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Freezing of Helium-4: Comparison of Different Density Functional Approaches

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Abstract Solidification of superfluid helium-4 has been addressed within the framework of density functional theory. Early studies used a variational approach, approximating the density distribution in the solid phase by a sum of Gaussians on each lattice site. Recently, we performed an unconstrained minimization of the functional describing the helium system as reported by Ancilotto et al. (Phys. Rev. B, **72**, 214522, 2005). At sufficiently high density, we find stable solid like solutions, which exhibit an anisotropic density profile around each lattice site. We compare these results to the previous variational approach, and attempt to improve the family of trial functions by adding a variational parameter to account for anisotropy.

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1 Introduction

Density functional theory (DFT) provides suitable tools to treat inhomogeneous systems, e.g. the liquid-vapor interface. An extreme case of inhomogeneity is the solid phase. DFT addresses the liquid-solid transition by assuming that the properties of the solid can be derived from periodic perturbations of a reference uniform liquid. DFT of freezing has been developed for classical systems (for reviews, see [1, 2]) and

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extended to quantum systems. Until recently, freezing of helium-4 had been treated within the frame of a second order (in the perturbation amplitude) approximation and using a variational approach for the density distribution in the solid; we present this method in Sect. 2. In Sect. 3, we describe how we went beyond the second order approximation and the variational level by performing an unconstrained minimization of the functional to find the solid solution [3]. However, as the description of the liquid differs between these approaches, the improvement over the variational treatment is difficult to assess. In order to do so, we repeat in Sect. 4 the variational calculation within the second order approximation, but with the same starting point; we also address the issue of the anisotropy of the density around the lattice sites in the solid, by enlarging the set of trial functions.

2 Second Order Approximation

This approach was introduced for classical systems by Ramakrishnan and Yussouff (RY) [4], and later used to study helium-4 [5]. 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 the phases is obtained by a Taylor expansion in the one particle density, truncated to second order:

$$\Delta E[\rho] = E_{\mathrm{id}}[\rho] + \int \mathrm{d}\mathbf{r} \left(\frac{\delta E_{\mathrm{int}}}{\delta\rho(\mathbf{r})} \right)_l \delta\rho(\mathbf{r}) + \frac{1}{2} \int \mathrm{d}\mathbf{r}\mathrm{d}\mathbf{r}' \left(\frac{\delta^2 E_{\mathrm{int}}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right)_l \delta\rho(\mathbf{r})\delta\rho(\mathbf{r}'), \tag{1}$$

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:

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

The second term on the right hand side of (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)

$$\left(\frac{\delta^2 E_{\mathrm{int}}}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \right)_l = v(|\mathbf{r} - \mathbf{r}'|; \rho_l), \tag{3}$$

which is the quantum analog of the classical Ornstein–Zernike DCF. The Fourier transform of v is related to the static density-density response function χ of the liquid:

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

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

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. This is usually done within a variational approach: the solid density is parameterized by Gaussians centered on the vectors $\{\mathbf{R}_j\}$ of a fcc lattice:

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

Using Fourier transform, one finds:

$$\frac{\Delta\Omega}{V} = \frac{E_{\rm id}}{V} + \frac{1}{2}\hat{v}(0;\rho_l)(\rho_s - \rho_l)^2 + \frac{1}{2}\rho_s{}^2 \sum_{\mathbf{k}_j} \exp\left(-\frac{|\mathbf{k}_j|^2}{2\alpha}\right)\hat{v}(|\mathbf{k}_j|;\rho_l), \tag{6}$$

where the $\mathbf{k}_j$ are the reciprocal lattice vectors (RLVs). For each liquid density ρ_l, the optimum solid density ρ_s and Gaussian width α are found. ρ_l is then varied until $\Delta\Omega$ is zero, corresponding to the two phases in equilibrium. If one neglects the overlap between Gaussians on neighboring lattice sites, $E_{\rm id}/V = \alpha\rho_s 3\hbar^2/(4m)$; Dalfovo et al. [6] have shown that this increases the equilibrium densities by only 3%, and we will use this approximation in the following.

