.

There is another important, purely classical, nonlocal contribution. Classically the surface tension may be thought of as arising because the surface atoms, having fewer neighbors than atoms in the bulk, have a higher potential energy. We therefore write a term

$$F_{\text{pot}}^{(b)} = \int n(\vec{r})n(\vec{r}+\vec{r}')K(\vec{r},\vec{r}')d\vec{r}d\vec{r}'. \quad (8a)$$

The kernel  $K(\vec{r})$  may be interpreted as the "attractive part" of the interparticle potential.

We will be considering two different geometries: a plane interface, in which case  $n(\vec{r})=n(x)$ , where  $x$  is the rectangular coordinate perpendicular to the interface; and a bubble, in which case  $n(\vec{r})=n(r)$ , with the origin taken at the center of the bubble. Especially in these cases, a substantial simplification is achieved if the following approximations, which preserve the physical content of Eq. (8a), are made. First write  $K(\vec{r}')=-K_0\delta(r'-a)$ , for which we choose the parameters  $K_0$  and  $a$  below. Then expand  $n(\vec{r}+\vec{r}')=n(\vec{r})+\vec{r}'\cdot\nabla n(\vec{r})+\frac{1}{2}\vec{r}'\vec{r}':\nabla\nabla n(\vec{r})+\dots$ . The following result:

$$F_{\text{pot}}^{(b)} = \frac{2}{3}\pi a^4 K_0 A \int_{-\infty}^{\infty} \left(\frac{dn}{dx}\right)^2 dx \quad (8b)$$

for the plane geometry, where  $A$  is the plane area, and

$$F_{\text{pot}}^{(b)} = \frac{8}{3}\pi^2 a^4 K_0 \int_0^{\infty} \left(\frac{dn}{dr}\right)^2 \left(1 - \frac{1}{10} \frac{a^2}{r^2}\right) r^2 dr \quad (8c)$$

for the bubble. The leading correction to (8b) is a term  $-(a^2/20)(d^2n/dx^2)^2$  in the integrand. Neglecting it leads to no qualitative and only a minimal quantitative error, since  $a$  is also the scale of variation of  $n$ . There are two sorts of corrections to (8c): higher-order derivatives, beginning with the term discussed above, and curvature terms, beginning with the term exhibited in (8c). This latter term is small because  $a^2/r^2 \ll 1$  when  $r$  is the order of the bubble radius ( $\geq 15 \text{ \AA}$ ), and additionally unimportant since it yields a contribution to the surface energy which is nearly independent of the bubble radius.<sup>15</sup>

### III. CALCULATIONS

#### A. Plane surface

We first discuss the predictions of the model for a plane free surface. Combining (3), (7), and (8b) we have the surface-tension functional

$$\begin{aligned} \sigma_{\text{bulk}} = & \frac{\hbar^2}{2m} \int_{-\infty}^{\infty} \left(\frac{d\sqrt{n}}{dx}\right)^2 dx + \frac{2}{3}\pi a^4 K_0 \int_{-\infty}^{\infty} \left(\frac{dn}{dx}\right)^2 dx \\ & + mc^2 n_0 \int_{-\infty}^{\infty} f(n/n_0) dx. \end{aligned} \quad (9a)$$

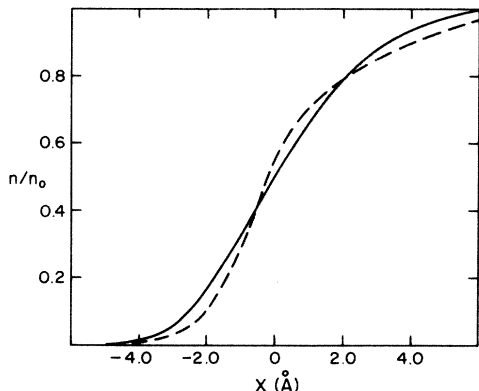


FIG. 2. Helium density profile at a plane free surface. Solid line is the numerical solution of Eq. (1) and the dashed line is the approximate profile of Chang and Cohen (Ref. 1).

