

Freezing of Liquid Helium at Zero Temperature: a Density Functional Approach.

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Abstract. – The liquid-solid phase transition of superfluid helium at zero temperature is studied in the framework of the density functional theory. The application of a second-order expansion of the energy of the system around the density of the liquid phase (Ramakrishnan-Yussouff method) is discussed. The role played by the static polarizability of the homogeneous liquid in characterizing the equation of state of the solid phase is explicitly pointed out.

Much work has been devoted in the last decade to the application of the density functional theory (DFT) to the liquid-solid transition in a wide variety of systems (for a recent review see, for instance, ref. [1]). The theory has proven successful in describing first-order phase transition in classical systems, from simple fluids to more complex situations. Moreover, it can be applied to investigate properties of quantum systems, such as the Wigner crystallization of electrons [2] and the freezing of a quantum hard-sphere liquid [3]. In this context superfluid ⁴He corresponds to a unique prototype of real quantum system where theory can be compared adequately with experiments. In ref. [4] a first quantitative analysis of the freezing transition in ⁴He, based on DFT, has been presented. The method requires, however, a high enough temperature in order to ignore exchange effects in the correlation functions. The aim of the present work is to show that reasonable predictions about the freezing transition of superfluid helium can be given with DFT also in the degenerate limit of zero temperature.

The density functional theory is based on the assumption that the energy of a many-body system can be expressed as a functional of the single-particle density. The minimum of the energy is located at the true equilibrium density of the system [5]. Since there is no *a priori* information about the exact form of the functional, different approximation schemes have

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been proposed to get sound functionals, containing the relevant symmetries of the system and having transparent physical ingredients. In the case of freezing a possible choice is a Taylor expansion of the energy about the density of a uniform reference liquid. If the expansion is truncated at second order the approximation is known as Ramakrishnan-Yussouff method (RY) [6]. The basic idea is that the correlation function in the solid phase, which is needed for the computation of the energy, can be approximated by the one of the liquid phase, or, equivalently, that the solid can be considered as a nonuniform perturbation of the liquid. This is equivalent to assuming

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

where $\delta \rho(\mathbf{r}) = \rho_s(\mathbf{r}) - \rho_l$ is the difference between the nonuniform density of the solid and the density of the liquid. The energy E_{id} is the ideal-gas energy, *i.e.* the energy of a noninteracting inhomogeneous system of particles. For a Bose system at zero temperature one has

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

while E_c is the nonideal part of the functional for the liquid. Its first derivative gives the chemical potential, while the second derivative is the quantum analog of the classical Ornstein-Zernike direct correlation function

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

The Fourier transform of $v(|\mathbf{r} - \mathbf{r}'|)$ is directly related to the static response function $G(q)$ of the liquid through the relation

$$\frac{1}{G(q)} = \frac{\hbar^2 q^2}{2m} + 2v(q; \rho_l) \rho_l. \quad (4)$$

Once the function $G(q)$ is given as input, the equilibrium density of the solid comes out by minimization of the grand potential difference per unit volume between the solid and the liquid phase $\Delta\Omega/V$ at the same chemical potential μ :

$$\frac{\Delta\Omega}{V} = \frac{\Delta E}{V} - \mu(\rho_s - \rho_l). \quad (5)$$

The density of the solid phase is usually parametrized as a sum of normalized Gaussians centred at the lattice sites positions $\{\mathbf{R}_j\}$ for a given crystalline structure:

$$\rho(\mathbf{r}) = \sum_{\{\mathbf{R}\}} \left(\frac{\alpha}{\pi} \right)^{3/2} \exp[-\alpha|\mathbf{r} - \mathbf{R}|^2], \quad (6)$$

where α is a localization parameter⁽¹⁾. With this choice the calculations can be carried out in

⁽¹⁾ Liquid helium at $T=0$ solidifies in a h.c.p. structure. As many authors did, we use a f.c.c. lattice, more simple to handle. The two closed-packed structures differ only beyond the third nearest neighbour in real space, and the expected differences in eq. (7) are small enough to be safely neglected in this context.

the reciprocal lattice $\{\mathbf{K}_j\}$ and the quantity to minimize is

$$\frac{\Delta\Omega}{V} = \frac{E_{\text{id}}}{V} + \frac{1}{2}v(0; \rho_1)(\rho_s - \rho_1)^2 + \frac{1}{2}\rho_s^2 \sum_{\{\mathbf{K}\}} \exp[-K^2/2\alpha]v(\mathbf{K}; \rho_1), \quad (7)$$

where E_{id} corresponds to the integral (2) with ρ given in eq. (6). In practice $\Delta\Omega/V$ is first minimized by variation of both the average solid density $\rho_s = N/V$ and of parameter α for a given liquid density ρ_1 , and then the procedure is repeated for different values of ρ_1 until the minimum occurs at $\Delta\Omega = 0$, to ensure the equality of the liquid and solid pressure. This is equivalent to the Maxwell double tangent construction for the liquid and solid equations of state.

