Density functional calculations for $^4$He droplets

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Abstract

A novel density functional, which accounts correctly for the equation of state, the static response function and the phonon-roton dispersion in bulk liquid helium, is used to predict static and dynamic properties of helium droplets. The static density profile is found to exhibit significant oscillations, which are accompanied by deviations of the evaporation energy from a liquid drop behaviour in the case of small droplets. The connection between such oscillations and the structure of the static response function in the liquid is explicitly discussed. The energy and the wave function of excited states are then calculated in the framework of time dependent density functional theory. The new functional, which contains backflow-like effects, is expected to yield quantitatively correct predictions for the excitation spectrum also in the roton wave-length range.

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I. INTRODUCTION

The study of Helium droplets, as a prototype of finite quantum fluid, has been the object of extensive experimental and theoretical investigations in the last decade (see Ref. [1] for a recent review). The ground state and the excited states of pure $^4$He droplets, as well as of droplets doped with atomic and molecular impurities, have been studied using different theoretical approaches. However, the overlap between theories and experiments is not yet satisfactory.

In this paper we investigate static and dynamic properties of $^4$He droplets using a density functional theory. We use a functional recently introduced by the Orsay-Trento collaboration [2]. It is an extension of a previous phenomenological functional [3], which has been extensively used in the last years to study the static and the dynamic properties of inhomogeneous phases of liquid helium (free surface, films, droplets). The Orsay-Trento functional improves, by construction, the description of relevant properties of the bulk liquid, such as the $q$-dependence of the static response function and the phonon-roton dispersion. We study here how this improvement affects the results for the static and dynamic properties of helium droplets. In particular, we look for deviations of the density profile and the evaporation energy from the liquid drop behaviour and we explore the effects of backflow correlations on the excitation spectrum at large momentum transfer.

The paper is organized as follows. In Sect. II we present briefly the functional (for a complete discussion we refer to [2]). In Sect. III we apply it to the ground state of the droplets. Then, in Sect. IV we sketch the formalism of time dependent density functional theory and present some results for excited states.

II. DENSITY FUNCTIONAL

A first systematic analysis of the ground state properties of $^4$He and $^3$He droplets in the framework of density functional theory was done in Ref. [4], using a simple functional based on a zero-range effective interaction. The same functional was later generalized to include finite-range effects [3]. This functional has been applied to investigate static properties of several inhomogeneous systems, such as helium films and wetting phenomena [5], vortices in bulk liquid [6] or droplets [7].

In density functional theory the energy of the system is written as

$$E = \int d\mathbf{r} \mathcal{H}[\Psi, \Psi^*]$$

with the complex function $\Psi$ in the form

$$\Psi(\mathbf{r}, t) = \Phi(\mathbf{r}, t) \exp \left( \frac{i}{\hbar} S(\mathbf{r}, t) \right) .$$

The real function $\Phi$ is related to the diagonal one-body density by $\rho = \Phi^2$, while the phase $S$ fixes the velocity of the fluid through the relation $\mathbf{v} = (1/m) \nabla S$. The ground state of the system is found by minimizing the energy with respect to the density, while the time dependent theory is formally equivalent to the RPA equations with an effective particle-hole interaction, as we will see in Sect. IV. We use the phenomenological density functional of
Ref. [2], containing a few parameters which are fixed to reproduce bulk properties of liquid helium. It has the form:

$$ E = E^{(\text{kin})}[\rho, \mathbf{v}] + E^{(c)}[\rho] + E^{(bf)}[\rho, \mathbf{v}], $$

(3)

where the first term is the kinetic energy of non-interacting bosons,

$$ E^{(\text{kin})}[\rho, \mathbf{v}] = \int d\mathbf{r} \frac{\hbar^2}{2m} |\nabla \Psi(\mathbf{r})|^2 $$

$$ = \int d\mathbf{r} \left\{ \frac{\hbar^2}{2m} (\nabla \sqrt{\rho})^2 + \frac{m}{2} \rho(\mathbf{r})|\mathbf{v}(\mathbf{r})|^2 \right\}, $$