The coefficient  $\frac{2}{3} \pi K_0 a^4$  can be estimated (recalling our interpretation of  $K(\bar{r})$  as something like the attractive part of the interparticle potential) from the Lennard-Jones parameters. One can alternatively use the measured value of the surface tension<sup>16</sup> to fit this parameter. We have done the latter, solving the second-order differential equation resulting from  $\delta\sigma_{\text{bulk}}/\delta n = 0$  numerically by a standard predictor-corrector technique. We find that (9) should be written

$$\begin{aligned} \sigma_{\text{bulk}} = & 0.130 \int_{-\infty}^{\infty} \left( \frac{d}{dx} (n/n_0)^{1/2} \right)^2 dx + 0.949 \\ & \times \int_{-\infty}^{\infty} \left( \frac{d}{dx} (n/n_0) \right)^2 dx + 0.592 \int_{-\infty}^{\infty} f(n/n_0) dx, \end{aligned} \quad (9b)$$

where  $\sigma_{\text{bulk}}$  will be given in  $^{\circ}\text{K}/\text{\AA}^2$ , and  $x$  is measured in  $\text{\AA}$ . Note that the classical nonlocal term is rather more important than the quantum nonlocal term.

Estimation of the unknown coefficient as suggested above leads to values close to the value used in (9b).<sup>17</sup>

The numerical solution is plotted in Fig. 2. The surface thickness (10%–90% density) is  $5.9 \text{ \AA}$ . The healing behavior on the high- and low-density sides is asymmetrical, the approach to zero being more rapid on the low-density side. This is principally a consequence of the asymmetry (with respect to the transformation  $n/n_0 \rightarrow 1 - n/n_0$ ) of  $F_{\text{kin}}$ . There is also a small asymmetry in  $f(n/n_0)$ , which is of lesser importance.

We also performed a variational solution of  $\delta\sigma_{\text{bulk}}/\delta n = 0$ . The trial function has the form

$$n(x) = \begin{cases} n_0 [1 - [1 + (x/\xi)^\gamma] e^{-\alpha/(x/\xi)^\gamma}], & x > 0 \\ 0, & x < 0. \end{cases} \quad (10)$$

The parameter  $\xi$  determines the thickness of the surface and  $\gamma$  can be used to control the asymmetry. We found that the choice  $\gamma = 1.7$ ,  $\xi = 3.78 \text{ \AA}$  is a good representation of the numerical solution (indistinguishable on the scale of the figure). Even a one-parameter trial function works very well. Thus with  $\gamma = 1$  (an initial choice) the variational energy is only 3% higher than the numerical value.

Plotted on the same graph (dashed curve) is the density profile calculated recently by Chang and Cohen,<sup>1</sup> who did a quasivariational microscopic calculation of the surface structure. The agreement is good, including the finding of an asymmetrical healing behavior. Earlier calculations by Brout and Nauenberg, Fitts, and Shih and Woo<sup>18</sup> give surface thicknesses ranging from half to nearly double our value. All these calculations suffer from the necessity of making an *ad hoc* guess about the two-particle correlations near the surface. We make guesses too, of course, but they are pegged to estimates based on experimental data.

#### B. Electron bubble

The structure of the negative ion in liquid helium has been the subject of much study, and it is now well accepted that the electron resides in a relatively large bubble whose radius is determined principally by a competition between the localization energy of the electron and the surface energy of the bubble.

