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Surface-Mode Renormalized Density-Functional Theory of the Free Surface of ^{4}He†

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We present a density-functional theory, renormalized to account self-consistently for the effects of the zero-point motion of surface modes, for the free surface of ^{4}He at zero temperature. Although detailed liquid-structure effects are included, no static density oscillations near the free surface are found in contrast to a theory of Regge. For the case of ^{4}He bounded by a single hard wall, density oscillations near the wall are obtained.

Recent years have seen the application of density-functional theory to a number of problems, principally those associated with the electron density in the vicinity of metal surfaces,[1] but also including some in the areas of liquid helium,[2] nuclear matter,[3] and classical liquids.[4] In this paper we present the results of a density-functional calculation of the density profile of the free planar surface of liquid ^{4}He at zero temperature. The theory used is a generalization of previous efforts, designed to take into account self-consistently the effects of changes in the long-wavelength (i.e., wavelengths greater than a few interatomic spacings) mode structure of the liquid when a free surface is formed in an otherwise uniform system. Specifically, we include the very important effects due to the zero-point motion of both the surface modes (ripplons) and surface-altered bulk modes (phonons reflected at the surface) on the density profile and on the surface tension. Our results resolve the intriguing question, raised by previous theories of the ^{4}He free surface,[5] as to whether or not there are oscillations in the density near the surface. We find no such oscillations even though we include hard-core effects (via a realistic structure factor) which might conceivably give rise to them. Further, we have applied our theory to the case where the liquid is bounded by a hard wall (ours is the first realistic calculation for this situation), and we find density oscillations similar to those found by Liu, Kalos, and Chester[6] for a hard-sphere boson system bounded by two hard walls. This contrasting behavior shows that a free surface is simply too soft to permit static oscillations in the density. It is worthwhile to point out that the oscillations we obtain in the case of a single hard wall may reasonably be expected to persist in the situation where the helium is in contact with a real substrate, next to which one or two solid ^{4}He layers are formed[7] (because of the substrate Van der Waals attraction), followed by the liquid. If so, one might expect a significant effect on the Kapitza boundary resistance in the temperature region (1–2° K) where the effective thermal-phonon wavelengths are comparable to those of the static density oscillations [recall that the phonons can strike the surface at an angle].

We begin with a description of what we term the bare density-functional (BDF) theory, "bare" in that it does not include the renormalizing effects of zero-point motion associated with the surface. Our approach is similar to that of Hohenberg and Kohn.[8] We approximate the exact energy functional $E[n]$ in terms of a local energy density plus an expansion in powers of the difference between densities at different points in the fluid; the series is terminated in second order, and the first-order term vanishes for reasons of symmetry. Thus,

$$E[n]=\int d^3r\,\epsilon(n(\vec{r}))+\int d^3r\,d^3r'\,W(\vec{r},\vec{r}')[n(\vec{r})-n(\vec{r}')]^2. \quad (1)$$

Here $\epsilon(n)$ is the energy density of a uniform system having density n and the kernel $W(\vec{r},\vec{r}')$ may be thought of as an effective interaction between different portions of the fluid arising from nonuniformity. To obtain an expression for $W(\vec{r},\vec{r}')$, we apply (1) to the limiting case of a weakly nonuniform fluid. Following an argument similar to that of Ref. 8, we find, in the stated limit, $W(r,r')=-\frac{1}{4}\sum_{\vec{q}}\exp[i\vec{q}\cdot(\vec{r}-\vec{r}')]\chi_q^{-1}(n_0)$, where χ_q is the density-density response function at wave number q for the uniform system having number density n_0. For the case of general nonuniformities, we will retain this form with the replacement $n_0 \to [n(\vec{r})+n(\vec{r}')]/2 \equiv \bar{n}$ in order to incorporate the density dependence. Since

$$\chi_q^{-1}(n) \underset{q\to\infty}{\longrightarrow} \chi_q^{0-1} = \hbar^2 q^2/4mn$$

(the free-particle limit), the integral in our expression for W is irregular at large q. It is convenient to separate out χ_q^0 in order to obtain a regular kernel, in which case (1) becomes

$$E[n]=\int d^3r\,\epsilon(n(\vec{r}))+(\hbar^2/2m)\int d^3r[\nabla n^{1/2}(\vec{r})]^2 - \tfrac{1}{4}\int d^3r\,d^3r'\{\textstyle\sum_q \exp[i\vec{q}\cdot(\vec{r}-\vec{r}')][\chi_q^{-1}(\bar{n})-\chi_q^{0-1}(\bar{n})]\}[n(\vec{r})-n(\vec{r}')]^2 . \quad (2)$$