(4)

the correlation energy $E^{(c)}$ is given by

$$ E^{(c)}[\rho] = \int d\mathbf{r} \{ \frac{1}{2} \int d\mathbf{r}' \rho(\mathbf{r}) V_f(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}') + \frac{c_2}{2} \rho(\mathbf{r})(\bar{\rho}_r)^2 + \frac{c_3}{3} \rho(\mathbf{r})(\bar{\rho}_r)^3 $$

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

(5)

and, finally, the backflow energy $E^{(bf)}$ is

$$ E^{(bf)}[\rho, \mathbf{v}] = -\frac{m}{4} \int d\mathbf{r} d\mathbf{r}' V_f(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}) \rho(\mathbf{r}') [\mathbf{v}(\mathbf{r}) - \mathbf{v}(\mathbf{r}')]^2. $$

(6)

The first term in the kinetic energy, which depends on gradient of the density, is a quantum pressure; it corresponds to the zero temperature kinetic energy of non-interacting bosons of mass $m$. The two-body interaction $V_f$ in the correlation energy $E^{(c)}$ is the Lennard-Jones interatomic potential, with the standard parameters $\alpha = 2.556$ Å and $\varepsilon = 10.22$ K, screened at short distance ($V \equiv 0$ for $r < h$, with $h = 2.1903$ Å). The two terms with the parameters $c_2 = -2.411857 \times 10^4$ K Å$^6$ and $c_3 = 1.858496 \times 10^6$ K Å$^9$ account phenomenologically for short range correlations between atoms. The weighted density $\bar{\rho}$ is the average of $\rho(\mathbf{r})$ over a sphere of radius $h$. Those terms are very similar to the functional of Ref. [3]. The last term in $E^{(c)}$, depending on the gradient of the density in different points, is new and has been added in order to improve the description of the static response function in the roton region. The function $F$ is a simple gaussian, $F(r) = \pi^{-3/2} \ell^{-3} \exp(-r^2/\ell^2)$ with $\ell = 1$ Å, while $\alpha_s = 54.31$ Å$^3$ and $\rho_{0s} = 0.04$ Å$^{-3}$. The energy $E^{(bf)}$ contains an effective current-current interaction accounting for backflow-like correlations. In Ref. [4] the simple parametrization

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

(7)

was chosen in order to reproduce the phonon-roton dispersion in bulk liquid. The parameters are given in Table [4].

A detailed discussion about the meaning of the different contributions to functional (3) and about the choice of the parameters is given in Ref. [4]. Here we apply this functional to the statics and the dynamics of droplets.
III. GROUND STATE

To find the ground state of the system one has to minimize the energy

\[ E_0 = E^{(c)}[\rho] + \int d\mathbf{r} \frac{\hbar^2}{2m} (\nabla \sqrt{\rho})^2 \]  

(8)

with respect to the particle density \( \rho \). This leads to the Hartree-type equation

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

(9)

The Hartree potential is given by \( U[\rho, \mathbf{r}] \equiv \delta E^{(c)}/\delta \rho(\mathbf{r}) \). The chemical potential \( \mu \) is introduced in order to ensure the proper normalization of the density to a fixed number of particles.

For helium droplets the Hartree equation has to be written in spherical geometry. It becomes a unidimensional integro-differential equation which requires an iterative procedure to be solved. The resulting density profile, normalized to the bulk value \( \rho_0 = 0.021836 \) \( \text{Å}^{-3} \), for small droplets \( (10 \leq N \leq 60) \) is shown in Fig. 1. One clearly notice the appearance of oscillations both in the interior of the droplets and on the surface. The central density approaches the bulk density for large droplets, but it deviates significantly from the smooth behaviour predicted for a drop of compressible liquid [4]. Such oscillations were not found with previous functionals.