The detailed structure of the bubble has been investigated using models of varying complexity. In most versions the energy of the bubble is written as

$$E_b = E_e + 4\pi\sigma a_b^2 + \frac{4}{3}\pi Pa_b^3, \quad (11)$$

where  $\sigma$  is the surface tension,  $a_b$  is the bubble radius, and  $P$  is the external pressure. The electronic energy  $E_e$  may be estimated by  $E_e \approx \hbar^2 \pi^2 \times (2m_e a_b^2)^{-1}$ , the energy of an electron in an infinite square well of radius  $a_b$ . Using the bulk surface tension and taking  $P = 0$ , one finds for  $T \approx 1 \text{ }^{\circ}\text{K}$  that  $a_b \approx 19 \text{ \AA}$ . A more elaborate model, taking into account the polarization energy (which has only a very minor effect) and using a Wigner-Seitz calculation for  $E_e$ , yields  $a_b \approx 17.5 \text{ \AA}$  under the same conditions.<sup>2, 8</sup> There exist a number of experimental determinations. The simplest to interpret are the mobility measurements of Schwarz and co-workers.<sup>2, 3</sup> The mobility results were analyzed classically using hydrodynamics and yield values ranging from  $15$  to  $19 \text{ \AA}$ . Partly because the theoretical values seem to be consistently a little high, it has been suggested that  $\sigma$  may be modified from its bulk value because

of the presence of the electron and/or the curvature of the surface.<sup>2, 8, 9</sup> In the Wigner-Seitz calculation referred to above, a surface tension  $\sigma = 1.7\sigma_{\text{bulk}}$  is required<sup>2</sup> in order to fit  $a = 15 \text{ \AA}$ . Other experiments, such as the trapping of ions on vortex lines and their subsequent escape,<sup>4</sup> yield larger radii (16 to 18  $\text{\AA}$ ), but the theoretical interpretation<sup>5</sup> of the experiments is more difficult. Photoejection experiments<sup>7</sup> yield a radius of about  $15\frac{1}{2} \text{ \AA}$ .

In order to analyze the bubble problem, we have to include in  $F$  contributions from the electron. We write

$$F = F_e + F_{\text{surf}}, \quad (12)$$

where

$$F_e = 4\pi \left( \frac{\hbar^2}{2m_e} \int_0^\infty \left| \frac{d\Psi_e}{dr} \right|^2 r^2 dr + V \int_0^\infty |\Psi_e|^2 m r^2 dr \right) \quad (13a)$$

and

$$F_{\text{surf}} = 4\pi \left[ \frac{\hbar^2}{2m} \int_0^\infty \left( \frac{d\sqrt{n}}{dr} \right)^2 r^2 dr + \frac{1}{2} m c^2 n_0 \times \int_0^\infty f \left( \frac{n}{n_0} \right) r^2 dr + \frac{2}{3} \pi a^4 K_0 \int_0^\infty \left( \frac{dn}{dr} \right)^2 r^2 dr \right]. \quad (13b)$$

The interaction of the electron with the He atoms is described by a point-interaction pseudopotential determined by the electron-He-atom scattering length<sup>19</sup>; this treatment is formally equivalent to the Wigner-Seitz approach described above. The factor  $K_0 a^4$  was chosen to be the same as in (9b).

Encouraged by the success of the variational approximation for the free surface, we attempted

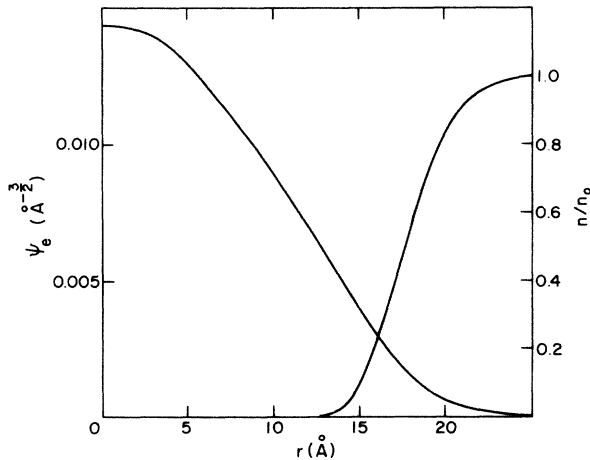


FIG. 3. Variational solution for the electron wave function and helium density for the electron bubble.

