1. INTRODUCTION

In the present contribution we present some of the most recent results of density functional theory for inhomogeneous systems of liquid $^4$He. Almost ten years ago, one of us (S.S.) introduced a simple density functional for liquid $^4$He and $^3$He. The functional was used to study the ground state properties of the free surface [1] and of droplets [2]. The theory has been later refined and extended in order to improve its accuracy and to make it applicable to a more microscopic level. Finite range correlations have been explicitly introduced [3] to explore strongly inhomogeneous systems, like layered structures of liquid helium on solid substrates [4] and near impurities [5] or vortices [6]. $^3$He-$^4$He mixtures have been also extensively studied with the same formalism [7].

It is a good time to see what the situation is. There are two major questions which have to be addressed. First, what is the present understanding of the foundations of density functional theory. For instance, what is the connection between phenomenological density functionals and microscopic approaches, as well as the applicability of the theory to dynamic problems through a time dependent formulation. Second, what is the predictive power of the theory and its accuracy. In the present contribution we will mainly concentrate on the second problem.

We will present a new density functional [8] (hereafter called Orsay-Trento functional), which is the result of a natural evolution and improvement of the theory starting from the original zero-range functional of Refs. [1,2]. We will focus on the key ingredients of the theory and we will show how they determine important predictions concerning inhomogeneous systems. These predictions turn out to be quite accurate even at the level of interatomic distances. We will present a selected set of results, referring to Refs. [8,9] for a more detailed discussion.
2. DENSITY FUNCTIONAL: EQUILIBRIUM PROPERTIES

Let us consider the complex wave function

\[ \Psi(r, t) = \Phi(r, t) \exp \left( \frac{i}{\hbar} S(r, t) \right), \quad (1) \]

where the real function \( \Phi \) is related to the one particle density by \( \rho = \Phi^2 \), while the phase \( S \) is related to the velocity of the fluid by \( v = (1/m)\nabla S \). In the density functional approach, the energy of the system at zero temperature is assumed to be a functional of \( \Psi \):

\[ E = \int \! dr \, \mathcal{H}[\Psi, \Psi^*]. \quad (2) \]

In the calculation of the ground state, only states with zero velocity are considered, so that the energy is simply a functional of the one-body density \( \rho(r) \). The ground state is then found by minimizing the energy with respect to \( \rho \). One usually write the energy as the sum of the kinetic energy of non-interacting particles ("quantum pressure") plus a term incorporating the effects of quantum fluctuations and correlations:

\[ E = \int \! dr \, \mathcal{H}_0[\rho] = \int \! dr \, \frac{\hbar^2}{2m} (\nabla \sqrt{\rho})^2 + E_c[\rho]. \quad (3) \]

Minimization with respect to the density leads to the Hartree equation

\[ \left\{ -\frac{\hbar^2}{2m} \nabla^2 + U[\rho, r] \right\} \sqrt{\rho(r)} = \mu \sqrt{\rho(r)}, \quad (4) \]

where \( U[\rho, r] \equiv \delta E_c/\delta \rho(r) \) acts as a mean field, while the chemical potential \( \mu \) is introduced in order to ensure the normalization of the density.

A derivation of functional \( \mathcal{H}_0 \) starting from first principle is not available. One then resorts to approximate schemes for the correlation energy. The phenomenological density functional approach consists of choosing a reasonable ansatz for \( \mathcal{H}_0 \), in which a few parameters are fixed to reproduce known properties of the liquid. For example, the functional of Refs. [1,2] was written in the form

\[ E = \int \! dr \left[ \frac{\hbar^2}{2m} (\nabla \sqrt{\rho})^2 + \frac{b}{2} \rho^2 + \frac{c}{2} \rho^{2+\gamma} + d(\nabla \rho)^2 \right], \quad (5) \]

