A non-perturbative approach to freezing of superfluid $^4$He in density functional theory

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Abstract. Freezing of various classical liquids is successfully described by density functional theory (DFT). On the other hand, so far no report has been published that DFT describes the freezing of superfluid $^4$He correctly. In fact, DFT gives too stable solid phase and the superfluid phase does not exist at finite positive pressures within a second order perturbation. In this paper we try a non-perturbative version of DFT, that is modified weighted density approximation (MWDA) to go beyond second order perturbation for the freezing of superfluid $^4$He. Via an exact zero temperature quantum Monte-Carlo (QMC) method we have computed the equation of state and the compressibility of superfluid $^4$He. By utilizing a recently introduced analytic continuation method (the GIFT method), we have obtained also density response functions at different densities from QMC imaginary time correlation functions. Contrary to second order perturbation, by employing these QMC data as DFT input we find a too stable superfluid phase, preventing freezing around the experimentally observed freezing pressure. We find the same pathological behavior by using another model energy functional of superfluid $^4$He (Orsay-Trento model). We conclude that the straightforward MWDA calculation gives such a poor result when liquid-gas transition is present.

1. Introduction

Density functional theory (DFT) is known to be a successful frame to describe freezing of various classical liquids [1]. As for the freezing of superfluid $^4$He, on the other hand, the frame has been suffering from too stable solid pathology [2] since when a reliable DFT input is obtained through quantum monte carlo simulation (QMC) at least for the version of second order truncation (SOT) which is a simple extension of Ramakrishnan-Yussouf theory of classical liquid freezing. Recently, we confirmed the same pathology [3] with use of recently invented analytic continuation method (GIFT method) [4], which enables us to extract another accurate input from the discrete imaginary time data by QMC. Therefore, the pathology should imply inapplicability of SOT rather than inaccuracy of input.

We shall try in this paper to go beyond SOT by employing a non-perturbative method named modified weighted density approximation (MWDA) [5]. In the next section, we introduce the frame of MWDA. In the third section, we give the ground state energy of superfluid and direct correlation functions for DFT inputs. We also touch an model energy functional, by which we have those inputs at any pressure easily within the model. In both cases, contrary to the result
of SOT, we find too stable liquid pathology: We will conclude in the final section that superfluid state is too stable and freezing never occurs around experimentally observed freezing pressure.

2. MWDA calculation
At zero temperature, let us assume that we obtain the ground state energy of liquid ⁴He per particle ɛ(ρ₁) and direct correlation function (DCF) \( \tilde{\psi}(q; \rho_1) \) at various wave number \( q \) and at various constant densities \( \rho_l \) over wide range. Then in the presence of density modulation, practically a periodic Gaussian packet on a fcc crystalline lattice \( \{\tilde{R}_j\} \) (to approximate hcp crystal of ⁴He):

\[
\rho_s(\vec{r}) = \sum_{\tilde{R}_j} \left( \frac{\alpha}{\pi} \right)^{3/2} \exp \left( -\alpha |\vec{r} - \tilde{R}_j|^2 \right) ,
\]

(1)

MWDA gives the ground state energy of the system per particle by \( \varepsilon_{MWDA}^{MWDA}[\rho_s] = \varepsilon_{id}[\rho_s] + \varepsilon(\tilde{\rho}(\alpha, \rho_s)) \). Here the constant density, named ‘weighted density’ \( \tilde{\rho} \) is a function of the average density \( \rho_s \) of (1) and the localization parameter \( \alpha \). \( \tilde{\rho} \) is obtained by solving the self-consistent equation:

\[
\tilde{\rho}(\alpha, \rho_s) = \rho_s \{1 + \frac{1}{2\varepsilon(\tilde{\rho})} \sum_{\mathbb{G} \neq 0} \exp^{-q^2/(2\alpha)} \tilde{\psi}(\mathbb{G}; \tilde{\rho})\},
\]

(2)

where \( \{\mathbb{G}\} \) is the reciprocal lattice vectors (RLVs) of the fcc direct lattice, and \( \mathbb{G} \) the magnitude of RLVs. \( \varepsilon_{id}[\rho_s] \) is the ground state energy of ideal Bose gas per particle and exactly calculable. Especially for sharp localization, we can neglect overlap of the Gaussian packets and have \( \varepsilon_{id}[\rho_s] \approx (3\hbar^2/4m)\alpha \), where \( \hbar \) and \( m \) are the Planck constant and bare atomic mass respectively. In this case, we have [5]

\[
\varepsilon_{MWDA}^{MWDA}[\rho_s] = \frac{3\hbar^2}{4m} \alpha + \varepsilon(\tilde{\rho}(\alpha, \rho_s)).
\]