The keypoint is the choice of the DCF, or equivalently of $\chi(q)$. Previous attempts used different inputs for the DCF, and got very different results [5]. In the following we will focus on the comparison between two methods with the same initial information on the liquid phase.

3 Exact Minimization

Recently, we used a different approach to go beyond the second order approximation and the variational level [3]. We used a functional describing correctly the liquid properties to compute the excess energy ΔE of any periodic perturbation, without truncating ΔE as in (1). The full, unconstrained, minimization is achieved by evolving a nonlinear Schrödinger equation derived from the functional, in a way similar to the Diffusion Monte-Carlo method. First we tried the Orsay-Trento functional (OT) [7], but it gives numerical instabilities. They disappear if we drop the gradient-gradient term introduced to reproduce $\chi(q)$ of liquid helium. Let us call the corresponding functional the truncated OT functional (OT-trunc). The equilibrium solid found for OT-trunc is a sum of isotropic Gaussians on each lattice site, but with an unphysically narrow width ($\alpha\sigma^2 = 49.2$). By introducing a penalty term that switches on only at high density, we were able to reproduce the experimental equation of state (EOS) of the solid. At equilibrium, the solid density is now wider around each lattice site, and anisotropic: the atoms extend in the directions of the empty spaces left between neighboring atoms.

4 Critical Comparison

The previous DFT calculations of freezing in helium-4 used other functionals than OT-trunc for their starting point. To allow a direct comparison, we first repeat the

Table 1 Comparison of the freezing parameters for the OT-trunc functional obtained with different methods ($\sigma = 0.2556$ nm). We show up to 4 digits to reveal the small differences

Method	P_f (MPa)	$\rho_l \sigma^3$	$\rho_s \sigma^3$	$\alpha \sigma^2$	τ
Exact [3]	3.41	0.45	0.55	–	–
Exact with penalty [3]	2.58	0.4385	0.4905	–	–
RY, isotropic	6.985	0.4973	0.5471	14.70	–
RY, anisotropic	6.975	0.4972	0.5468	14.69	0.0103

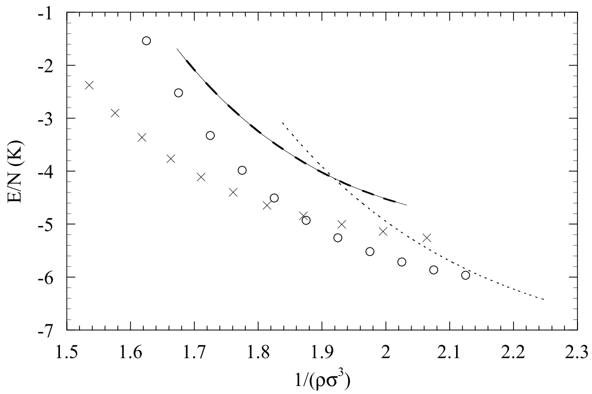

Fig. 1 Comparison of the EOSs obtained with different methods. The energy per particle is plotted as a function of $1/(\rho\sigma^3)$. All data were obtained using the OT-trunc functional. The *dotted line* shows the EOS for the liquid (which reproduces the experimental data by construction). The *crosses* show the solid EOS obtained by exact minimization, the *circles* give the EOS when the penalty term is included [3]. The *solid and dashed lines* are the solid EOS predicted by the second order approximation with isotropic (5) and anisotropic trial functions (7), respectively. The last two EOSs are not distinguishable at this scale

second order approximation with the OT-trunc functional, using the usual Gaussian ansatz for the solid density (5). As this method can only deal with Bravais lattices, we consider a fcc lattice instead of hcp for the exact minimization. This should not affect the comparison: the coordination and packing fraction of the two lattices are the same, and Monte-Carlo simulations [8] have found their energies per particle to differ by less than 20 mK. Following the procedure described in Sect. 2, and keeping only the 5 first shells of RLVs, we obtain the freezing parameters; they are given in Table 1, along with the results from [3]. We can also derive the solid EOS: as shown in Fig. 1, it disagrees with the results of the exact minimization. Let us emphasize that, as the penalty term introduced in [3] vanishes at low density, the second order approximation is the same whether the penalty is included or not. This points out a limitation of the second order approximation.