where \( b, c, \gamma \) and \( d \) are phenomenological parameters fixed to reproduce the ground state energy, density and compressibility in the homogeneous liquid at zero pressure, as well as the free surface energy. Non locality effects have been included in a more adequate way by Dupont-Roc et al. [3], who generalized Eq. (5) accounting for the finite range of the atom-atom interaction and the existence of the hard-core. In that case, the term quadratic in the density is replaced by a two-body potential energy, containing a Lennard-Jones interaction, and the term with the power \( \gamma \) is taken to depend on a "coarse grained density", i.e., the density averaged on a sphere of atomic size. The three parameters of the functional are fixed to reproduce the bulk equation of state and the energy per particle at zero pressure. The most important feature
Figure 1. Static response function in liquid $^4$He at zero pressure. Points: experimental data [10]; dotted line: from functional of Refs. [1,2]; dashed line: from Ref. [3]; solid line: from the Orsay-Trento functional.

of this approach is that the static response function of the liquid turns out to be strongly $q$-dependent, with a peak at the roton wave length, in qualitative agreement with the experimental data [10].

The static response function $\chi(q)$ plays a key role in density functional theory, since it fixes the response of the system to static density perturbations. It is consequently a quantity which, in principle, must be exactly accounted for by the theory. It is easily calculated from the density functional by taking the second functional derivative of the energy in $q$-space. Actually the functional of Ref. [3] provides a static response function which underestimates significantly the height of the peak in the roton region. For this reason we have corrected that functional, introducing a new non local term depending on gradients of the density. The new term is fixed to reproduce the experimental static response function in the liquid. The function $H_0$, entering Eq. (3), is then written in this way:

$$H_0 = \frac{\hbar^2}{2m} (\nabla \sqrt{\rho})^2 + \frac{1}{2} \int d\mathbf{r}' \rho(\mathbf{r})V_l(|\mathbf{r} - \mathbf{r}'|)\rho(\mathbf{r}') + \frac{c_2}{2} \rho(\mathbf{r})(\bar{\rho}_r)^2 + \frac{c_3}{3} \rho(\mathbf{r})(\bar{\rho}_r)^3$$

$$- \frac{\hbar^2}{4m} \alpha_s \int d\mathbf{r}' F(|\mathbf{r} - \mathbf{r}'|) \left(1 - \frac{\rho(\mathbf{r})}{\rho_{0s}}\right) \nabla \rho(\mathbf{r}) \cdot \nabla \rho(\mathbf{r}') \left(1 - \frac{\rho(\mathbf{r}')}{{\rho}_{0s}}\right).$$

(6)

The two-body interaction $V_l$ is the Lennard-Jones interatomic potential, with the standard parameters $\sigma = 2.556$ Å and $\varepsilon = 10.22$ K, screened at short distance.
\( V = 0 \) for \( r < h \), with \( h = 2.1903 \text{Å} \). The weighted density \( \bar{\rho} \) is the average of \( \rho(r) \) over a sphere of radius \( h \). Thus the two terms containing \( \bar{\rho} \), with the parameters \( c_2 = -2.411857 \times 10^4 \text{ K Å}^6 \) and \( c_3 = 1.858496 \times 10^6 \text{ K Å}^9 \), account phenomenologically for short range correlations. The last term corresponds to a non local correction to the kinetic energy. The function \( F \) is a simple gaussian \( F(r) = \pi^{-3/2} \ell^{-3} \exp(-r^2/\ell^2) \) with \( \ell = 1 \text{ Å} \), while \( \alpha_s = 54.31 \text{ Å}^3 \). The factors \( (1 - \rho/\rho_0) \), with \( \rho_0 = 0.04 \text{ Å}^{-3} \), are included in order to obtain a pressure dependence of the static response function close to the one predicted by Diffusion Monte Carlo simulations [11]. In conclusion, the function \( H_0 \) is such that the theory reproduces two important features of the liquid, namely the equation of state and the static response function. The situation, as concerns the quantity \( \chi(q) \) is shown in Fig. 1, where the experimental data are compared with the results of three different functionals. The \( q = 0 \) limit is fixed by the compressibility of the system, which, in all cases, is an input of the theory. It ensures the correct behaviour in the long wavelength limit and, consequently, the correct description of systems characterized by slow density variations. The peak of the static response function in the roton region, \( q \simeq 2 \text{ Å}^{-1} \), is very significant in characterizing structural properties on the interatomic length scale.