Despite the lack of rigorous arguments about the validity of the second-order truncation, the RY method has been applied with reasonable success in different contexts, suggesting the occurrence of important cancellation effects in the higher-order terms. Various attempts have been recently made to go beyond the RY approximation, as in the case of the MWDA method employed by Denton *et al.* [3] to study the quantum hard-sphere liquid. However, the applicability of these methods to Lennard-Jones systems at zero temperature is not yet well established [3]. In this context the relative simplicity of the RY method and the clear interpretation of its physical ingredients make it a useful starting point to discuss the freezing transition of liquid helium.

An important point to stress is that in liquid ^4He the static response function $G(q)$, key ingredient of the theory, is accessible via inelastic neutron scattering experiments. In fact, at zero temperature, $G(q)$ is related to the inverse energy-weighted moment of the dynamic form factor $S(q, \omega)$:

$$G(q) = \frac{1}{N} \int (\hbar\omega)^{-1} S(q, \omega) d\omega. \quad (8)$$

The sum rule (8), also known as the compressibility sum rule in the low- q limit, is well suited for experimental investigation in superfluid ^4He . In fact the discretization of the elementary excitations (phonon-maxon-roton branch) ensures a regular behaviour of the integrand in the low-frequency region. On the other hand the $1/\omega$ factor makes the integral rapidly convergent at high ω . To date measurements of $G(q)$ are however available only at zero pressure [7]. They reveal a characteristic bump in the roton region ($q \approx 2 \text{ \AA}^{-1}$). This bump implies the tendency to favour self-consistent density oscillations with wavelength of the order of the interparticle distances, *i.e.* the localization of atoms on a lattice. For a quantitative use of the RY expansion one has to know the static response function for a reference liquid at density higher than that at vapour pressure. We point out that, with the available experimental techniques of neutron scattering, the required knowledge on $G(q)$ should not be difficult to obtain.

In the absence of experimental data on $G(q)$ at higher pressure one can simply try the Feynman relation [8]

$$v(q; \rho) = \frac{\hbar^2 q^2}{4m\rho} \left(\frac{1}{S^2(q)} - 1 \right) \quad (9)$$

connecting the static response function to the static form factor $S(q)$, known with good accuracy at different densities. We have taken the values of $S(q)$ given by the Monte Carlo calculations with the Lennard-Jones potential of ref. [9] and tabulated for three densities (similar results are obtained in ref. [10] using the Aziz potential). The resulting static response function at zero pressure (dashed line) is compared with the experimental data of

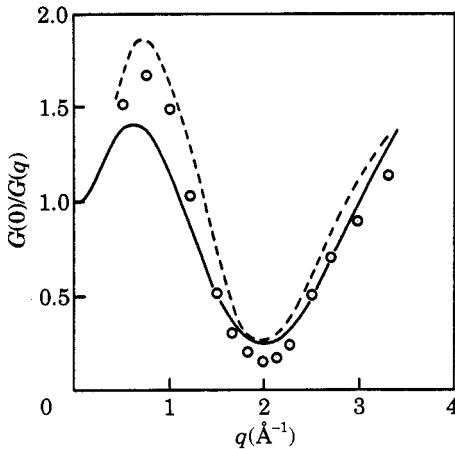


Fig. 1.

Fig. 1. – Inverse static response function $G^{-1}(q)$ at zero pressure normalized to its $q=0$ value. The latter is fixed by the compressibility sum rule for the homogeneous liquid. Circles: experimental data as extracted from ref. [7]; full line: ref. [13]; dashed line: eq. (9) with S_q given by GFMC calculations [9].

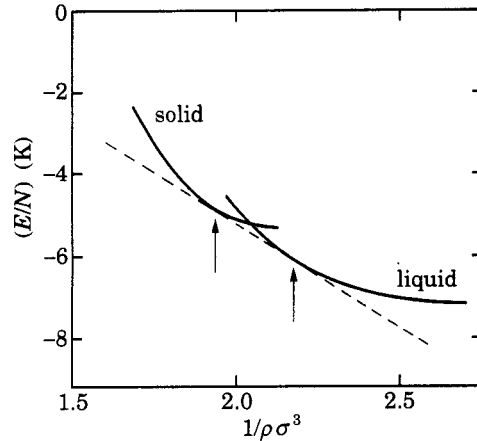


Fig. 2.

Fig. 2. – Solid and liquid equations of state as predicted in the present work using the RY method. The arrows show the densities of the solid and liquid phases at the freezing transition. The quantity in abscissa corresponds to the volume per atom in σ^3 units ($\sigma = 2.556 \text{ \AA}$).

ref. [7] in fig. 1. Performing the RY minimization procedure with the three available values of ρ_1 , we obtain minimum values of $\Delta\Omega$ very far from zero, *i.e.* we do not find any solid in equilibrium with the liquid at density ρ_1 . As already pointed out by other authors [11], this drawback of the Feynman relation, in providing a reasonable equation of state of solid ${}^4\text{He}$, follows mainly from the fact that it does not properly account for the multiphonon contribution to the dynamic structure function and provides only a lower bound of $G(q)$ [12].

