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Variational calculations of liquid ^{4}He with free surfaces*

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Results of variational calculations of the surface profile and energy of the free surface of liquid helium are presented. The trial wave function is taken to be a product of two-body Jastrow factors and one-body factors. We performed the numerical computations using Monte Carlo techniques. The obtained suface energy is 0.21 °K/Å^2 compared with the experimental value of 0.27 °K/Å^2. The density profile is found to have a very weak layered structure near the free surface. A scheme is proposed and carried out to test the consistency of other approximate microscopic calculations of the surface profile and energy. We also suggest that experiments be considered to probe the surface structure.

I. INTRODUCTION

Recently, many attempts[1–7] have been made to construct a theory of the free surface of ^{4}He. This simple inhomogeneous system already poses a substantial challenge to theorists to build a model for an inhomogeneous, strongly interacting quantum system. The task is, of course, only a first step toward dealing with more complicated and more interesting inhomogeneous systems like quantum vortex lines, atomic rearrangements around ions and neutral impurities, thin films, and excited states of all these systems. In the present article, we restrict ourselves to the problem of the free surface.

Assessments of earlier papers[1–3] have been made in recent publications[4–7] and, therefore, we confine our review to the latter. Roughly they fall into one of two categories, namely, phenomenological and variational treatments. In the first category, Regge[4] and Padmore and Cole[7] proposed different local energy functionals and, not unnaturally, came to different conclusions about the density profile, the first exhibiting oscillatory behavior and the second showing monotonic behavior. Since neither approach has been derived from any microscopic theory it is very hard to judge their merits. The only possible case where one can test these theories against exact calculations is the system of quantum hard spheres confined to a channel. In that case, the calculated[8,9] density profile exhibits a pronounced layered structure. We presume that application of Padmore and Cole's theory to this case would give results rather like those predicted by the weakly interacting Bose-gas model[10] which produces results in qualitative disagreement with the exact results. On the other hand, Regge's approach will produce results qualitatively similar to the exact results. In the second category of theories variational calculations are performed in an approximate fashion. Shih and Woo[5] and Chang and Cohen[6] made very similar approximations to relate the two-particle correlation function for the inhomogeneous system to the bulk two-particle correlation function at a suitable scaled density. Having made this approximation, it is possible to start the computation with a given density profile rather than a given variational wave function. (See Sec. IV for details). Another point worth mentioning about these calculations is that though it is easier to perform the calculation by prescribing a given density profile, it is also easy thereby to introduce unnecessary curvature into the single-particle factors in the wave function and thus raise the energy of the system.

The purpose of the present calculation is to present variational calculations without invoking any additional approximations. Hopefully we can thus focus our attention on the merits of the trial wave functions, and perhaps in so doing gain some insight as to whether any improvements are called for.

A variational calculation[8] similar to the present one has been carried out for quantum hard spheres in a channel. In that case the results of Monte Carlo numerical integration of the Schrödinger equation are available.[9] While the results of the variational calculation show a definite layered structure in the density profile, it is not nearly as pronounced as that revealed by the exact calculation. We therefore anticipate that application of a variational calculation to the present case would give an adequate qualitative description of the structure near a free surface and that any structure found is likely to appear enhanced in an exact treatment.

In Sec. II the model and the method will be explained. Results of the variational calculations will be reported in Sec. III. A check on the consistency of the approximate-integral-equation approach[6,7] will be presented in Sec. IV. Our conclusions are given in Sec. V; we believe that the recent work based upon approximate integral equations is seriously inconsistent and the resulting density profiles are not convincing. Our own results for the surface energy show reasonable agreement with experiment and reveal a weak oscillatory structure in the density profile near the surface. Further numerical and laboratory experiments are needed to accurately determine the surface structure.

II. MODEL

The system is composed of N particles interacting through a pairwise Lennard-Jones potential. In our simulations, we work with a thick film with two surfaces. This is thought to be the simplest way to simulate a free surface for self-binding liquids without complicating the calculation by introducing a substrate. Periodic boundary conditions are imposed on the two directions (x and y) parallel to the free surfaces.

The Hamiltonian of the system is given by

$$H=-\sum_i \frac{\hbar^2}{2m}\nabla_i^2+\frac{1}{2}\sum_{i\neq j} V(|\vec{r}_i-\vec{r}_j|), \qquad (1a)$$

here

$$V(r)=4\epsilon_0[(\sigma/r)^{12}-(\sigma/r)^6]\,;$$

$$\epsilon_0=10.22\,^\circ\mathrm{K},\ \sigma=2.556\ \text{Å}. \qquad (1b)$$

The special boundary condition on the wave function ψ arising from the presence of the free surface is that $\psi\to 0$ for any $|z_i|\to\infty$. The trial wave function we have investigated is of the form

$$\psi_t=\psi_0\prod_{i=1}^{N} h(z_i)=\psi_0\exp\Big(-1/2\sum_i t(z_i)\Big), \qquad (2)$$

where $\psi_0=\exp(-\frac{1}{2}\sum u_{ij})$ with $u(r)=(1.16\sigma/r)^5$ taken from the ground-state calculation for the uniform system.[11]