With the functional described above we have studied the properties of the free surface, droplets and films. Here we restrict ourselves to a few relevant results for helium droplets, where a detailed comparison between the predictions of different density functionals with the ones of Monte Carlo calculations, is possible. In this case the Hartree equation (4) has to be solved in spherical geometry. The ground state energy and density of small droplets are shown in Fig. 2 and Fig. 3, respectively, as a function of the number of atoms. The density profile of a droplet of 70 atoms is shown in Fig. 4, together with the predictions of other calculations. Some relevant comments follow:

- The predictions of density functional theory for the energy of droplets become closer and closer to the results of \textit{ab initio} simulations, as the accuracy of the static response function is improved. We note that the three functionals give practically the same surface energy, very close to the experimental one, and the same bulk equation of state, while they differ in the behaviour of the static response function. The close agreement between the predictions of the Orsay-Trento functional and the ones of \textit{ab initio} simulations seems to indicate that the new non-local kinetic energy term in Eq. (6) accounts properly for correlations on the atomic length scale. The detailed form of the functional is not crucial; different parametrizations give very similar results provided the static response function in bulk liquid is reproduced.

- The density profiles exhibit small regular oscillations. These oscillations were not found with previous functionals, because the latter underestimated the height of \( \chi(q) \) at the roton wave length. The connection between the oscillations of the density profile and the behaviour of the static response function was suggested twenty years ago by Regge and Rasetti [14]. Subsequent microscopic calculations did not provide any conclusive evidence of this effect. The results of the density functional approach support the Regge's idea. These oscillations have a regular behaviour when one goes from small to very large clusters, up to limit of a planar free surface. The density oscillations are found to affect also the the evaporation energy, \([E(N-1) - E(N)]\), characterizing the mass distribution of
Figure 2. Energy per particle of helium droplets. The results of the present Orsay-Trento functional (solid line) are compared with the ones of functional of Refs. [1,2] (dotted line) and of Ref. [3] (dashed line), as well as with Monte Carlo simulations of Ref. [12] (crosses) and Ref. [13] (circles).

Figure 3. Density profile of helium droplets with $N = 8$ to 60. The density is normalized to the one of the bulk liquid.
Figure 4. Density profile of a droplet with 70 $^4$He atoms. Solid line: present work; triangle: DMC simulations of Ref. [15]; dashed line: Variational (HNC) calculations [16]; circles: most recent DMC calculations by Barnett and Whaley [17].

Droplets in experimental beams: deviations of the order of 0.1 K with respect to a pure liquid drop model are predicted. These deviations are signatures of a shell structure (”soft sphere close packing”) induced by quantum correlation at the liquid surface.

- Density oscillations have been recently found in Diffusion Monte Carlo (DMC) calculations on small droplets by Chin and Krotscheck [15], even if their results are probably affected by large statistical errors. The same authors have more recently employed a variational (HNC) method, and found oscillations closer to the ours [16]. A very good agreement with the density functional results has been very recently obtained by Barnett and Whaley in their most recent DMC calculations [17].

In other systems, like the free surface, films, porous media, doped clusters, less information are available from ab initio methods. The accuracy of the density functional approach is expected to be similar to the one shown for helium droplets. We emphasize again that the freedom in the choice of the parametrization of the starting functional is only a minor source of indetermination in the predictive power of the theory, provided the crucial ingredients (equation of state and static response function in bulk liquid) are properly accounted for.
Table 1

Values of the parameters used in $V_J(r)$.