a variational solution of the bubble problem. We chose for  $\Psi_e$  the trial function

$$\Psi_e(r) = \begin{cases} A[(\sin kr)/r], & r < a_e \\ B(e^{-\kappa r}/r), & r > a_e \end{cases} \quad (14)$$

which has the form of the ground-state function for a square well of radius  $a_e$ . For  $n(r)$  we took

$$n(r) = \begin{cases} 0, & r < a_{\text{He}} \\ n_0 \left\{ 1 - \left[ 1 + \left( \frac{r - a_{\text{He}}}{\xi} \right)^\gamma \right] \times \exp \left[ - \left( \frac{r - a_{\text{He}}}{\xi} \right)^\gamma \right] \right\}, & r > a_{\text{He}} \end{cases} \quad (15)$$

with  $\gamma = 1.7$ , in analogy with the one-dimensional solution. We treated  $a_{\text{He}}$ ,  $a_e$ ,  $\xi$ , and  $k$  as variational parameters, while  $A$ ,  $B$ , and  $\kappa$  were determined so  $\Psi_e$  would be smooth and correctly normalized.

The result of the variational calculation was

$$\begin{aligned} a_{\text{He}} &= 12.6 \pm 0.2 \text{ \AA}, & \xi &= 3.41 \pm 0.05 \text{ \AA}, \\ a_e &= 15.8 \pm 0.2 \text{ \AA}, & k &= 0.167 \pm 0.002 \text{ \AA}^{-1}, \\ F &\approx 2138 \text{ }^\circ\text{K}. \end{aligned} \quad (16)$$

The variationally determined functions are shown in Fig. 3.

The total energy is quite flat in the vicinity of the minimum and the accuracy attainable was limited by the accuracy of the numerical evaluation of the quadratures. The probable errors given in (16) also include an estimate of the inaccuracy of the variational wave function. (The values of the variational parameters are highly correlated, however, and an arbitrary choice of values consistent with the quoted errors will lead only rarely to the minimum energy.)

Questions as to the effect of curvature and surface "tightening" were also investigated. As remarked above, there is a negligible term of order  $(a/a_{\text{He}})^2$ , which has already been dropped in Eq. (13b) for the surface energy. Additionally there are correction terms to the bulk value of order  $\xi/a_{\text{He}}$  and  $(\xi/a_{\text{He}})^2$ , which arise from the  $r^2$  weighting factor. By defining an appropriate effective surface at  $\bar{a}_{\text{He}} \approx 17.2 \text{ \AA}$ , the linear terms can be made to vanish, leaving only small  $(\xi/a_{\text{He}})^2$  terms. (At  $\bar{a}_{\text{He}}$  the density is  $0.42n_0$ .)

Defining a surface tension by

$$\sigma = F_{\text{surf}} / (4\pi\bar{a}_{\text{He}})^2, \quad (17)$$

we find that the surface tension is nearly identical to the bulk value. Comparison of (16) with the result for the plane free surface  $\xi = 3.78 \text{ \AA}$  indi-

cates that the surface is tightened only about 10%; our variational calculations would lead us to expect this to make a difference of less than 1% in the surface energy, consistent with the finding above. One reason that the surface is not very much tightened is that the electron density decays much more slowly than the variation in  $n$ . In contrast, a sharp hard-wall interaction with the helium would produce (because of the quantum kinetic-energy term) a slightly higher surface tension than for a free surface.

We conclude that the curvature and surface-tightening effects are probably *not* important in determining the bubble structure.

