

Surface Structure of Liquid Helium 4

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A wavefunction for liquid He^4 with a surface is constructed, and a variational calculation to minimize the additional surface energy gives an integro-differential equation for the function characterizing the surface. The surface structure can be determined in terms of bulk properties provided certain approximations are made for the density and pair correlation functions near the surface.

§ 1. Introduction

In a recent paper,¹⁾ the problem of bound states of He^3 atoms on the surface of liquid He^4 is reduced to that of the motion of a particle in an effective potential. This potential is defined in terms of correlation functions which depend on the surface structure of pure He^4 . There are several other problems, for example those of surface energy and surface excitations, which depend for their resolution on knowledge of surface structure.

In this paper an attempt is made to calculate this structure by setting up a wavefunction with a surface, and minimizing the energy associated with the existence of the surface. This approach is different from that used in,²⁾ where exact formal expressions for the surface energy are derived in terms of the ground state wavefunction, without the latter being specified. The method used here is designed to determine the wavefunction, and may thus also be used to calculate the surface tension.

§ 2. Surface energy

Consider a system of N He^4 atoms in a box of side L , with Hamiltonian

$$H = -\frac{\hbar^2}{2m} \sum_{i=1}^N \nabla_i^2 + \sum_{i<j} v(|\mathbf{r}_i - \mathbf{r}_j|), \quad (1)$$

ground state wavefunction $\Phi(\mathbf{r}_1 \cdots \mathbf{r}_N)$, and energy E :

$$H\Phi = E\Phi. \quad (2)$$

By specifying periodic boundary conditions, Φ is defined in all space, but in (2), E is understood to be the energy of a system of N He^4 atoms.

We now impose a surface at one face of the box (e.g. the one at $z=0$) by taking the wavefunction

$$\Psi = S\Phi, \quad S = \prod_{i=1}^N s(z_i). \quad (3)$$

This choice of a Hartree product is the simplest possible one giving Bose symmetry and a precisely defined surface, and wavefunctions of the type (3), with various choices for Φ , have been widely used in studying Bose systems.^{9)~10)} The function $s(z)$, which is to be determined, tends to unity deep inside the fluid, and goes to zero outside. The energy of the fluid now contains a surface term E_s , which we will define by

$$E_s = \int d^N \mathbf{r} \Psi H \Psi \Big/ \int d^N \mathbf{r} \Psi^2 - E. \quad (4)$$

The integration in (4) is limited to $[0, L]$ for each x and y coordinate, but extends from $-L$ to $+\infty$ for each z coordinate. Using (1), (2) and (3) we find

$$\begin{aligned} E_s &= \frac{N\hbar^2}{2m} \frac{\int d^N \mathbf{r} (\nabla_1 S)^2 \Phi^2}{\int d^N \mathbf{r} (S\Phi)^2} \\ &= \frac{N\hbar^2}{2m} \frac{\int d^N \mathbf{r} (s'(z_1)/s(z_1))^2 \Psi^2}{\int d^N \mathbf{r} \Psi^2}. \end{aligned} \quad (5)$$

In terms of the number density $n(z)$ defined by

$$n(z_1) = N \int d^{N-1} \mathbf{r} \Psi^2 \Big/ \int d^N \mathbf{r} \Psi^2, \quad (6)$$

the surface term can be written

$$E_s = \frac{\hbar^2}{2m} \int d\mathbf{r} n(z) (s'(z)/s(z))^2 \quad (7)$$

or

$$E_s/L^2 = \frac{\hbar^2}{2m} \int dz n (s'/s)^2.$$

Thus the energy of the state Ψ is greater than that of Φ by a positive-definite term proportional to the surface area. The usual definition of surface energy is^{2),4)}

$$\mathcal{E}_s = \int d\mathbf{r} [\epsilon(z) - (\epsilon_0/n_0) n(z)], \quad (8)$$

where

$$\epsilon(z) = \int d^{N-1} \mathbf{r} \Psi H \Psi \Big/ \int d^N \mathbf{r} \Psi^2 \quad (9)$$

is the energy density in the system (tending to ϵ_0 in the bulk), and n_0 is the bulk number density. The expression for \mathcal{E}_s is arrived at by postulating that the surface energy is

$$\mathcal{E}_s = \int d^N \mathbf{r} \Psi H \Psi / \int d^N \mathbf{r} \Psi^2 - N\epsilon_0/n_0. \quad (10)$$

Thus E_s and \mathcal{E}_s are the same if $N\epsilon_0/n_0$ is identified with E .

