

Density Functional Theory of the Interface between Solid and Superfluid Helium 4

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We report a calculation of the equilibrium profile of the interface between superfluid helium 4 and its solid phase at 0 K. To calculate the excess energy of the interface, we use the density functional theory that allowed us to obtain the equilibrium density of both phases. We compare our result to the experiment and to a previous microscopic calculation.

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1. INTRODUCTION

How far can superfluid helium be pressurized before it crystallizes? Recent experiments¹ have quenched the liquid as far as 140 bar above the freezing pressure $P_f = 25.3$ bar at low temperature without observing nucleation of crystals. This contradicts the standard nucleation theory which predicts the formation of crystals around only 40 bar above P_f .²

One of the key parameters in this theory is the interfacial tension γ between the liquid and solid phases. Helium is among the few substances for which this quantity has been directly measured: $\gamma = 0.17$ mN m⁻¹.³ However, the relevance of the equilibrium value at freezing to describe deep quenches of the liquid phase can be questioned, and an effective interfacial tension varying with pressure has been recently proposed.⁴

Density functional theory (DFT) should be able to clarify this issue. Using a functional designed for superfluid helium, the Orsay-Trento functional⁵ (OTF), we have shown how to reproduce the equilibrium parameters and the equation of state of the solid in a satisfactory way.⁶ We shall now use the same input to compute the equilibrium interfacial profile. Many DFT ap-

proaches to this problem have been explored for classical systems;⁷ some of them rely on the simplifying approximation of a broad interface. The purpose of this paper is to rewrite this approximation in the quantum case, and to determine whether it is valid for helium.

We shall first briefly recall the quantum DFT formalism and our previous results. We will then present the application of DFT to the calculation of a broad interface, and compare the results obtained for helium at freezing to the available information.

2. DENSITY FUNCTIONAL FORMALISM

We first recall the main lines of our previous calculation.⁶ The solid is treated as a spatially periodic perturbation (density $\rho_s(\mathbf{r})$) of the uniform liquid (density ρ_l). The difference in energy between both phases is obtained by a Taylor expansion in the one particle density, truncated to second order:

$$\Delta E[\rho] = E_{\text{id}}[\rho] + \int d\mathbf{r} \left(\frac{\delta E_{\text{int}}}{\delta \rho(\mathbf{r})} \right)_1 \delta \rho(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \left(\frac{\delta^2 E_{\text{int}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right)_1 \delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}') \quad (1)$$

with $\delta \rho(\mathbf{r}) = \rho_s(\mathbf{r}) - \rho_l$, E_{id} the energy of the noninteracting inhomogeneous system and E_{int} the interacting part of the energy. For Bose particles of mass m , E_{id} is the kinetic energy:

$$E_{\text{id}} = \frac{\hbar^2}{2m} \int d\mathbf{r} \frac{[\nabla \rho(\mathbf{r})]^2}{4 \rho(\mathbf{r})} \quad (2)$$

The second term on the right hand side of Eq. 1 is the mass term: the derivative of E_{int} is the chemical potential μ_l of the liquid. The third term involves the direct correlation function (DCF)

$$\left(\frac{\delta^2 E_{\text{int}}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} \right)_1 = v(|\mathbf{r} - \mathbf{r}'|; \rho_l) \quad (3)$$

which is the quantum analog of the classical Ornstein-Zernike DCF. Dealing with a periodic density, the calculations are more conveniently carried out in Fourier space; the Fourier transform of v is related to the static density-density response function χ of the liquid:

$$v(q; \rho_l) = \frac{1}{\chi_0(q)} - \frac{1}{\chi(q)} \quad (4)$$

where χ_0 is the non-interacting limit: $\chi_0(q) = -(4m\rho_l)/(\hbar^2 q^2)$.

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For a given liquid density, the grand potential difference $\Delta\Omega = \Delta E - \mu V(\rho_s - \rho_l)$ is minimized to find the most stable solid. We use a variational approach, parameterizing the solid by gaussians centered on a fcc lattice:

$$\rho_s(\mathbf{r}) = \sum_{\mathbf{R}_j} \left(\frac{\alpha}{\pi}\right)^{3/2} \exp\left(-\alpha|\mathbf{r} - \mathbf{R}_j|^2\right) \quad (5)$$

For each liquid density ρ_l , we determine the optimum solid density ρ_s and gaussian width α . ρ_l is then varied until $\Delta\Omega$ is zero, corresponding to the two phases at equilibrium.