The bubble radius of about  $17.2 \text{ \AA}$  ( $\bar{a}_{\text{He}}$ ) that we have found, is somewhat larger than the  $15 \text{ \AA}$  implied by the viscosity-limited ( $T \geq 2^\circ\text{K}$ ) mobility measurements,<sup>2</sup> although consistent with the less precise phonon-limited mobility results,<sup>3</sup> and with other measurements.<sup>4-6</sup> These determinations treat the diffuse surface crudely at best. Considering the substantial surface thickness that we find and the probability that classical hydrodynamics fails on a scale of Angstroms, one does not expect the experimental determinations to be more accurate than 1 or 2  $\text{\AA}$ , so the agreement between experiment and experiment and experiment and theory is actually quite satisfactory.

A further experimental consequence of the diffuse surface is that different experiments will measure different radii. For example, the electronic radius  $a_e \approx 15.8 \text{ \AA}$  is almost  $1\frac{1}{2} \text{ \AA}$  smaller than  $\bar{a}_{\text{He}}$ , and in agreement with the photoejection measurement of Zipfel and Sanders.<sup>7</sup> The effective mass is a hydrodynamic induced mass arising from the kinetic energy of the velocity field around the sphere. The velocity field is determined classically by the vanishing of the normal velocity component at a surface, and quantum mechanically by the vanishing of the density. The latter condition can be shown,<sup>20</sup> however, to reduce to the former at a well-defined surface. The density profile of the bubble is very close to what one

would obtain if a spherical surface were introduced at  $r \approx a_{\text{He}}$ . One would expect, then, that the effective mass measures a rather small radius ( $a_{\text{He}} \approx 12.6 \text{ \AA}$ ). Indeed, using the results of Padmore and Fetter,<sup>20</sup> we estimate that the effective mass would be that appropriate to a sphere of radius slightly more than  $14 \text{ \AA}$ . The effective-mass radius measured in a recent somewhat surprising experiment<sup>21</sup> was  $11.4 \text{ \AA}$ . Our result may provide part of the explanation.

#### IV. CONCLUSIONS

We have developed a convenient and, hopefully, fairly realistic model for the structure of an inhomogeneous quantum fluid and applied it to calculate the structure of the free surface and the electron bubble in helium. The surface shape compares well with the results of a more elaborate calculation and the bubble parameters are consistent with experiment. The model is especially easy to treat variationally, and such an approach seems to yield very accurate representations of the exact solutions.

It will be interesting to apply the model to other situations of physical interest, such as He films on solid surfaces [in which case a term  $\int n(\vec{r}) \times V_{\text{ex}}(\vec{r}) d\vec{r}$ , where  $V_{\text{ex}}(\vec{r})$  is an external "wall potential," should be added to  $F$ ] and He in other restricted geometries (pores, powders, channels). Problems with potential flow can be treated with the addition of a term  $\int n(\vec{r})(\nabla\phi(\vec{r}))^2 d\vec{r}$  to  $F$ . An extension to finite temperatures is possible via a study of the periodic solutions of the equations resulting from small perturbations of the equilibrium solutions. These solutions describe the low-lying excitations of the system. The study of the different surface excitations that result will be of considerable interest.

#### ACKNOWLEDGMENTS

We would like to acknowledge useful conversations with Michael Fisher and Josef Sak.

\*Work supported by the National Science Foundation through Grant No. GH-36457 at Cornell University and Grant No. 11-5608 at the University of Washington.

†Present address: Dept. of Physics, University of Toronto, Toronto, Canada.

<sup>1</sup>C. C. Chang and Michael Cohen, *Phys. Rev. A* **8**, (1973).

<sup>2</sup>K. W. Schwarz, *Phys. Rev. A* **6**, 837 (1972); R. M. Ostermeier and K. W. Schwarz, *Phys. Rev. A* **5**, 2510 (1972).

<sup>3</sup>K. W. Schwarz and R. W. Stark, *Phys. Rev. Lett.* **21**, 967 (1968); and K. W. Schwarz, *Phys. Rev.* **6**, 1958

(1972).

<sup>4</sup>R. L. Douglass, *Phys. Rev. Lett.* **13**, 791 (1964); W. P. Pratt and W. Zimmermann, *Phys. Rev.* **177**, 417 (1969).