§ 3. Variational calculation

We shall take variations in s to minimize E_s . Now n is a functional of s , and is subject to the constraint

$$\int dz n(z) = n_0 L. \quad (11)$$

Thus for arbitrary L we would need to introduce a Lagrange multiplier corresponding to this constraint. However, here we shall consider only the limit $L \rightarrow \infty$, and it is then sufficient to replace (11) by the boundary condition $n \rightarrow n_0$, $s \rightarrow 1$ in the bulk.

Taking variations in s , and setting $\delta E_s = 0$ gives the equation

$$\int d\mathbf{r} \{ \delta n (s'/s)^2 + 2n (s'/s) [\delta s'/s - s' \delta s/s^2] \} = 0. \quad (12)$$

The variation δn can be determined in terms of δs from the defining equation (6): we have

$$\delta n(z_1) \int d^N \mathbf{r} \Psi^2 + 2n(z_1) \int d^N \mathbf{r} \left(\frac{\delta S}{S} \right) \Psi^2 = 2N \int d^{N-1} \mathbf{r} \left(\frac{\delta S}{S} \right) \Psi^2. \quad (13)$$

Using

$$\frac{\delta S}{S} = \sum_{i=1}^N \frac{\delta s(z_i)}{s(z_i)}, \quad (14)$$

and defining a pair density function,

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int d^{N-2} \mathbf{r} \Psi^2 / \int d^N \mathbf{r} \Psi^2, \quad (15)$$

gives the functional relation

$$\delta n(z_1) = 2 \frac{\delta s(z_1)}{s(z_1)} n(z_1) + 2 \int d\mathbf{r}_2 \frac{\delta s(z_2)}{s(z_2)} [n_2(\mathbf{r}_1, \mathbf{r}_2) - n(z_1)n(z_2)]. \quad (16)$$

Thus we have

$$\begin{aligned} \int d\mathbf{r}_1 \delta s(z_1) \left(\frac{n(z_1) s'(z_1)}{s^2(z_1)} \right)' &= \int d\mathbf{r}_1 \left(\frac{s'(z_1)}{s(z_1)} \right)^2 \int d\mathbf{r}_2 \frac{\delta s(z_2)}{s(z_2)} [n_2(\mathbf{r}_1, \mathbf{r}_2) - n(z_1)n(z_2)] \\ &= \int d\mathbf{r}_1 \frac{\delta s(z_1)}{s(z_1)} \int d\mathbf{r}_2 \left(\frac{s'(z_2)}{s(z_2)} \right)^2 [n_2(\mathbf{r}_1, \mathbf{r}_2) - n(z_1)n(z_2)], \end{aligned} \quad (17)$$

and the equation for s reads

$$L^2 \left(\frac{n(z_1) s'(z_1)}{s^2(z_1)} \right)' = \frac{1}{s(z_1)} \int dx_1 dy_1 \int dr_2 \left(\frac{s'(z_2)}{s(z_2)} \right)^2 [n_2(\mathbf{r}_1, \mathbf{r}_2) - n(z_1)n(z_2)]. \quad (18)$$

It is convenient to define a pair correlation function g in terms of the pair density function n_2 :

$$n_2(\mathbf{r}_1, \mathbf{r}_2) = n(z_1)n(z_2)g(\mathbf{r}_1, \mathbf{r}_2). \quad (19)$$

Then we can write, in the limit of large L ,

$$\frac{s(z_1)}{n(z_1)} \left(\frac{n(z_1) s'(z_1)}{s^2(z_1)} \right)' = \int dz_2 n(z_2) \left(\frac{s'(z_2)}{s(z_2)} \right)^2 G(z_1, z_2), \quad (20)$$

where

$$G(z_1, z_2) = \lim_{L \rightarrow \infty} L^{-2} \int dx_1 dy_1 \int dx_2 dy_2 [g(\mathbf{r}_1, \mathbf{r}_2) - 1]. \quad (21)$$

From the definition of the problem we see that $g(\mathbf{r}_1, \mathbf{r}_2)$ is a function of $|x_1 - x_2|$ and $|y_1 - y_2|$, apart from regions of negligible volume near the edges of the box. It thus follows from the result

$$L^{-1} \int_0^L dx_1 \int_0^L dx_2 f(|x_1 - x_2|) = 2 \int_0^L dx f(x) \left(1 - \frac{x}{L}\right) \quad (22)$$

that the limit on the right-hand side of (21) exists if $g(\mathbf{r}_1, \mathbf{r}_2) - 1$ goes to zero faster than the inverse of $|x_1 - x_2|$ or $|y_1 - y_2|$ as one or both of these tend to infinity. Thus provided this mild requirement is satisfied, Eqs. (19) ~ (21) give a formal solution to the problem of the surface structure of a Bose fluid, subject only to the assumption that the surface can be described by a wavefunction of the type given in Eq. (3).