It is a very pleasing feature of the present theory that the well-known quantum pressure term[9] [that involving $\nabla n^{1/2}(\vec{r})$] emerges in a completely natural fashion and does not have to be put in by hand, as has been done in the essentially phenomenological theory of Padmore and Cole.[2]

In order to make practical use of (2) we require a reasonable approximation for χ_q. Our choice is to employ the result of the Feynman theory[10]: $\chi_q^{-1}=\hbar^2q^2/4mS_q^2n$, where S_q is the usual liquid-structure factor. This approximation includes the structure of the liquid in a very reasonable way and renders actual computation of χ_q as a function of density sensibly tractable.

Now the equilibrium configuration assumed by the system is the solution (subject to appropriate boundary conditions) of $\delta E[n]/\delta n(\vec{r})=\mu$, where μ is the chemical potential. Thus, from (2) we find a nonlinear integro-differential equation which may be solved for $n(\vec{r})$.

The quantities $\epsilon(n)$ and $S_q(n)$ have been obtained via application of the theory of Mihara and Puff.[11] This theory yields an S_q at the equilibrium density for zero pressure in excellent agreement with experiment. At higher densities the peaks in S_q become more pronounced and move to slightly larger values of q, whereas the peak structure gradually disappears as the density is reduced from its zero-pressure value.

We have solved numerically the integro-differential equation subject to the boundary conditions $n(z=-\infty)=0$ and $n(z=+\infty)=n_0$, appropriate to a bath of ^{4}He with a planar free surface. The solution, which we call the bare density and denote by $n_b(z)$, is depicted in Fig. 1.

The surface tension σ_b associated with $n_b(z)$ is given by

$$\sigma_b = E[n_b(z)] - \int_{-\infty}^{\infty} dz\,\mu n_b(z) . \quad (3)$$

Calculation yields the result $\sigma_b = 0.003$ erg/cm^2, which, when compared to the experimental surface tension $\sigma = 0.378$ erg/cm^2,[12] is a clear indication that some very important physics is missing from the BDF. A clue as to what has been ignored is found in the original paper of Atkins[13] on the surface tension of ^{4}He. In that paper he estimates the contribution of the zero-point motion of the ripplons to be of the same order of magnitude as the experimental surface tension. Of course, an exact density-functional theory would incorporate this effect. However, all extant practical theories of this nature,[1] the above one included, embark from the uniform-system limit and thus contain no information about surface modes. Reconciling this sort of theory with one like that of Atkins, which commences in

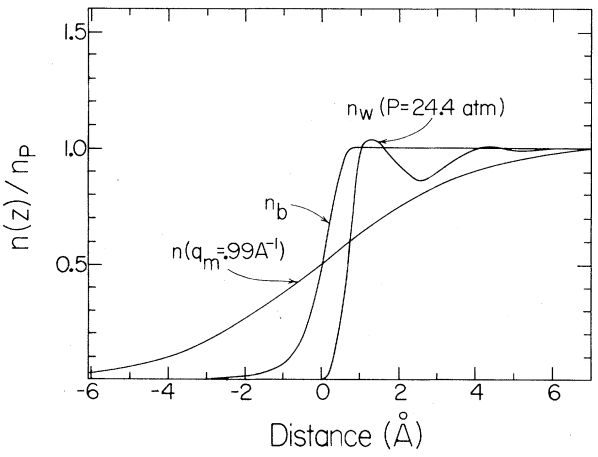

FIG. 1. The bare (n_b) and renormalized (n) densities at the free surface and the density at a hard wall (n_w) as functions of z. n_P is the bulk equilibrium density at pressure P.

zeroth order from a model with a perfectly sharp surface, is the problem to which we now address ourselves.