<sup>5</sup>R. J. Donnelly and P. H. Roberts, *Proc. R. Soc., Lond. A* **312**, 519 (1969); T. C. Padmore, *Phys. Rev. Lett.* **28**, 469 (1972).

<sup>6</sup>B. E. Springett, *Phys. Rev.* **155**, 139 (1967).

<sup>7</sup>C. Zipfel and T. M. Sanders, *Proceedings of the Eleventh International Conference on Low Temperature Physics, St. Andrews, 1968*, edited by J. F. Allen, D. M. Finlayson, and D. M. McCall (St. Andrews Uni-

- versity, St. Andrews, Scotland, 1969).
- <sup>8</sup>B. E. Springett, M. H. Cohen, and J. Jortner, *Phys. Rev.* **159**, 183 (1967).
- <sup>9</sup>K. Hiroike, N. R. Kestner, S. A. Rice, and J. Jortner, *J. Chem. Phys.* **43**, 2625 (1965). The bubble surface tension calculated in this paper is large, but the bulk surface tension predicted by this model is equally large.
- <sup>10</sup>A. Widom, Ph.D. thesis (Cornell University, 1968) (unpublished); P. C. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
- <sup>11</sup>At low densities we have, approximately, an ideal gas with  $S = \frac{5}{2}Nk + Nk \ln[(kT)^{3/2}VN^{-1}]$  plus a constant independent of  $T$  and  $V$ .
- <sup>12</sup>We do not know how  $\mathcal{F}$  varies for  $n \rightarrow 0$ . The choice  $\mathcal{F}(n) \propto n$  for  $n \rightarrow 0$  is motivated by an unconvincing mean-field argument. The consequences of error here are minute, however, as  $\mathcal{F}$  is already well determined by its behavior at  $n = n_0$  and the condition on  $\mathcal{F}(0)$ .
- <sup>13</sup>D. J. Amit, *Phys. Lett.* **23**, 665 (1966); *J. Low Temp. Phys.* **3**, 645 (1970).
- <sup>14</sup>Built in here is a Lagrange multiplier term which incorporates Eq. (2). For our free-energy functional the Lagrange multiplier will turn out to be zero, so it will not be mentioned again.
- <sup>15</sup>The bubble structure is determined principally by the vanishing of the *derivative* with respect to the bubble radius of the total free energy.
- <sup>16</sup>H. M. Guo, D. O. Edwards, R. E. Sarwinski, and J. T. Tough, *Phys. Rev. Lett.* **27**, 1259 (1971).
- <sup>17</sup>For example the condition  $\int_0^\infty V_{6-12} r^2 dr = -K_0 \int_0^\infty \delta(r-a) \times r^2 dr$  for  $a = 2^{1/6}\sigma$  gives about 1.25 in Eq. (9b) rather than 0.949, and a consequent surface energy about 15% too high.
- <sup>18</sup>R. Brout and M. Nauenberg, *Phys. Rev.* **112**, 1451 (1958); D. D. Fitts, *Physica (Utrecht)* **42**, 205 (1969); Yu Ming Shih and Chia-Wei Woo, *Phys. Rev. Lett.* **30**, 478 (1973).
- <sup>19</sup>T. F. O'Malley, *Phys. Rev.* **130**, 1020 (1963). Choosing the scattering length  $l$  as a single parameter characterizing the interaction is an oversimplification in the sense that  $l$  represents some combination of long-range attraction and short-range repulsion for the single-atom problem that will not be identical for the many-atom problem. Because the bubble is large, however, the attractive part contributes relatively little, so that the repulsion dominates in both cases. Thus this method may be rather accurate.
- <sup>20</sup>T. C. Padmore and A. L. Fetter, *Ann. Phys. (N. Y.)* **62**, 293 (1971).
- <sup>21</sup>J. Poitrenaud and F. I. B. Williams, *Phys. Rev. Lett.* **29**, 1230 (1972).