For the DCF, we used the one obtained with the Orsay-Trento functional (OTF).⁵ To obtain freezing at $\rho_l\sigma^3 = 0.4346$ (near the experimental value 0.4345⁸), where $\sigma = 0.2556$ nm, we had to rescale the DCF at non-vanishing q 's by a factor 0.9369.⁶ With no more adjustable parameters, this gives a solid density at equilibrium $\rho_s\sigma^3 = 0.5127$, in reasonable agreement with the experiment⁸ (0.4793). Given this shift in the melting density, the experimental pressure dependence of the solid EOS is well reproduced.

As the equilibrium liquid-solid surface tension can be found within the same formalism with no additional fitting parameters, its calculation would provide a consistent check of our DFT approach. We now turn to our attempt in this direction.

3. THE SQUARE GRADIENT APPROXIMATION

Let us consider the one dimensional problem of a flat interface extending perpendicularly to an axis $\hat{\mathbf{z}}$. The density profile can be written as:

$$\rho(\mathbf{r}) = \rho_l \left(1 + \sum_j \mu_j(z) e^{i\mathbf{k}_j \cdot \mathbf{r}} \right) \quad (6)$$

where the \mathbf{k}_j 's are the reciprocal lattice vectors (RLVs) and the order parameters μ_j vary through the interface, from the solid to the liquid values.

The excess energy of the interface is again given by Eq. 1. When the μ_j 's vary slowly on the distance between two atomic layers, their second order Taylor expansion may be used to calculate the interacting part. In the classical case, as E_{id} includes only local terms of the density, this square gradient approximation (SGA) leads to:⁷

$$\Delta\Omega = \Delta\Omega^{\text{local}}[\rho(\mathbf{r})] + \frac{\rho_l^2}{4} \int d\mathbf{r} \sum_j (\hat{\mathbf{k}}_j \cdot \hat{\mathbf{z}})^2 v_j'' \left| \frac{\partial \mu_j}{\partial z} \right|^2 \quad (7)$$

where $\Delta\Omega^{\text{local}}$ groups all local terms, $\hat{\mathbf{k}}_j = \mathbf{k}_j/|\mathbf{k}_j|$, and $v_j'' = v''(|\mathbf{k}_j|)$.

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An intrinsic failure of the SGA appears in this expression: if one of the v_j'' is negative, a steep μ_j is favored and the energy has no lower bound! This is usually fixed by forcing all μ_j 's to have the same profile; a reason invoked for this for the non zero values of j is the positiveness of the density reconstructed from the μ_j 's.¹⁰ v_0'' is more problematic and it should be negative for most classical systems; this drawback is fixed either by forcing μ_0 to follow the common profile, or by setting $v_0'' = 0$ because its magnitude is smaller than other v_j'' 's.

To compute the v_j'' 's in the case of superfluid helium, we use the rescaled OTF.⁶ However, the DCF is not accurate for low q 's and the value it gives for $v_0'' \simeq 45 \hbar^2 \sigma^3 / m$ is not reliable. We can still estimate it by using the Feynmann approximation, relating the DCF and the energy spectrum to the static response function $S(q)$. The phonon dispersion relation $\omega(q) = cq(1 + \alpha_2 q^2 + \dots)$ (see Ref. 9) leads to

$$v_0'' = \frac{4mc^2\alpha_2}{\rho_1} - \frac{\hbar^2}{2m\rho_1} \quad (8)$$

Near freezing, superfluid helium exhibits normal phonon dispersion:⁹ α_2 is small and negative and $v_0'' \simeq -\hbar^2/(2m\rho_1) = -1.1 \hbar^2 \sigma^3 / m$. Therefore we have to deal with the same problem as for classical systems; however, in the quantum case positive terms coming from the non local part of the kinetic energy could balance the negative ones in the interaction energy. In this paper we will set v_0'' to zero.

4. RESULTS AND DISCUSSION

In the quantum case, extra terms arise in Eq. 7 because of the non-local character of the kinetic energy. To evaluate its contribution, we first have to choose a family of profiles. Following Ref. 10, we take a linear combination of the equilibrium densities:

$$\rho(\mathbf{r}) = [1 - f(z)] \rho_1 + f(z) \rho_s(\mathbf{r}) \quad (9)$$

where f is a function going from 1 on the solid side to 0 on the liquid side. All the μ_j 's then follow the same profile determined by f . We have:

$$\nabla \rho = f(z) \nabla \rho_s(\mathbf{r}) + f'(z) [\rho_s(\mathbf{r}) - \rho_1] \hat{\mathbf{z}} \quad (10)$$

The integral giving the extra energy may be divided into a sum of integrals over unit cells of the lattice; in the case of a broad interface, the rapidly varying coefficients of f and f' can be replaced by their average