We begin by noting that we may regard, after Gross[9] and Pitaevskii,[9] the BDF result as a semiclassical equation determining a classical field $n_b(z)$. The small oscillations of the density are then, when quantized, the elementary excitations of the system. Since the bare surface $n_b(z)$ is quite sharp, we may obtain all but the very short-wavelength excitations (whose effects are at least partially accounted for in the BDF through the density dependence in ϵ and W) from the theory of quantum hydrodynamics for a liquid which has a sharp surface characterized by surface tension σ_b. The contribution $\sigma_{zp}(\sigma_b)$ to the surface tension (surface energy per unit area) due to the difference between the zero-point motion of the system with a surface and an equivalent amount of bulk liquid is thus found to be a sum of two terms[14]:

$$\sigma_{zp}(\sigma_b)=\sigma_{zp}{}^{\text{ripplon}}(\sigma_b)+\sigma_{zp}{}^{\text{phonon}}(\sigma_b), \tag{4}$$

and each of these contributions may be expressed in terms of the ^{4}He density ρ, velocity of sound s, and a cutoff wave number q_m (determined below) in addition to σ_b.

Were we simply to add σ_{zp} to σ_b, the resulting σ would be inconsistent for two reasons. The first, and most obvious, is that σ_b appears in $\sigma_{zp}(\sigma_b)$, whereas the real modes are determined by σ. Self-consistency requires the replacement $\sigma_{zp}(\sigma_b)\to\sigma_{zp}(\sigma)$, an effective mode renormalization. Secondly, we must include the fact that there will be zero-point motion of the surface as a consequence of the surface modes. Let $\zeta(x,y)$ be the displacement of the surface from its equilibrium value (at $z=0$ in the sharp-surface model). Then, the renormalized density is approximately[15] $n(z,\sigma_b)=\langle 0|n_b(z+\zeta(x,y))|0\rangle$, $|0\rangle$ being the ground state. Use of the fact that $\zeta(x,y)$ is expressible in the form

$$\sum_{\vec{q},l} e^{i\vec{q}\cdot\vec{r}}[\zeta_{-\vec{q},l}{}^{*}a_{-\vec{q},l}{}^{\dagger}+\zeta_{\vec{q},l}\,a_{\vec{q},l}{}^{\dagger}],$$

where $\vec{q}$ is a wave vector parallel to the surface, l is an index describing both ripplons and phonons, $\zeta_{\vec{q},l}$ is a mode amplitude, and $a_{\vec{q},l}{}^{\dagger}$ creates an excitation characterized by $\vec{q}$ and l, allows one to put $n(z,\sigma_b)$ in the form

$$n(z,\sigma_b)=\int_{-\infty}^{\infty}dz'\,n_b(z-z')\times\exp(-z'^2/2\zeta_0{}^2)(2\pi\zeta_0{}^2)^{-1/2}, \tag{5}$$

where the mean-square displacement $\zeta_0{}^2\equiv\langle 0|\zeta^2(x,y)|0\rangle$ may be simply expressed in terms of σ_b, ρ, s, and q_m. The zero-point motion thus produces a Gaussian broadening of the surface. Mode renormalization of the density is effected by the replacement $n(z,\sigma_b)\to n(z,\sigma)$, and renormalization of the density-functional contribution to the surface tension is then handled by substituting $n(z,\sigma)$ for $n_b(z)$ in (3). Consequently, the total surface tension is

$$\sigma=E[n(z,\sigma)]-\int_{-\infty}^{\infty}dz\,\mu n(z,\sigma)+\sigma_{zp}(\sigma). \tag{6}$$

This result, together with (5), provides us with a fully self-consistent set of equations from which we have determined σ, $n(z,\sigma)$, and ζ_0 as functions of q_m.

To determine q_m we relate it to the surface width[16] (governed by ζ_0 since the bare surface is very sharp) by the statement $q_m\zeta_0(q_m)=\gamma$, where γ is a constant of order π (as the width is approximately $2\zeta_0$). Now, for large q_m (~ 1 Å^{-1}), $\zeta_0(q_m)$ is a decreasing function of q_m because increasing q_m increases σ, forcing the surface to become stiff for high-wave-number ripplons in a compressible fluid (one result being the high-q limit, sq, of the ripplon frequency). This has the consequence that $q_m\zeta_0(q_m)$ possesses a maximum. Its value (and our choice of γ) $\gamma_m=3.28$ at the maximum is the smallest value of γ for which $\gamma=q_m\zeta_0(q_m)$ and (6) possess unique solutions, given numerically by $q_m=0.99$ Å^{-1} and $\sigma=0.384$ erg/cm^2. The resulting renormalized density $n(z,\sigma)$ is plotted in Fig. 1. The experimental surface tension is 0.378 erg/cm^2. The contribution of σ_{zp} to σ is typically one-half as large as the contribution from the density functional. Our calculated free-surface width is somewhat greater than that found by calculations based on approximate wave functions.[17] This predicted width could probably most easily be given an experimental test by elastic scattering of polarized light near the Brewster angle.[18]