Two different forms for the function $h(z)$ were chosen,

$$\text{(i)}\ \ h_a(z)=\{1+\exp[k(|z|-z_0)]\}^{-1} \qquad (3a)$$

$$\text{(ii)}\ \ h_b(z)=\begin{cases}1, & |z|<z_0\\ 2\{1+\exp[k(|z|-z_0)^q]\}^{-1}, & z_0<|z|.\end{cases} \qquad (3b)$$

It is clear that z_0 controls where the free surface will be located and k (and q) determines its width.

Let E_0 and E_t be the ground-state energy per particle of the uniform system and the present case, respectively, then the surface energy E_s (which is equal to the surface tension at $T=0$) is given by

$$E_s=N(E_t-E_0)/A, \qquad (4)$$

where A is the total surface area.

The single-particle density function $\rho_1(z)$ is defined as

$$\rho_1(z)=\frac{N\int\psi_t^2(\vec{r}_1,\vec{r}_2,\cdots\vec{r}_n)\,d\vec{r}_2\cdots d\vec{r}_n}{\langle\psi_t|\psi_t\rangle}\,. \qquad (5)$$

Given a trial wave function defined in Eqs. (2) and (3), the energy and the single-particle density function can be computed without any further approximation by standard Monte Carlo methods.[12,13] To get an accuracy in energy of about 1%, it is sufficient to generate a random walk with 10^5 configurations. However, to obtain sufficient accuracy in the density profile, it is necessary to carry out several independent runs each consisting of about a million configurations. The number of particles used was either 256, 512, or 1024. It turns out that the structures that we are particularly interested in are more or less indistinguishable in these three cases.

We choose $\bar{\rho}$, the average density in the interior of the film to be $\bar{\rho}=0.9\rho_0$, the density at which the Lennard-Jones potential with the given form of u gives the minimum energy for the bulk system. This ensures that the material on the interior of the film resembles bulk helium as closely as possible. An effective width of the film L_z is defined by the relation $\bar{\rho}=N/AL_z$.

III. RESULTS

Of the two trial wave functions given by Eqs. (3a) and (3b), a lower energy is found if h_b in Eq. (3b) is used. The surface-energy found is 0.21 ± 0.01 °K/Å^2 for the optimal parameters $k=0.3/\sigma$, $\tilde{z}_0=\frac{1}{2}L_z-z_0=3.0\,\sigma$, and $q=2$ for $N=512$. The values quoted in Refs. 5 and 6 are 0.26 and 0.29 °K/Å^2, respectively. However, direct comparison of these numbers is not very meaningful since either a different average density or a different potential was used. It is worth emphasizing that the percentage difference of our surface energy as compared to the experimental value (0.27 °K/Å^2) is 25%. This is similar to the percentage difference (16%) between the variational ground-state energy (−5.9 °K) and the exponential binding energy (−7.16 °K).

The density profile calculated from wave functions with parameters giving nearly the same energies all exhibit a rather weak oscillatory behavior near each free surface. In Fig. 1 we show such a density profile for a rather thick film (~ 19 σ wide) where the two free surfaces are so far apart that one can reasonably assume that they behave independently of each other. On both free surfaces, one can clearly identify at least a weak first peak. Regge's phenomenological treatment[4] also predicted a similar oscillation in the density profile, though his estimate suggested a much larger ripple. The surface thickness (defined as the interval of density profile between 90% and 10% of $\bar{\rho}$, the

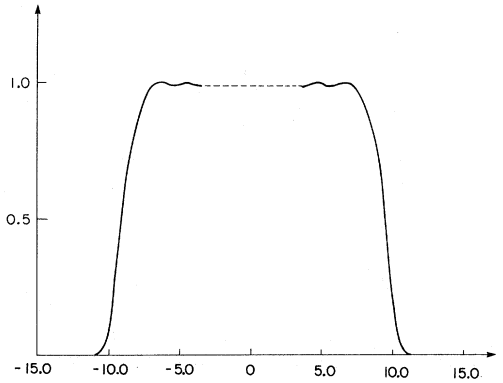

FIG. 1. Density profile of the free surface of liquid helium calculated variationally, $\sigma = 2.56$ Å; $\bar\rho$ is the mean density in the film, $\bar\rho = 0.9$ (measured equilibrium density).

average density in the interior) is about 2σ (i.e., about 5 Å).

