

Density Functional Theory of Freezing of Superfluid Helium 4

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*We discuss freezing of superfluid helium 4 in the frame of density functional theory. We first review the previous attempts made with different inputs for the liquid properties. We then present a new calculation based on a more recent input. Our result confirms the finding by Likos et al. [C.N. Likos, S. Moroni, and G. Senatore, Phys. Rev. B, **55**, 8867 (1997)] that the solid is always too stable. However, a slight rescaling leads to freezing parameters and an equation of state for the solid consistent with the experiments. We discuss the physical origin of this rescaling.*

PACS numbers: 64.70.Dv, 67.40.Kh, 67.80.-s

1. INTRODUCTION

One of the numerous peculiarities of helium is that it does not exhibit any triple point, where solid, liquid and gas phases coexist. This behaviour is attributed to the zero point energy of helium atoms.¹ To give a quantitative prediction of the freezing pressure P_f at zero temperature, one can resort to Monte-Carlo simulations or density functional theory (DFT). We are interested in the latter, because it appears to be a more flexible tool and potentially provides a way to describe properly the nucleation of the solid phase in the metastable superfluid. This issue has been raised by recent experiments² which use a focused ultrasonic wave to quench the superfluid far above P_f : despite the huge pressures reached (up to 165 bar), helium remains liquid, in contradiction with standard nucleation theory which predicts nucleation of crystals below 67 bar.³

DFT of freezing was first developed to describe classical systems (for

a review, see Refs. 4 and 5). This approach does not only provide predictions for the freezing parameters, but also information on the solid-liquid interfacial properties and on nucleation. The attempts to adapt DFT to the freezing of quantum systems fall in two categories: at temperatures high enough for the interparticle exchange to be neglected,^{6–8} and at zero temperature in the degenerate limit. We are concerned with the latter. We first recall the formalism and then give a review of the corresponding results. One of the keys to this theory is the liquid properties input; using an input different from the previous studies, we find a solid which is always more stable than the liquid. We will finally consider a possible correction of the input which gives freezing parameters and an equation of state (EOS) for the solid in reasonable agreement with the experiments.

2. DFT OF QUANTUM FREEZING AT ZERO TEMPERATURE

DFT assumes that the energy of interacting particles can be written as a functional of the one particle density. We will focus here on the quantum version of the so-called Ramakrishnan-Yussouff method (RY).^{9,10} We recall only the main lines of RY and refer the reader to Refs. 11 and 12 for more details. RY treats the solid 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 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:

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

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 linear 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: $\chi_0(q) = -(4m\rho_l)/(\hbar^2 q^2)$.

To find equilibrium one usually considers the grand-canonical system. Choosing a liquid density ρ_l in a fixed volume V , one finds the most stable solid at the same chemical potential $\mu = \mu_l$ by minimizing the grand-potential difference $\Delta\Omega = \Delta E - \mu V(\rho_s - \rho_l)$. Instead of performing the full minimization, one usually resorts to a variational approach, parameterizing the solid by gaussians centered at the lattice sites.^{11,12} The fcc lattice is usually chosen, although helium actually freezes into hcp at zero temperature; fcc is easier to handle, and the two symmetries were found to give scarcely distinct results.¹³ The minimum in $\Delta\Omega$ results from the competition between the interaction term in Eq. 1, which favours localization, and the kinetic term which tends to homogenize the system.

Then ρ_l is varied until the minimum $\Delta\Omega$ is zero: the pressure of the two phases is then also the same and this corresponds to liquid-solid coexistence; it is equivalent to the Maxwell double tangent construction. From other values of ρ_l , one obtains $\mu_s(\rho_s)$ which is integrated to give the solid EOS.

The key point of this theory is to supply the correct DCF, or equivalently by Eq. 4 the correct function χ . It is related to the inverse energy-weighted moment of the dynamic form factor $S(q, \omega)$ obtained in neutron scattering experiments:

$$\chi(q) = -2\rho_l \int_0^{+\infty} d\omega \frac{S(q, \omega)}{\omega} \quad (5)$$

Unfortunately these experimental data are at the moment available at low pressure only.¹⁴ We will see in the next section which inputs were chosen.

3. PREVIOUS RESULTS

The first attempt to describe freezing of a degenerate quantum system within the frame of DFT was made by Denton *et al.*¹³ on the Bose hard-sphere liquid. In fact they used a development different from RY: the so-called modified weighted-density approximation, which goes beyond the second-order truncation. However, the principle is similar and they also need the function χ as an input; it was evaluated within the Feynman approximation (FA):

$$\chi(q) = [S(q)]^2 \chi_0(q) \quad (6)$$

with $S(q)$ the zeroth moment of $S(q, \omega)$, obtained from simulations (see Refs. 13, 15 and 16 for details). It is known that FA provides only a lower bound for χ ; furthermore, it does not satisfy the compressibility sum rule: $v(0; \rho_1) = mc^2/\rho_1$, where c is the sound velocity, which should be used at $q = 0$. To correct this, Denton *et al.* (i) rescaled χ by the same factor ($\simeq 1.2$) for all q 's^{13,15} or (ii) used the compressibility sum rule for $v(0)$ and kept the raw DCF for non-vanishing q 's.¹⁶ They find that freezing does occur. In case (i), the agreement with variational Monte-Carlo simulations¹⁷ is reasonable, both for the freezing parameters and for the solid EOS, whereas it is poor in case (ii). Denton *et al.* also tried the RY method in case (i): they find freezing, with less satisfactory parameters.

