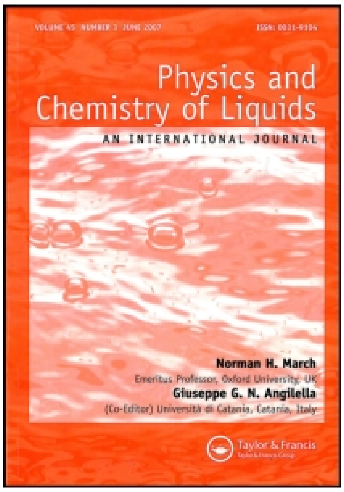

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Letter

FREE SURFACE THICKNESS OF LIQUID ^{4}HE AT ZERO TEMPERATURE RELATED TO SURFACE ENERGY TIMES BULK COMPRESSIBILITY

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In a low-order density gradient version of density functional theory, the surface energy σ of liquid ^{4}He at $T = 0$ is written alternatively in terms of (i) the gradient $\nabla\rho$ of the particle density profile $\rho(z)$ for a planar surface and (ii) the 'local' energy density. As a byproduct of (ii), it is shown that the product $\sigma\kappa$, with κ the bulk compressibility, is related to the surface thickness.

Keywords: Density functional theory; surface energy and thickness

In classical liquids Frenkel, followed by Cahn and Hilliard [1], was already aware of a relation between surface tension σ and bulk isothermal compressibility κ, namely

$$\sigma\kappa \approx \ell \tag{1}$$

with ℓ a measure of the surface thickness. The relation of Eq. (1) to experiment was established especially by the work of Egelstaff and Widom [2]. The later study of Bhatia and March [3] derived Eq. (1) from a low-order density gradient expansion of the free energy, based on the work of Yang *et al.* [4] for classical liquids. A quantal derivation

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of Eq. (1) was already established for simple $s-p$ liquid metals near freezing in the investigation of Brown and March [5]. Electron-hole liquids were dealt with in the study of Singwi and Tosi [6].

Recent work of Tozzini and Tosi [7] on lattice vacancies in solid ^{4}He has caused us to re-open the above area, with specific reference to liquid ^{4}He in its ground state. This is because, in a simple $s-p$ liquid metal such as Al, the electron density profile around a vacancy is hardly distinguishable from that at a liquid metal surface [8]. Of course, no such simple reasoning will work in ^{4}He but the above results were the initial motivation for the present study (see also more on the vacancy formation energy E_v in the concluding remarks).

Using Jastrow-like trial wave functions, much microscopic theory has been carried out on the free surface of liquid ^{4}He. Some of this is summarized in the work of Krotscheck *et al.* [9]. However, these workers also considered a phenomenological treatment based on density functional theory plus the assumption of low-order gradient expansions. After a modest generalization of their phenomenology set out below, we use the resulting treatment of surface energy to regain the form (1) for the ground state of liquid ^{4}He.

The basic assumption of the phenomenology is then that there is an energy functional for the ground state of liquid ^{4}He with a free surface of the form

$$E = T + E_c = \int d\mathbf{r}\varepsilon[\rho(\mathbf{r}), \nabla\rho(\mathbf{r})]. \tag{2}$$

Here the energy density ε is a sum of a free-particle kinetic energy $t(\mathbf{r})$ and a correlation energy contribution $\varepsilon_c(\mathbf{r})$, where

$$t(\mathbf{r}) = \frac{\hbar^2}{2m}\left|\nabla\sqrt{\rho(\mathbf{r})}\right|^2, \tag{3}$$

with m the mass of the ^{4}He atom and $\rho(\mathbf{r})$ the atomic density profile in the inhomogeneous quantal fluid.

Following Krotscheck *et al.* [9], who refer to early work of Skyrme,

$$\varepsilon_c(\mathbf{r}) = \varepsilon_c(\rho(\mathbf{r})) + d|\nabla\rho(\mathbf{r})|^2. \tag{4}$$

In Ref. [9] a form of the 'local' term $\varepsilon_c(\rho(\mathbf{r}))$ in Eq. (4) is specified in parametrized form, but we shall leave here the form of $\varepsilon_c(\rho(\mathbf{r}))$ as quite general.

The equation to determine the density profile then follows from Eqs. (2)–(4) *via*

$$\frac{\delta(E-N\mu)}{\delta\rho(\mathbf{r})}=0 \tag{5}$$

where μ is the (constant) chemical potential in the inhomogeneous fluid, taking care of the normalization condition

$$\int d\mathbf{r}\rho(\mathbf{r})=N. \tag{6}$$

Following Krotscheck *et al.* [9], one is then led to one form of the surface energy σ as

$$\sigma=2T+2d\int dz|\rho'(z)|^2 \tag{7}$$

for a planar surface in the (x, y) plane. The kinetic energy T is evidently now, in Eq. (6), to be taken per unit area in the (x, y) plane. We note that Eq. (6), being determined solely by density gradients (see Eq. (3) for $T=\int d\mathbf{r}t(\mathbf{r})$), can be viewed as the quantal analogue of the very early treatment of van der Waals.

However, to reach a form equivalent to Eq. (1), we now seek a 'local' equation for the pressure p across the inhomogeneity caused by the free surface. To motivate this, we note first the thermodynamic relation

$$p=\rho\mu-\rho\frac{E}{N} \tag{8}$$

and writing the 'local' version of this we are led to

$$\begin{aligned} p &= \mu\rho(z)-t(z)-\varepsilon_c(z) \\ &= p(\rho(z))+p_{\text{density gradient}}(z). \end{aligned} \tag{9}$$

Returning to Eq. (7), which is equivalent from Eq. (9) to

$$\sigma=2\int dz p_{\text{density gradient}}(z) \tag{10}$$

we use Eq. (9), with

$$p(\rho(z)) = \mu\rho(z) - \varepsilon_c(\rho(z)) \tag{11}$$

to find

$$\sigma = 2\int dz[p - \mu\rho(z) + \varepsilon_c(\rho(z))]. \tag{12}$$

Following Bhatia and March [3], we note that $p_{\text{density gradient}}(z)$ in Eq. (10) is only non-zero over a distance of the order of the surface thickness. Therefore the integration in Eq. (12) extends only over such a range of z. Expanding around the bulk liquid density ρ_ℓ and using $\kappa^{-1} = \rho^2 d^2\varepsilon_c(\rho)/d\rho^2$, one is led back to a form of Eq. (1). The length ℓ one thereby obtains using experimental values of σ and κ is 0.15 Å which is of the same order as for classical liquids such as Ar or the liquid metal Na near freezing.

Quantitative error for liquid ^{4}He is, no doubt, introduced by expanding around the bulk liquid density in Eq. (12). However, its merit is that one is thereby able to retain a general form of $\varepsilon_c(\rho)$, whereas to evaluate the van der Waals form (7) of the surface tension one must evidently solve for the density profile $\rho(z)$ for a specified form of $\varepsilon_c(\rho)$ as in Ref. [9].

A final comment takes us back to the vacancy formation energy E_v. In Ref. [7], this is estimated in cubic phases to be ≈ 10 K. Estimates for classical crystals indicate that E_v is of the order of magnitude of $B\Omega$ with B the isothermal bulk modulus and Ω the atomic volume. However, for ^{4}He $B\Omega$ is ≈ 70 K and this warns against pressing too far the analogies between defect (and perhaps also surface) properties of quantal and classical systems.

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