Another limitation of the RY method is the restriction to isotropic trial functions. To estimate its effect, we repeat the variational calculation with a more general, anisotropic ansatz, recently used in DFT of freezing of hard sphere [9] and soft core

[10] fluids:

$$\rho_s(\mathbf{r}) = \sum_{\mathbf{R}_j} \left(\frac{\alpha}{\pi}\right)^{3/2} \exp(-\alpha|\mathbf{r}-\mathbf{R}_j|^2)\,[1+\tau\alpha^2 f_{\mathrm{a}}(\mathbf{r}-\mathbf{R}_j)], \tag{7}$$

where $f_{\mathrm{a}}(\mathbf{r}) = x^4 + y^4 + z^4 - 3r^4/5$ is the leading term for the unit cell anisotropy in cubic lattices, and τ is an anisotropy parameter. The grand potential difference between the liquid and the solid now writes:

$$\begin{aligned}\frac{\Delta\Omega}{V} = {}& \alpha\rho_s\frac{3\hbar^2}{4m}\left(1+\frac{12}{5}\tau^2-\frac{108}{25}\tau^3+\frac{3204}{25}\tau^4+\mathcal{O}(\tau^5)\right)\\ &+\frac{1}{2}\hat{v}(0;\rho_l)(\rho_s-\rho_l)^2\\ &+\frac{1}{2}\rho_s{}^2\sum_{\mathbf{k}_j}\exp\left(-\frac{|\mathbf{k}_j|^2}{2\alpha}\right)\hat{v}(|\mathbf{k}_j|;\rho_l)\left(1+\frac{\tau}{16\alpha^2}f_{\mathrm{a}}(\mathbf{k}_j)\right).\end{aligned} \tag{8}$$

To compute E_{c}, we have neglected the overlap between neighboring atoms and used an expansion in powers of τ. The value of the isotropic ansatz (5) is recovered for $\tau = 0$. As usual, for any given value of ρ_l, (8) is minimized to find the most stable solid, and the EOS derived. The results are displayed on Fig. 1: on this scale, they cannot be distinguished from those obtained with isotropic trial functions. When $\rho_l\sigma^3$ varies from 0.445 to 0.545, the corresponding τ decreases from 0.013 to 0.008. E_s/N for the anisotropic ansatz is lower than for the isotropic one by less than 5 mK.

We shall mention a technical problem arising with (7): it leads to singularities in the integral for E_{c} (2) because the density can be negative (consider for example the direction (111): $\rho_s \le 0$ for $x^4 \ge (5/12)\tau\alpha^2$). As this happens in a region where the integrand of (2) is small, it should not affect the results. One can obtain a more regular ansatz by multiplying f_{a} by a Gaussian factor $\exp(-\alpha|\mathbf{r}-\mathbf{R}_j|^2)$ in (7); then for $-(5/8)e^2 < \tau < (15/16)e^2$, ρ_s is positive everywhere. We have checked that this gives values of E_s/N between those of the two other ansätze.

5 Conclusion

We have compared the predictions of two methods for the solid EOS and the freezing parameters of helium-4. Both methods are based on the same description of the liquid, namely the OT-trunc functional. The exact minimization is able to find the ground state of the system with the full functional and without any constraint on the density profile. On the other hand, the RY method uses a second order approximation for the solid energy, and resorts to a variational calculation of the density. The two methods give very different results. We have shown that the use of anisotropic trial functions does not improve the RY result. The shortcoming of the RY method must thus be attributed to the poor quality of the second order approximation.

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