Shell effects in \( ^3\text{He} \) droplets, originating from Fermi statistics and shell closure in the single particle spectrum [3], are expected to be important. On the contrary, the existence of a shell structure in bosons droplets is still under debate. Twenty years ago Regge and Rasetti [8] suggested the possibility to have “magic” droplets by looking at the structure of the elementary excitations in the bulk. In particular they showed that the surface of the liquid drop could act as a source of excitations producing static ripples on the density profile. In this approach the static ripples of the surface profile are connected to the pronounced peak of the static response function of bulk liquid at the roton wave length. The authors of Refs. [4] also commented about the possibility that those oscillations could be washed out by the zero-point motion of the surface, whose thickness is expected to be larger than the interatomic distance. Indeed the subsequent theoretical predictions for the surface profile in helium droplets [4, 10, 12], predicted a thickness of the order of \( 6 \div 8 \) \( \text{Å} \) and no density oscillations. A systematic analysis of small droplets with Green’s Function Monte Carlo techniques was presented by Melzer and Zabolitzky [13] in a work entitled “No magic numbers in neutral \( ^4\text{He} \) clusters”. However, the problem has been re-opened by the most recent Diffusion Monte Carlo calculations by Chin and Krotscheck [14] which show clear structures in the density profile of droplets with 20, 40, 70, and 112 atoms.

In order to check the relation between the density oscillations in Fig. 1 and the behavior of the static response function \( \chi(q) \) we calculate the latter using our density functional theory. It can be evaluated by taking the second functional derivative of the energy through the relation

\[ -\chi^{-1}(q) = \frac{\hbar^2 q^2}{4m} + \frac{\rho}{V} \int d\mathbf{r} d\mathbf{r}' \frac{\delta^2 E^{(c)}}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')}, \]  

(10)
where $V$ is the volume occupied by the system. A major advantage of liquid helium is that $\chi(q)$ is known experimentally since it is also equal to the inverse energy moment of the dynamic structure function $S(q, \omega)$ which is measured in neutron scattering. In the upper part of Fig. 2 the experimental value of the static response function at zero pressure \[^{[15]}\] is compared with the predictions of three functionals: the one of the present work \[^{[2]}\] and the ones of Refs. \[^{[3,4]}\]. The static response function is strongly $q$-dependent, showing a peak at the roton wave length. According to the theory of Regge and Rasetti this peak is also related to density oscillations in the profile of the free surface and of droplets. In the lower part of Fig. 2 we show the predictions for the density profile of the free surface with the three functionals. Indeed, while the three surface profile have a similar thickness, of the order of 6 to 8 Å, they have a different structure. Only the functional of the present work, which reproduce completely the peak of $\chi(q)$ at the roton wave length, exhibits density oscillations. We note also that the same physical effect can be understood in terms of the static structure factor $S(q)$, which has also a peak in the roton wavelength region. The relation between the quantities $\chi(q)$ and $S(q)$ in the framework of the present density functional theory is discussed in Ref. \[^{[2]}\]. It is worth mentioning that small density oscillations at the liquid-vapour interface have been recently predicted in classical fluids interacting through short ranged potentials \[^{[16]}\]. In that case, the connection with the behavior of the radial distribution function, $g(r)$, has been investigated in detail. For classical fluids the static response function and the radial distribution function are related through the Ornstein-Zernike equation.

The oscillations of the free surface profile are very small; they are not expected to give rise to measurable effects. The surface energy is practically the same for the three profiles in Fig. 2 (about 0.27 KÅ$^2$) and, moreover, the available experimental data on the surface reflectivity \[^{[17]}\] are not sensitive to such small oscillations in the profile. In the case of small droplets, however, the oscillating structure of the surface can combine with finite size effects, i.e., the tendency to form closed shell of atoms. This seems the case for the profile in Fig. 1. We notice that the structure in the density of the droplets is not related to a “solid-like” behaviour; the oscillations originate at the surface, while a solid structures are not favoured in general by the presence of surfaces.