(3)

Fixing \( \rho_s \), we obtain \( \varepsilon_{MWDA}^{MWDA}[\rho_s] \) as a function of \( \alpha \) by the procedure above. If \( \varepsilon_{MWDA}^{MWDA}[\rho_s] \) has a minimum at some value \( \alpha^*_s \) such a density modulation specified by \( (\alpha^*_s, \rho_s) \) is mechanically stable and called ‘solid’. Hereafter, we shall call the density modulation (1) ‘solid density’, regardless of its stability. We will conclude in Fig.3 that no such a stability appears not only for the melting density of solid hcp ⁴He, \( \rho_s = 0.0286 \text{Å}^{-3} \), but also for the higher density 0.030Å⁻³.

3. DFT inputs: The ground state energy of superfluid and direct correlation function
In our QMC calculations ⁴He atoms have been modeled as structureless zero-spin bosons, interacting through a realistic two-body potential, that we have assumed to be the HFDHE2 Aziz potential [6]. We calculate directly the ground state energy per particle \( \varepsilon(\rho_l) \) by using the “exact” zero–temperature shadow path integral ground state (SPIGS) method [7]. We find

\[
\varepsilon(\rho_l) = a + b(\rho_l/\rho_0 - 1)^2 + c(\rho_l/\rho_0 - 1)^3
\]

(4)

with parameters \( a = -7.3509 \pm 0.0021 \), \( b = 13.65 \pm 0.25 \), \( c = 7.58 \pm 0.46 \) in Kelvin and \( \rho_0 = 0.022064 \pm 0.000018 \text{Å}^{-3} \).

As for DCF, we have proceeded in the same way as in our previous report [3], but this time at seven liquid densities \( \rho_l = 0.0200, 0.0218, 0.0240, 0.0260, 0.0273, 0.0290, 0.0300 \text{Å}^{-3} \). We extract real time dynamics from SPIGS imaginary time correlation functions by using the GIFT method [4]. Note that superfluid state at \( \rho_l > 0.0260 \) is metastable, and the solid phase is the true stable phase for densities above the melting one; however, starting from a disordered configuration, the metastable liquid phase was found persistent with no sign of crystallization, allowing us to
perform calculations also in metastable liquid states. Also superfluid at $\rho_l < 0.0221$ was found uniform liquid, although it is metastable against cavitation. Since MWDA requires DCF as a continuous function of $\rho_l$ over wide range, we linearly interpolate those DCFs of seven densities for each wave number $q$. Since the range of $q$ is sufficiently wide in our DCFs, we perform the summation up to 15th reciprocal lattice shell in (2).

4. Result and discussion

![Figure 1](image1.png)

**Figure 1.** The self-consistent equation (2) is graphically illustrated at $\rho_s = 0.0286 \text{Å}^{-3}$. See the text for the detail.

![Figure 2](image2.png)

**Figure 2.** The 'normal' weighted density versus localization parameter at $\rho_s = 0.0286 \text{Å}^{-3}$ (open circles) and $0.030 \text{Å}^{-3}$ (filled circles). There is no solution for $\alpha > \alpha^*$, where $\alpha^*$ is the positions denoted by asterisk.