3. DENSITY FUNCTIONAL: EXCITED STATES

Starting again from functional (2) one can develop a time dependent density functional theory in order to study the dynamics of inhomogeneous systems. In this case one has to apply the least action principle

$$\delta \int_{t_1}^{t_2} dt \int dr \left[ H[\Psi^*, \Psi] - \mu \Psi^* \Psi - \Psi^* i\hbar \frac{\partial \Psi}{\partial t} \right] = 0 \ .$$

(7)

The equations of motion for the excited states of the fluid can be derived by making variations with respect to $\Psi$ or $\Psi^*$. One finds a Schrödinger-like equation of the form

$$(\tilde{H} - \mu) \Psi = i\hbar \frac{\partial \Psi}{\partial t} ,$$

(8)

where $\tilde{H} = \delta E/\delta \Psi^*$ is an effective Hamiltonian. If one looks for linearized solutions $\Psi(r, t) = \Psi_0(r) + \delta \Psi(r, t)$

(9)

the Hamiltonian $\tilde{H}$ takes the form $\tilde{H} = \tilde{H}_0 + \delta \tilde{H}$, where the static Hamiltonian $\tilde{H}_0$ fixes the equilibrium state as in Eq. (4). The term $\delta \tilde{H}$ is linear in $\delta \Psi$ and accounts for changes in the Hamiltonian induced by the collective motion of the system. The Schrödinger equation (8) has to be solved using a self-consistent procedure. This linearized theory concides with the Random Phase Approximation for bosons. More detailed aspects of the theory were discussed by S. Stringari in the same Workshop.

To solve the equations of motion of the time dependent density functional theory one has to consider explicitly the velocity dependence of the function $\mathcal{H}$. We write

$$\mathcal{H} = \mathcal{H}_0[\rho] + \mathcal{H}_v[\rho, \mathbf{v}] \ ,$$

(10)

where $\mathcal{H}_0$ is the velocity independent function given in Eq. (6), while $\mathcal{H}_v$ is taken to be [8]

$$\mathcal{H}_v = \frac{m}{2} \rho(r)|\mathbf{v}(r)|^2 - \frac{m}{4} \int d\mathbf{r}' V_J(|r - r'|) \rho(r)\rho(r') \ (\mathbf{v}(r) - \mathbf{v}(r'))^2 .$$

(11)

The first term is the usual kinetic energy for free particles. The second term plays the role of a non local kinetic energy, accounting for backflow effects through an effective current-current interaction $V_J$. A similar functional was introduced long time ago by Thouless [18] to study the flow of a dense superfluid. We fix $V_J(r)$ using the phonon-roton dispersion in bulk liquid as input. We have chosen the simple parametrization

$$V_J(r) = (\gamma_{11} + \gamma_{12} r^2) \exp(-\alpha_1 r^2) + (\gamma_{21} + \gamma_{22} r^2) \exp(-\alpha_2 r^2) ,$$

(12)

where the parameters are given in Table I. With this choice the phonon-roton spectrum of the uniform liquid at zero pressure is well reproduced, and its pressure dependence also agrees with the experimental data. The theory is then used to predict dynamic properties of non uniform systems.
We show here what happens in the case of the free surface. The time dependent part of the wave function \((9)\) has to be expanded in plane waves in the direction parallel to the surface. The equations of motion are solved for the \(z\)-dependent coefficients, where \(z\) is the orthogonal coordinate. In practice, we expand the solutions on a basis of eigenfunctions of the static Hamiltonian, in order to write the equations in the form of a matrix diagonalization. One gets the transition density, the energy and the strength associated with each excited state, for any given value of the parallel wave vector \(k\). The same procedure can be easily applied to the case of helium films, by adding the external potential of the substrate.

In Fig. 5 we show the excitation spectrum of the free surface. Up to \(k \simeq 1.15 \text{ Å}^{-1}\), the state with lowest energy is localized at the surface. In the long wave length limit \(k \rightarrow 0\) its dispersion coincides with the hydrodynamic dispersion of ripplons (dotted line). It deviates significantly from the hydrodynamic law when approaching the threshold energy \(\Delta = 8.7\) K for rotons. A similar deviation has been found in the dispersion of surface modes in helium films measured in neutron scattering experiments \([19]\) (points with error bars). The bulk phonon-roton dispersion (upper solid line) is also plotted, together with the experimental data. We stress again that, while the phonon-roton dispersion in the bulk is used as input to fix the velocity dependent part of the functional, the theory becomes predictive for the dynamic properties of inhomogeneous systems, like the free surface.