The comparison between our results for the density profile and the ones of \textit{ab initio} calculations is given in Fig. 3 for droplets with 20 and 70 particles. The solid line is the result of the present density functional calculation, while the DMC results of Ref. \[^{[14]}\] are represented by solid circles. The DMC data exhibit more pronounced oscillations, but possible spurious effects of metastable states, slowing down the convergence in the Monte Carlo algorithm, cannot be completely ruled out \[^{[14]}\]. Recently the same authors have found oscillations in $\rho(r)$ even with a variational approach based on the HNC approximation \[^{[18]}\] (dashed line). Even though the HNC method underestimates the central density, it predicts oscillations with amplitude and phase in remarkable agreement with the ones of density functional theory. An even better agreement is found in the most recent DMC calculations by Barnett and Whaley \[^{[19]}\] (empty circles), where the statistical error is significantly reduced with respect to Ref. \[^{[14]}\].

Our predictions for the energy per particle are shown in Fig. 4 (solid line), together with the results of previous Monte Carlo and density functional calculations. The energy is a smooth function of the particle number $N$. Indeed $^4$He clusters behave “grosso modo” as liquid droplets and the energy can be easily fitted with the liquid drop formula.
\[
\frac{E}{N} = a_v + a_s N^{-1/3} + a_c N^{-2/3} + a_0 N^{-1}, \tag{11}
\]

where the volume coefficient \(a_v\) is the chemical potential in bulk, the surface coefficient is fixed by the free surface energy, while \(a_c\) and \(a_0\) can be taken as fitting parameters. The energy calculated with the density functional differs from the liquid drop fit by less than 0.02 K for all droplets with \(N > 30\). This seems to rule out apparently any shell effect in the energy systematics. However, one must keep in mind that the most relevant quantity determining the mass distribution of droplets is the evaporation energy \([E(N-1) - E(N)]\). The latter is not as smooth as the energy per particle. In Fig. 1 we show the evaporation energy predicted by the density functional (solid line) and the one obtained with the liquid drop formula (11) (dashed line). The difference between the two curves is also shown (dot-dashed line). When the difference is positive the droplets are more stable than it is predicted by the liquid drop formula. We note clear oscillations, having decreasing amplitude and increasing periodicity as a function of \(N\). The same kind of oscillations appear in the central density of the droplets, as seen in Fig. 1. Since the distance between two crests of the surface ripples is practically constant and the droplet radius goes approximately like \(N^{1/3}\), the period of oscillations of the central density as a function of \(N\), as well as the one of the evaporation energy, increases as \(N^{1/3}\).

These results support quantitatively the original pictures proposed in Ref. [9], where the surface ripples have been discussed in terms of soft sphere closed packing. However the predicted deviations of the evaporation energy from the liquid drop behaviour are very small (less than 0.1 K). This makes their detection quite difficult since the temperature of the droplets in the experimental beams is presently expected to be about 0.4 K.

In conclusion, we have shown some evidence for the occurrence of shell effects in neutral \(^4\)He droplets. They are predicted by a density functional theory and physically originate by the strong peak in the static response function of liquid helium at the roton wave length. The shell effects are visible in the density profiles and the evaporation energy as a function of the number of particles in the droplet. Our results are in agreement with recent Monte Carlo simulations [14] and seem to confirm the previous predictions by Regge and Rasetti [9].

IV. EXCITED STATES

A. Density-density response

The first theoretical investigations of the elementary excitations of \(^4\)He droplets have been based on a generalized Feynman theory within the framework of microscopic Monte Carlo calculations of the ground state [10,12,20,14]. A systematic discussion, using a Diffusion Monte Carlo algorithm, has been presented in [14]. In general, within this framework, it has been found that the dispersion with transferred momentum of the collective energies approaches the Feynman spectrum for bulk \(^4\)He as the cluster size increases. The convergence is very fast and already at small sizes \((N \approx 70)\) there seems to be a well defined roton minimum. The Feynman spectrum is known however to overestimate by almost a factor two the experimental roton energy.
Since the Orsay-Trento functional reproduces the bulk phonon-roton spectrum, it is interesting to explore what it gives for the dynamics of helium droplets. In the following we study the behaviour of monopole ($L = 0$) and quadrupole ($L = 2$) excitations at low $q$, where the effect of the velocity dependent term turns out to be negligible, as well as the behaviour of monopole excitations at large $q$, where the spectrum is shown to approach the correct phonon-roton dispersion. We discuss the deviations from the results of a liquid drop model and the comparison with previous theories.