§ 4. An approximate reduction

It is possible to determine s in terms of the bulk pair correlation function of the fluid provided two further approximations are made. The first of these is to assume that g is a function of $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ only. This approximation is exact when both \mathbf{r}_1 and \mathbf{r}_2 are deep inside the fluid, and thus identifies $g(r_{12})$ with $g_0(r_{12})$, the bulk pair correlation function. It also holds in the limit of no interactions among the particles, i.e. when $\Phi = 1$, $\Psi = Hs(z_i)$ (in which case $g \equiv 1$). Approximating g by $g_0(r_{12})$, and using (22),

$$\begin{aligned} G(z_1 - z_2) &= \lim_{L \rightarrow \infty} 4 \int_0^L dx \int_0^L dy [g_0(\{x^2 + y^2 + (z_1 - z_2)^2\}^{1/2}) - 1] \\ &= 2\pi \int_{|z_1 - z_2|}^{\infty} dr r [g_0(r) - 1]. \end{aligned} \quad (23)$$

We note in passing that the Fourier transform G_k of $G(z)$ may be determined

directly from the experimentally known liquid structure factor F_k ,

$$\begin{aligned} F_k &= N^{-1} \langle \sum_i \sum_j \exp(ik \cdot (r_i - r_j)) \rangle \\ &= 1 + \frac{4\pi n_0}{k} \int_0^\infty dr r \sin kr [g_0(r) - 1]. \end{aligned} \quad (24)$$

For,

$$\begin{aligned} G_k &= \int_{-\infty}^\infty dz e^{ikz} G(z) \\ &= 4\pi \int_0^\infty dz \cos kz \int_z^\infty dr r [g_0(r) - 1] \\ &= \frac{4\pi}{k} \int_0^\infty dr r \sin kr [g_0(r) - 1] \\ &= n_0^{-1} (F_k - 1). \end{aligned} \quad (25)$$

It remains to find the relation between n and s . Equation (16) suggests the functional form

$$n(z) = n_0 s^2(z) e^{u(z)}; \quad (26)$$

taking variations of (26) and using (16) and (19), we find that u satisfies

$$\delta u(z_1) = 2 \int dr_2 \frac{\delta s(z_2)}{s(z_2)} n(z_2) [g(r_1, r_2) - 1]. \quad (27)$$

An approximate solution of this equation can be obtained by replacing $g(r_1, r_2)$ by $g_0(r_{12})$. Then we have

$$\delta u(z_1) = n_0 \int dr_2 2\delta s(z_2) s(z_2) e^{u(z_2)} [g_0(r_{12}) - 1] \quad (28)$$

which, to lowest order in n_0 , has the solution

$$\begin{aligned} u(z_1) &= n_0 \int dr_2 [s^2(z_2) e^{u(z_2)} - 1] [g_0(r_{12}) - 1] \\ &= n_0 \int dz_2 [s^2(z_2) e^{u(z_2)} - 1] G(z_1 - z_2). \end{aligned} \quad (29)$$

With these approximations, s is determined in terms of g_0 by the non-linear integro-differential equation

$$\frac{s''(z_1)}{s(z_1)} + \frac{u'(z_1)s'(z_1)}{s(z_1)} = n_0 \int dz_2 e^{u(z_2)} \{s'(z_2)\}^2 G(z_1 - z_2). \quad (30)$$

This equation has some unexpected properties. For example, it cannot have a solution which goes to zero exponentially outside the fluid (as does the most obvious trial form for s , namely a Fermi function, or a power of such a function¹⁰). This is because for such functions the left side of (30) tends to a constant outside

the fluid, while the right side tends to zero. It is not clear at present whether the indicated long-range behaviour is a consequence of the approximations made, or whether it is an intrinsic property of the surface of a Bose fluid.

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