We carry out calculation for $\rho_s = 0.0286 \text{Å}^{-3}$ and $0.030 \text{Å}^{-3}$ which correspond respectively to the melting density and the density well above the melting density of solid $^4$He at low temperature [8]. In Fig.1, we illustrate the self-consistent Eq.(2) graphically at average solid density $\rho_s = 0.0286 \text{Å}^{-3}$. The variable $\hat{\rho}$ of the left hand side of Eq.(2) is shown as a function of $\hat{\rho}$ of the right hand side by solid curves at three localization parameters $\alpha$. Since we obtain $\hat{v}(q; \rho_l)$ at seven densities $\rho_l$, we show the seven sets of diamonds, crosses and asterisks respectively at $\alpha = 1.4, 1.9$ and $2.5 \text{Å}^{-2}$. The solid curves are obtained by using the linearly interpolated DCFs noted in the previous section. The weighted density is determined by intersection between the solid curves and the dashed line of unit slope. For a trivial case $\alpha = 0$, we expect that the weighted density coincides with $\rho_s$. In fact, Eq.(2) would have such a solution if $\epsilon'(\hat{\rho}) \neq 0$: In the present case, however, Eq.(4) implies $\epsilon'(\rho_0) = 0$ at density $\rho_0$ due to the attraction of HFDHE2 potential. As a result, the solid curves are separated by divergence (the vertical line of dots in Fig.1) at $\rho_0$. We are concerning the right hand side region because of $\rho_s > \rho_0$. There the divergence squeezes the curves near $\rho_0$ downwards sharply, and we have two weighted densities even at the trivial case $\alpha = 0$: one is $\rho_s$ and the other is $\rho_0$. In Fig.1, we see two weighted densities at filled and open circles on the curve of $\alpha = 1.4$. They approach with each other with lifting $\alpha$ and merge at $\alpha = 1.9$. See the solid curve contacts with the dashed unit slope at $\alpha = 1.9$ and leaves at $\alpha > 1.9$: Eq.(2) does not have solution to give the weighted density at $\alpha > \alpha^* = 1.9$. The critical value $\alpha^*$ depends on $\rho_s$: we find $\alpha^* = 2.4$ for $\rho_s = 0.030 \text{Å}^{-3}$. The denser weighted density denoted by open circle seems 'normal' because it approaches to $\rho_s$ with lowering $\alpha$ as expected. From this point, we shall discard the 'anomalous' weighted density (filled circle) hereafter and use the symbol $\hat{\rho}$ for the normal weighted density (we use the same symbol as the variable of axes because of no confusion).
In Fig.2, the normal weighted density $\hat{\rho}$ is plotted as a function of localization parameter $\alpha$ at two fixed $\rho_s$. Note that in both cases $\hat{\rho}$ drops, hence $\epsilon(\hat{\rho})$ drops with $\alpha$ monotonically. On the other hand, $\epsilon_{id}$ increases linearly with $\alpha$, so the total ground state energy per particle $\varepsilon^{MWDA}$ in (3) is expected to have minimum at some finite $\alpha = \alpha_s$. Since $\rho_s = 0.0286\,\text{Å}^{-3}$ is the density of solid lcp $^4$He at melting pressure [8], we can very expect such a minimum. The drop in $\epsilon(\hat{\rho})$ is, however, negligibly small and $\varepsilon^{MWDA}$ increases just simply with $\alpha$ as in Fig.3. Even for the higher density $\rho_s = 0.030\,\text{Å}^{-3}$ the result does not change. $\varepsilon^{MWDA}$ terminates at points denoted by asterisk in Fig.3 because $\hat{\rho}$ does not exist for $\alpha > \alpha^*$. We note that $\alpha^* \sigma^2 \approx 14$, where $\sigma = 2.6\,\text{Å}$ is the hard core diameter of HFDHE2 potential, is large enough to cover realistic solid state localization $\alpha_s$. The result pathologically asserts that fcc solid is mechanically unstable and the superfluid never solidifies around experimentally observed freezing pressure.

We did the same calculation by employing model energy functional (Orsay-Trento functional (OTF)) [9] as DFT input. OTF gives both equation of state and phonon-roton spectrum at various pressures, and the coincidence with experiment is satisfactory. Then $\epsilon(\rho_l)$ and DCF are easily extracted at any density $\rho_l$ and at any wave number, although DCF does not include multi-particle excitation contribution. Caupin et. al employed them as DFT inputs and found that solid is always stable within SOT [10]. In opposite, we find by MWDA that superfluid state is again always stable. This pathology is essentially due to the presence of the zero in $\epsilon'(\rho_l)$, namely liquid-gas transition. In fact, the freezing of hard sphere Bosons are quite well described by MWDA [5], in which liquid-gas transition does not exist.

Figure 3. Total ground state energy per particle $\varepsilon^{MWDA}$ versus localization parameter $\alpha$ for the HFDHE2 Aziz Boson fcc crystal at average solid density $\rho_s = 0.0286\,\text{Å}^{-3}$ (open circles) and $0.030\,\text{Å}^{-3}$ (filled circles).

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