The formalism of the time dependent density functional theory has been already introduced, for instance, in Refs. [21,22,2] for applications to the dynamics of the free surface, of droplets, and films of helium on solid substrates. The same theory is here developed using the formalism of Green’s Functions, allowing for a direct evaluation of the dynamic response function. We consider elementary excitations which are induced by an external field that couples to the particle density in the droplet. For sufficiently weak external fields the response can be treated linearly within the Random-Phase approximation. The response function to a transition operator $Q(r)$ is defined as

$$ \mathcal{R}(\omega) = \int d\vec{r}d\vec{r}' Q^\dagger(\vec{r})G(\vec{r},\vec{r}';\omega)Q(\vec{r}) , \tag{12} $$

where $G$ is the retarded Green’s function, which is defined in terms of the ground state ($|0>\rangle$), excited states ($|n>\rangle$) and their corresponding excitation energies $\omega_{n0}$, and the creation operator $\psi^\dagger(\vec{r})$ (assuming time-reversal invariance of the matrix elements):

$$ G(\vec{r},\vec{r}';\omega) = - \sum_n <0|\psi^\dagger(\vec{r})\psi(\vec{r})|n> <n|\psi^\dagger(\vec{r}')\psi(\vec{r}')|0> \frac{1}{\omega_{n0} - \omega - i\eta} + \frac{1}{\omega_{n0} + \omega + i\eta} . \tag{13} $$

From Eq. (13) it is clear that the excitation energies are at the poles of $G$, and that they produce sharp peaks in the imaginary part of $\mathcal{R}(\omega)$.

Within the RPA the Green’s function is calculated from the equation

$$ G(\vec{r},\vec{r}';\omega) = G^{(0)}(\vec{r},\vec{r}';\omega) + \int d\vec{r}_1d\vec{r}_2 G^{(0)}(\vec{r},\vec{r}_1;\omega)V_{ph}(\vec{r}_1,\vec{r}_2)G(\vec{r}_2,\vec{r}';\omega) , \tag{14} $$

where $G^{(0)}$ is the Green’s function for a helium droplet with $N$ atoms within the single-particle model, i.e., expressed in terms of single particle wave functions $\varphi_i$ and energies $\varepsilon_i$:

$$ G^{(0)}(\vec{r},\vec{r}';\omega) = -N\varphi_0^*(\vec{r})\varphi_0(\vec{r}')\sum_n \varphi_n(\vec{r})\varphi_n^*(\vec{r}') \left( \frac{1}{\varepsilon_n - \varepsilon_0 - \omega - i\eta} + \frac{1}{\varepsilon_n - \varepsilon_0 + \omega + i\eta} \right) , \tag{15} $$

and $V_{ph}$ is the residual (particle-hole) interaction. The sum in Eq. (13) extends, in principle, to all states $\varphi_n$, including those lying within the energy continuum (see Appendix). Once this is obtained, the RPA equation can be solved as a matrix equation in coordinate space and, finally, the response function can be obtained from Eq. (12).

In principle, the external field to be used in density-density response is the plane wave, with transferred momentum $q$, $Q(\vec{r}) = \sum_{i=1}^N e^{i\vec{q}\cdot\vec{r}_i}$. However, with the multipole expansion indicated in the Appendix, one can calculate separately the response to each multipole $Q_L =$
$\sum_{i=1}^{N} j_L(q r_i) Y_{L0}(\hat{r}_i)$. In the limit of low $q$ this external field reduces to $Q_L = \sum_{i=1}^{N} r_i^L Y_{L0}(\hat{r}_i)$. Within the previous formulation of the response we will include exactly the coupling with the particle continuum. This may have some importance, especially for the response at high momentum transfer.