In order to be certain that our theory is indeed capable of producing oscillations in a physical situation where there is little doubt that they exist, we have applied it to the case where the free surface is replaced by a hard wall [i.e., boundary conditions $n_w(0)=0$, $n_w(+\infty)=n_P$, a constant, determined by the pressure P required to hold the liquid against the wall]. In this case we did not solve $\delta E[n_w]/\delta n_w(z)=\mu$ but used the (in principle equivalent) procedure of minimizing $\sigma_{\text{wall}}=E[n_w]-\int_0^{\infty}dz\,[\mu n_w(z)-P]$ with respect to variations in $n_w(z)$.[19] A ten-parameter minimization produced the result shown as n_w in Fig. 1. No zero-point renormalization of the density is

required here since the surface is not free to move. It is quite gratifying that n_w shows behavior similar to that found by Liu, Kalos, and Chester[6] in their direct integration of the Schrödinger equation for a system of hard-sphere bosons between two hard walls.

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[1]For an excellent review, see N. D. Lang, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1973), Vol. 28, p. 255.

[2]See, e.g., T. C. Padmore and M. W. Cole, Phys. Rev. A 9, 802 (1974).

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[6]K. L. Liu, M. H. Kalos, and G. V. Chester, in *Monolayer and Submonolayer Helium Films*, edited by J. G. Daunt and E. Lerner (Plenum, New York, 1973), p. 95.

[7]See, e.g., J. H. Scholtz, E. O. McLean, and I. Rudnick, Phys. Rev. Lett. 32, 147 (1974).

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[15]This ignores the contributions from zero-point density fluctuations below the surface. Detailed calculations show these to be negligible.

[16]Use of separate two- and three-dimensional Debye cutoffs $q_m^{\,r}=\sqrt{8\pi}\,n_0^{1/3}=1.395$ Å^{-1} and $q_m^{\,p}=(18\pi^2 n_0)^{1/3}=1.568$ Å^{-1} for phonons and ripplons gives $\sigma=0.429$ erg/cm^2, expected to be an overestimate since, for example, the bulk-phonon spectrum ceases to be phononlike near $q=0.8$ Å^{-1}. Determination of both cutoffs by the requirement [the imaginary part of the ripplon frequency $\omega_q{}^r$ has been computed by W. F. Saam, Phys. Rev. A 8, 1918 (1973)] $\mathrm{Im}\omega_q{}^r/\mathrm{Re}\omega_q{}^r=1$ gives $q_m=0.973$ Å^{-1} and $\sigma=0.379$ erg/cm^2. Thus, all cutoffs give fairly reasonable σ's, but our choice is to be preferred since it is determined self-consistently within our theory. In a single (but variable) cutoff theory, for q_m between 0.95 and 1.05 Å^{-1}, $n(z,\sigma)$ varies at most by $0.02n_0$ relative to the curve in Fig. 1, while σ varies between 0.369 erg/cm^2 ($q_m=0.95$ Å^{-1}) and 0.414 erg/cm^2 ($q_m=1.05$ Å^{-1}).

[17]The variational calculations of Shih and Woo and Chang and Cohen (Ref. 5) are similar to our theory in that σ is obtained by varying $n(z)$. Their theories, based on the variational principle, automatically, but implicitly, contain zero-point motion, while ours isolates this motion and carefully examines its important effects.

[18]One measures the ellipticity of the scattered light. See P. Drude, *Theory of Optics* (Longmans, Green & Co., New York, 1907), p. 292.

[19]The form used for the trial function is

$$n_w(z)=n_0[1-(1+\sum_{p=1}^{N}\alpha_p z^p)\exp(\beta z^2)]^2,$$

where the α_p and β are varied. The reason for using this method of solution is that in repeated iteration of the integro-differential equation for $n_w(z)$, each succeeding solution is very sensitive to small errors in the density oscillations in the preceding one and a convergent solution was not obtained, in contrast to the free-surface case.