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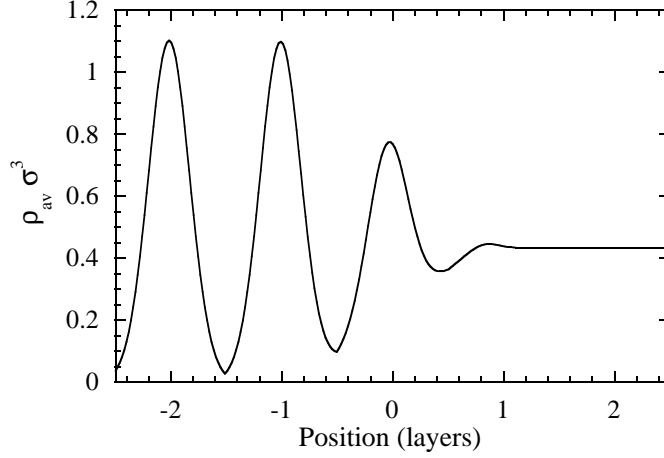


Fig. 1. Equilibrium profile obtained with the SGA and the complete kinetic energy. The density has been averaged on planes parallel to the 100 interface.

value over each cell. In the following we consider the 100 interface. For the moment, let us just keep the local term in f in the kinetic energy, while keeping the gradient terms in the interacting part. The problem becomes analytical if we neglect $(1-f)\rho_l$ in the denominator of E_{id} ; in doing so we overestimate the first term in $\Delta\Omega$. Using $\Delta\Omega_s = 0$ we find for an area S :

$$\frac{\Delta\Omega_{(100)}}{S} = \rho_s \int dz f(z)[1-f(z)]E_{id,s} + \frac{\rho_s^2}{4} \int d\mathbf{r} \sum_j (\hat{\mathbf{k}}_j \cdot \hat{\mathbf{z}})^2 v_j'' \left| \frac{\partial \mu_j}{\partial z} \right|^2 \quad (11)$$

where $E_{id,s} = 3\hbar^2\alpha/(4m)$. The minimization is then equivalent to solving the differential equation:

$$E_{id,s}(1-2f) - \frac{\rho_s^2}{2} \left[\sum_j (\hat{\mathbf{k}}_j \cdot \hat{\mathbf{z}})^2 v_j'' e^{-\mathbf{k}_j^2/(2\alpha)} \right] f'' \equiv a(1-2f) - 2bf'' = 0 \quad (12)$$

The solution connecting both phases is $f(z) = \{1 - \sin[\pi z/(2\xi)]\}/2$ where $\xi = \sqrt{b/a}$ and $|z| \leq \xi$. The corresponding surface tension is $\gamma = (\pi/4)\sqrt{ab}$. Keeping the first five sets of RLVs as in our equilibrium calculation, this gives $2\xi = 0.33$ nm and $\gamma = 0.72$ mN m $^{-1}$. As the distance between lattice planes is 0.25 nm, we see that the assumption of a wide interface fails.

Let us now take the complete denominator and the gradient terms in E_{id} into account. We note that the cross term from Eq. 10 vanishes by parity, when averaged over a unit cell. We still use $f(z) = \{1 - \sin[\pi z/(2\xi)]\}/2$ and solve for the value of ξ that minimizes Eq. 1. If we keep only the local term in E_{id} , this leads to $2\xi = 0.53$ nm and $\gamma = 0.45$ mN m $^{-1}$; if we take the gradient term into account, we find $2\xi = 0.56$ nm and $\gamma = 0.47$ mN m $^{-1}$.

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Method	Ref.	$\rho_l \sigma^3$	$\rho_s \sigma^3$	γ (mN m ⁻¹)	ξ (nm)
Exp.	3	0.4345	0.4793	0.17	
VMC	11	0.449 ± 0.001	0.456 ± 0.002	0.25 ± 0.1	1-1.25
DFT	present	0.4346	0.5127	0.47	0.56

Table 1. Comparison between available values of the interface parameters.

The interface obtained extends only over three lattice planes: this is not sufficient to justify the SGA. However, it appears that in the classical hard spheres system,¹⁰ the single order parameter SGA gave results close to the one from a direct numerical calculation of Eq. 1. Thus we may still compare our result to the available experimental³ and theoretical¹¹ data, as is done in Table 1. The experimental value for γ is within the error bars of the previous theory, which used a variational Monte Carlo simulation (VMC); the poorer agreement on the densities is of little concern, since the main contribution to γ comes from the change in localization. The VMC calculation gives also access to the width of the interface (4 or 5 layers), which has not yet been measured. We think that the failure of the SGA agrees with such a narrow interface, and the value we obtain for γ , although large, encourages us to turn to the full calculation.

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