Freezing of helium 4 at zero temperature was investigated with the RY method by two groups.^{11,12} They use the sum rule value for $v(0)$. Both of them notice that when using for the input Eq. 6 with $S(q)$ from Green's-function Monte-Carlo simulations (GFMC),¹⁸ freezing does not occur for reasonable densities. Moroni and Senatore tried two empirical corrections for non-vanishing q 's: (i) to rescale the DCF by a constant (1.23) or (ii) to shift the DCF by a constant (-1.52 K). These values were chosen to get freezing at the same liquid density than GFMC; they lead to solid density values close to GFMC¹⁸ and experimental¹⁹ ones. Dalfovo *et al.*¹¹ used a different input for χ , obtained from the so-called Orsay-Paris functional (OPF).²⁰ This leads to freezing, although at quite high densities. Both groups have shown that because of the large delocalization of solid atoms, it is required to take the overlap between lattice sites into account. Neglecting it causes a few percent error in the densities.

The last approach to date²¹ used yet another input for χ , directly calculated by quantum Monte-Carlo calculations,²² instead of resorting to FA. This leads to a pathological result: $\Delta\Omega$ is not bounded from below at high densities; even for low liquid densities, it exhibits a negative minimum. This means that the solid is predicted to be always the stable phase. The origin of this failure has been pointed out: the simulated DCF is negative for all values of the reciprocal lattice vectors, thus leading to strong localization.²¹

4. THE ORSAY-TRENTO SUPERFLUID

An improvement of the OPF, called the Orsay-Trento functional (OTF), was built by adding to the hamiltonian of the system a nonlocal correction to the kinetic energy.²⁴ The parameters involved were chosen to reproduce the experimental value of χ at low pressure.¹⁴ It should be noted that, due to the lack of other experimental data, Dalfovo *et al.*²⁴ included a density factor

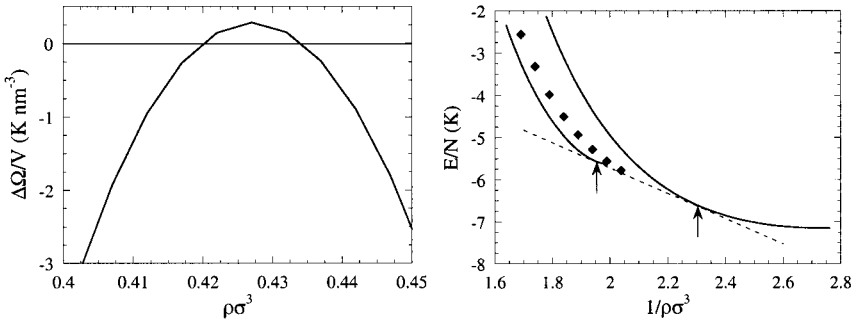


Fig. 1. (a) Grand-potential difference per unit volume as a function of liquid density for OTF rescaled by 0.9306. (b) Solid and liquid energy per particle as a function of volume per particle as predicted in the present work. The diamonds are the experimental data for the solid.²³ The arrows indicate the calculated coexistence values. The dashed line illustrates the Maxwell construction.

to obtain a pressure variation of χ close to the direct simulation results:^{22,21} the peak in χ changes by about 10% between 0 and P_f .

We have used this OTF as the input to treat freezing with the RY method, neglecting the overlap between gaussians. We do not find any freezing: $\Delta\Omega$ is always negative. However, in contrast with Ref. 21, we do not find any pathology: $\Delta\Omega$ always remains bounded from below. This difference arises from the fact that the present DCF oscillates around zero instead of being always negative in the roton region.

Following Ref. 12, we have tried to rescale the DCF at non-vanishing q 's. As shown on Fig. 1 (a), the factor 0.9306 leads to freezing at $\rho_l\sigma^3 = 0.4343$, near the experimental value (0.4345), where $\sigma = 0.2556$ nm. The retracing of $\Delta\Omega$ at low density seems unphysical, and may be related to the poor quality of the second order truncation far away from coexistence. Now with no more adjustable parameter, we find a solid density at equilibrium $\rho_s\sigma^3 = 0.5122$, in reasonable agreement with the experiment¹⁹ (0.4793). As shown on Fig. 1 (b), we also find a solid EOS in semi-quantitative agreement with experimental data.²³

5. DISCUSSION

We have shown that a slight rescaling (about 7%) of the DCF obtained with the OTF was sufficient to obtain a satisfactory description of freezing of superfluid helium 4 at zero temperature. We see two possible reasons for

the need of such a rescaling. The first one is that the pressure variation for χ used in OTF (see Sec. 4.) could be overestimated. Clearly an analysis of neutron scattering data at high pressure is needed. The second reason is that the superfluidity of the liquid does not appear explicitly in the DFT of freezing; as the condensate fraction of the liquid amounts to roughly 8% at saturated vapour pressure,²⁵ we wonder if it plays a role in the rescaling.

Our calculation was performed for a fcc crystal, neglecting the overlap between neighbouring atoms; we plan to study hcp and to take the overlap into account. The next check of the DFT is to estimate the liquid-solid surface tension and compare with the experiment.²⁶ It would open the way to the theory of homogeneous nucleation in the overpressurized superfluid.

One of us (TM) thanks S. Balibar for his hospitality in Paris. Part of this work was supported by Yoshida Science Fundation and ENS-PR0135.

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