Below \(\Delta\) the surface mode is undamped, while above \(\Delta\) it couples with the continuum of bulk modes (rotons with negative and positive group velocity) propagating...
at different angles \((q_z \neq 0)\). This results in a spreading of the strength associated with the surface mode. Actually the spreading predicted by our theory is rather small. This can be seen by plotting the dynamic structure function \(S(k, \omega)\), defined by

\[
S(k, q_z, \omega) = \sum_b \left| \hat{\rho}_{q z k, b} \right|^2 \delta(\omega - \omega_{k, b}).
\]

In Fig. 6 (top) we show the dynamic structure function for scattering at grazing angle \((q_z = 0)\) on a slab (liquid between two parallel surfaces at a distance of 50 Å). For graphical convenience we have replaced the \(\delta\)-functions with gaussians of width 0.4 K. The strength of the surface mode is well localized also above \(\Delta\), even though the strength is partially distributed among bulk modes coupled to ripplons. The position of the peak above \(\Delta\) is shown also in Fig. 5 as a dashed line. The hybridization mechanism between ripplons and rotons is discussed on a general ground in Ref. [9].

The form of the spectrum can change significantly in liquid helium films on solid substrates, where the substrate-helium potential produces a layering of the helium density and the bulk modes are discretized by the finite size of the system along \(z\). An example is given in Fig. 6 (bottom), where we show the dynamic structure function for a film on Sodium. The areal density of helium is 0.23 Å\(^{-2}\), which corresponds to approximately 4 liquid layers. The surface mode is clearly visible. Near the roton minimum one notes a new structure coming from the first liquid layer close to the substrate. It is interpreted as a 2D roton, whose energy becomes significantly lower than \(\Delta\) in the case of more attractive substrates, reflecting the tendency to solidification. Similar structures have been also seen in the experimental spectrum [19].

Finally, we note that the density functional method is also suitable to investigating the properties of reflection and evaporation of bulk excitations at the surface. Liquid helium is very peculiar from this viewpoint. For instance, one can study the one-to-one process of a roton impinging the surface and ejecting an atom (quantum evaporation). Experimental data about evaporation and condensation rates are now becoming available [20]. The threshold for quantum evaporation at zero temperature is shown in Fig. 5 (dot-dashed line). The \(q = 0\) value is the chemical potential \(|\mu| = 7.15\) K. Above this curve the solutions of the time dependent density functional theory are combinations of free atom states, outside the liquid, and bulk states (phonons and rotons). From their coupling one can extract the evaporation and condensation probabilities. This work is in progress.

4. CONCLUSIONS

In this contribution we have briefly traced the evolution of phenomenological density functional theories, from the one of Refs. [1,2] to the most recent Orsay-Trento functional [8]. We have emphasized the crucial role of the static response function of the bulk liquid; together with the equation of state, this quantity has to be considered the main ingredient of the density functional approach. We have shown how the predictions of the theory improve when the static response function is properly reproduced. For the time dependent version of the theory one can introduce backflow effects through an effective current-current interaction. In that case the
Figure 6. Dynamic structure function for a 50 Å thick slab (top) and a film on Sodium (bottom), with coverage of 0.23 Å⁻².
phonon-roton dispersion in the uniform liquid is used as input. This makes the theory quantitative in the prediction of the excited states of inhomogeneous systems. We have shown results for the dispersion of ripplons on the free surface and for the excitations of films. An accurate description of the excitations in bulk is particularly important to study the ripplon-roton hybridization mechanism [9] and the process of quantum evaporation.

The predictions of the theory compare well with available results of Monte Carlo simulations in small systems. The density functional approach can be easily applied to large systems too, and consequently can be considered a reliable tool to exploring the properties of inhomogeneous liquid helium in a rather systematic way.

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