IV. TEST OF AN APPROXIMATE-INTEGRAL-EQUATION APPROACH

Given ψ_t in Eq. (2), it is easy to derive the following exact integral equation in the Bogolyubov, Born, Green, Kirkwood, Yvon (BBGKY) hierarchy,

$$\nabla\rho_1(r) = \rho_1(\vec r)\nabla t + \int d\vec r\,'\rho_2(\vec r, \vec r\,')\nabla_{\vec r}\, u(\vec r, \vec r\,'), \quad (6)$$

where $\rho_2(\vec r, \vec r\,')$ is the two-particle correlation function.

In Refs. 5 and 6, an approximation is made to make Eq. (6) a closed equation between $\rho_1(r)$ and $t(r)$. The approximation is to write

$$\rho_2(\vec r, \vec r\,') = \rho_1(\vec r)\rho_1(\vec r\,')g_B(|\vec r - \vec r\,'|;\ \rho_{\text{eff}}(\vec r, \vec r\,')), \quad (7)$$

where $g_B(r;\rho)$ is the pair correlation of the corresponding uniform system at a density ρ. Three somewhat different forms of ρ_{eff} were proposed, namely,

$$\text{(i)}\quad \rho_{\text{eff}}(z, z') = [\rho_1(z)\rho_1(z')]^{1/2}, \quad \text{(8a)}$$

$$\text{(ii)}\quad \rho_{\text{eff}}(z, z') = \tfrac{1}{2}[\rho_1(z) + \rho_1(z')], \quad \text{(8b)}$$

$$\text{(iii)}\quad \rho_{\text{eff}}(z, z') = \rho_1[\tfrac{1}{2}(z + z')]. \quad \text{(8c)}$$

In Ref. 6 it was reported that (8c) gives a poorer estimate of E_s as compared with (8a) or (8b), which give essentially the same result. We have also checked that in solving Eqs. (6) and (7) for t from a given $\rho_1(z)$, there is little difference whether one uses (8a) or (8b). We will pick (8a) to be combined with Eqs. (6) and (7) for the following discussion.

From Eqs. (6), (7), and (8a), given a $\rho_{1A}(z)$, one can solve for $t_A(z)$. We now use this $t_A(z)$ in Eq. (2) to calculate the single-particle density function $\rho_1(z)$ without further approximation. We followed this scheme to check if any inconsistency is introduced as a consequence of the approximations made in Eqs. (7) and (8a). Values of $g_B(r;\rho)$ for $0 < \rho \leq \bar\rho$, which are needed in Eq. (7), were obtained from Monte Carlo calculations. Then, given $\rho_{1A}(z) = (1 + e^{4.0z/\sigma})^{-1}$, we solved for $t_A(z)$ from Eqs. (6), (7), and (8a). With this input into Eq. (2), we computed both the surface energy and the density profile. The surface energy was found to be 20% higher than our previous estimate. The density profile $\rho_1(z)/\bar\rho$, $h_A^2(z) = e^{t_A(z)}$, and the input $\rho_A(z)$ are plotted in Fig. 2. Three comments are in order First, pronounced first peaks near each free surface are present in the final $\rho_A(z)$ as compared with the originally assumed $\rho_A(z)$. This is a clear inconsistency in the approximate treatment. Secondly, we notice that the $t_A(z)$ obtained shows considerable curvature, which in turn is responsible for raising the estimate of the surface energy. Finally, the fact that the interior density has changed is not an inconsistency. With the fixed number of particles used in the Monte Carlo, the redistribution of density near the surface forces a change of interior density.

In Fig. 3, results similar to those shown in Fig. 2 are given for a film whose thickness is $\frac{1}{2}$ that of the former. The departure of the average interior density from unity is much larger, since a larger fraction of the particles are displaced into the surface region. It is striking that the surface peak is present and has almost exactly the same height as in the thicker film. This suggests very strongly that the surface peak will persist largely

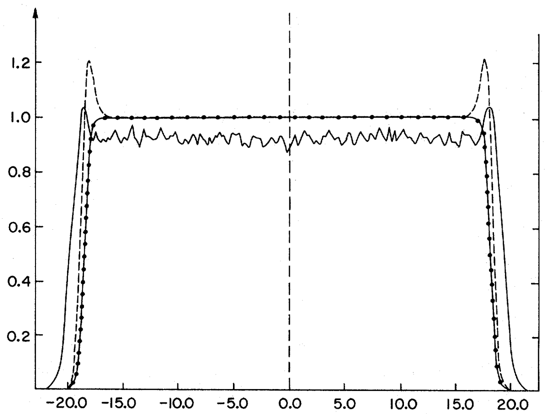

FIG. 2. Dotted curve is the average density profile which forms the starting point for the approximate treatment embodied in Eqs. (6), (7), and (8a). Dashed curve is the function t_A calculated from Eqs. (6), (7), and (8a) using the dotted curve as input. Solid curve is the density profile calculated variationally from t_A.