In ref. [13, 14] a phenomenological approach to inhomogeneous liquid ${}^4\text{He}$ has been recently developed and successfully applied to the study of the free surface as well as of ${}^4\text{He}$ films. The theory provides an expression for the energy of the nonuniform liquid, which includes the equation of state in the uniform limit, the effects of short-range correlations, through the use of the average weighted density method [15], and the correct long-range behaviour of the interparticle potential. In fig. 1 we plot the resulting predictions for the static response function $G(q)$ at zero pressure (full line). The comparison with the experimental points has the same quality as the Feynman prediction (9) in the roton region (2 \AA^{-1}), with some improvement at higher q 's. We stress here that the first nearest neighbour in the reciprocal lattice is typically at distances of 2 \AA^{-1} , so that the relevant contribution of $G(q)$ to the sum in eq. (7) comes out from the range between 2 and 3 \AA^{-1} . The crucial point is that the difference between the predictions of ref. [13] and the Feynman approximation for $G(q)$ is much more pronounced at high pressure, where the Ramakrishnan-Yussouff method is actually employed. In particular the quantity $v(q; \rho)$ calculated with the method of ref. [13] is systematically lower than the Feynman one in the relevant range of q . A lower curve for $v(q; \rho)$ in the roton region implies a larger negative energy contribution in eq. (7) and, consequently, more binding for the solid phase.

The pressure dependence of $G(q)$ can also be tested looking at the ratio between the f -sum rule $\int \hbar\omega S(q, \omega) d\omega = N\hbar^2 q^2/2m$ and the inverse energy-weighted moment (8). The square

root of this ratio provides an estimate of the phonon-roton excitation energy. Using $G(q)$ from ref. [13], the resulting dispersion relation shows the correct trend for the energy in the roton region (the roton minimum lowers, as a function of pressure, following the behaviour of the experimental data).

Performing the complete minimization of functional (7) one finds a solid phase in equilibrium with the liquid. The equation of state of the solid is shown in fig. 2 and the values of the thermodynamic parameters at the freezing transition are given in table I, together with the experimental data [16] and the results of GFMC simulations [10]. The difference in the molar volumes for the solid and liquid phases at the transition obtained with the RY method is of the same order as in the GFMC simulation, while the predictions for the freezing pressure are significantly higher. The transition is also characterized by the Lindemann parameter, defined as the ratio between the average quadratic displacement of one atom from its lattice position and the nearest-neighbour distance. Using a f.c.c. lattice one has $L = \sqrt{3}/(\alpha a^2)$, where a is the lattice constant, directly related to ρ_s . We find $\alpha = 1.85 \text{ \AA}^{-2}$ and then $L = 0.25$, a value close to the results of Monte Carlo simulations [9, 17]. We note that in solid ^4He the atomic delocalization is strongly influenced by quantum effects and the Lindemann parameter turns out to be much larger [3, 9, 18] than the typical values for classical systems. For this reason ignoring the overlapping among the Gaussians of eq. (6), which would correspond to assuming $E_{id}/V = (3\hbar^2/4m) \alpha \rho_s$, is a worse approximation here than in the classical case. In particular it yields a Lindemann parameter 10% lower and values of ρ_s and ρ_l about 3% higher, corresponding to a freezing pressure of 47 atm.

TABLE I. – *Thermodynamic parameters at the freezing transition. Experimental and GFMC data are taken from ref. [17] and ref. [10], respectively.*

	$\rho_l \sigma^3$	$\rho_s \sigma^3$	Δv (cm ³ /mol)	P (atm)
exp	0.434	0.478	2.165	25
GFMC	0.438	0.491	2.47	26.7
RY	0.459	0.515	2.51	41

Our results suggest that the Ramakrishnan-Yussouff approximation can provide a reasonable starting point to describe the helium freezing transition in the context of DFT. The resulting predictions depend however in a critical way on the assumption made for the static response function $G(q)$. The Feynman approximation (9) does not seem to be enough accurate in this context, while more reasonable results are obtained employing the static response function of ref. [13], which better accounts for the pressure dependence of $G(q)$.

A more systematic knowledge of the static response function $G(q)$, based on new neutron scattering data and on *ab initio* calculations, seems to be crucial in order to draw more definitive predictions for the solid-liquid transition. In particular it will permit to appreciate the quality of the RY method, as well as of different density functional theories [1, 3, 15] beyond the RY approximation. The progress in this direction is expected to stimulate new interest in the theoretical study of inhomogeneous helium systems, including the liquid-solid interface and the layer structure of helium films.

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