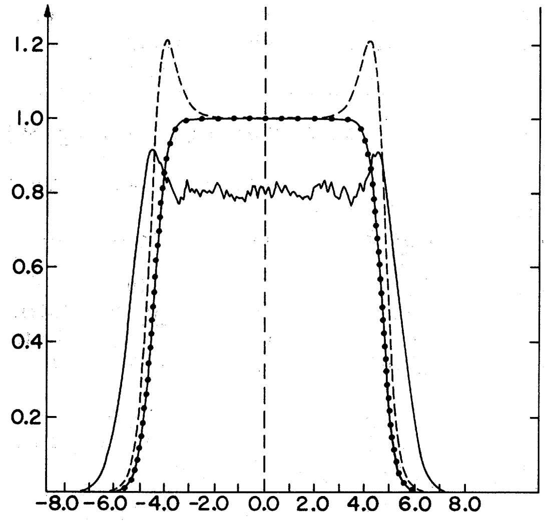

FIG. 3. Dotted curve is the average density profile which forms the starting point for the approximate treatment embodied in Eqs. (6), (7), and (8a). Dashed curve is the function t_A calculated from Eqs. (6), (7), and (8a) using the dotted curve as input. Solid curve is the density profile calculated variationally from t_A. These results are for a film $\frac{1}{2}$ the thickness of that in Fig. 2.

unaltered as one passes to a very thick film. The final density profiles shown in Figs. 2 and 3 have not been smoothed.

We believe a very useful analogy for the relationship between $t(z)$ and $\rho_1(z)$ is that between $u(r)$ and $g_B(r)$ in a variational calculation for a uniform system. In such a calculation, it is well known that a smooth monotonic $u(r)$, representing strong short-ranged repulsion, will lead to an oscillatory $g_B(r)$, and furthermore, it is not hard to find a $u(r)$ which gives a $g_B(r)$ which agrees well with the experimental results.[11] However, if one were to choose instead a smooth monotonic g_B, and then try to find $u(r)$ through a similar approximate scheme, it is inevitable that a $u(r)$ with considerable curvature will result. For this reason it is generally believed that varying $u(r)$ is more practical then varying $g_B(r)$. This analogy thus leads us to suggest that for the free-surface problem, varying $t(z)$ instead of $\rho_1(z)$ is likely to markedly improve the situation.

It is regrettable that we have not been able to precisely establish the difference between the approximate ρ_2 (Eqs. 7 and 8) and the more accurate ρ_2 calculated by Monte Carlo methods from the variational trial function used in this paper. Since, presumably, the significant differences are confined to the surface region, good statistics for the three-dimensional function $\rho_2(r_1, r_2)$ would be very time consuming to accumulate. This task would be more appropriate as part of the exact calculations of the surface profile now in progress.

V. CONCLUSIONS

We have presented a series of variational calculations to study a large class of wave functions as well as to examine carefully some recent microscopic calculations. The basic conclusions are sixfold:

(i) The surface energy found from most of these methods is in reasonable agreement with the experimental result.

(ii) Our current results suggest a very weak layered behavior in the density profile at a free surface. This differs markedly from the results found in Refs. 5–7.

(iii) The previous calculations[5–7] are based on a monotonic density profile and are, without doubt, subject to the criticism that if the same approaches were adopted in the narrow-channel problem they would lead to entirely incorrect results.

(iv) There is a serious internal inconsistency in the approximate treatments contained in Refs. 5 and 6.

(v) We believe that there are, therefore, considerable difficulties in attempting to close $\rho_1(r)$ *a priori* in problems with any geometrical complexity. On the other hand, we know that wave functions must always be chosen to be as smooth as the geometry allows and that this kind of choice leads to nonobvious consequences for ρ_1.

(vi) We draw the reader's attention again to Figs. 2 and 3 which represent calculations of films whose thicknesses differ by a factor of 2, but whose surface profiles are almost the same. We conclude that we have attained a regime in which size effects on the surface profile are small.

Of course, our treatment, being variational in character, has to be tested against an exact treatment to verify that the results reported here are not an artifact of the trial wave functions assumed. Our experience in the channel problem suggests that the structures found in variational calculations tend to be reinforced in an exact calculation, which in turn suggests that this might also be the case for the present problem.

We hope that the present work and the exact results we shall shortly have available will arouse the interest of experimentalists. We would very much like some experimental data on the surface profile. This is important, since so many different theoretical approaches, with all their inherent deficiencies, are able to give reasonable estimates of the only experimental datum at $T=0$, namely the surface energy. In our view, a neutron diffraction like the one reported recently by Kjems, Passell, Taub, and Dash,[14] or a light scattering experiment might be a good choice. Perhaps, a low-energy-electron-diffraction (LEED) experiment would serve as a better probe into the density profile near the surface, since electrons tend to interact mostly with surface atoms.

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