**B. Residual particle-hole Interaction**

The particle-hole interaction entering Eq. (14) is obtained, within density-functional theory, from the second variation of the energy functional. For functionals depending just on particle density $\rho(\mathbf{r})$ and its gradients it may be obtained in the following way.

Let the density be written, in general, in terms of the single particle basis $\varphi_i(\mathbf{r})$ as

$$\rho(\mathbf{r}) = \sum_{ij} \rho_{ij} \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}).$$  \hspace{1cm} (16)

The second variation of the correlation energy $E_c$ with respect to $\rho_{ij}$’s, taken at the ground state, provides the two-body interaction $V_{ph}$:

$$<ij|V_{ph}(\mathbf{r}_1, \mathbf{r}_2)|kl> = \frac{\delta^2 E_c[\rho]}{\delta \rho_{ik} \delta \rho_{jl}}.$$  \hspace{1cm} (17)

The variation in this equation may be calculated as

$$\frac{\delta^2 E_c[\rho]}{\delta \rho_{ik} \delta \rho_{jl}} = \int d^3 r_1 d^3 r_2 \left( \frac{\delta^2 E_c[\rho]}{\delta \rho(\mathbf{r}_2) \delta \rho(\mathbf{r}_1)} \right)_{g.s.} \frac{\delta \rho(\mathbf{r}_1)}{\delta \rho_{ik}} \frac{\delta \rho(\mathbf{r}_2)}{\delta \rho_{jl}}$$

$$= \int d^3 r_1 d^3 r_2 \varphi_i^*(\mathbf{r}_1) \varphi_j^*(\mathbf{r}_2) \left( \frac{\delta^2 E_c[\rho]}{\delta \rho(\mathbf{r}_2) \delta \rho(\mathbf{r}_1)} \right)_{g.s.} \varphi_k(\mathbf{r}_1) \varphi_l(\mathbf{r}_2),$$  \hspace{1cm} (18)

and, consequently, we obtain the well known result

$$V_{ph}(\mathbf{r}_1, \mathbf{r}_2) = \left( \frac{\delta^2 E_c[\rho]}{\delta \rho(\mathbf{r}_2) \delta \rho(\mathbf{r}_1)} \right)_{g.s.}.$$  \hspace{1cm} (19)

The Fourier transform of this quantity enters the definition of the static response function $\chi(q)$ in bulk liquid, as in Eq. (11). From a practical viewpoint, the functional derivative implies the calculation of derivatives of the integrands in Eq. (5) with respect to $\rho$ and $\nabla \rho$.

The inclusion of the backflow term in the functional requires a generalization of the previous scheme. This term introduces a dependence on the current density $\mathbf{j}$, defined as

$$\mathbf{j}(\mathbf{r}) = \frac{\hbar}{2m} \sum_{ij} (\nabla - \nabla') \rho_{ij} \varphi_i^*(\mathbf{r}) \varphi_j(\mathbf{r}')(\mathbf{r} = \mathbf{r}').$$  \hspace{1cm} (20)

Since the current density vanishes for the ground state, the only term contributing to the residual (backflow) interaction will be

$$\frac{\delta^2 E^{bf}[\rho, \mathbf{j}]}{\delta \rho_{ik} \delta \rho_{jl}} = \int d^3 r_1 d^3 r_2 \left( \frac{\delta^2 E^{bf}[\rho, \mathbf{j}]}{\delta \mathbf{j}_\nu(\mathbf{r}_2) \delta \mathbf{j}_\nu(\mathbf{r}_1)} \right)_{g.s.} \frac{\delta \mathbf{j}_\nu(\mathbf{r}_1)}{\delta \rho_{ik}} \frac{\delta \mathbf{j}_\nu(\mathbf{r}_2)}{\delta \rho_{jl}}.$$  \hspace{1cm} (21)
where the index $\nu$ spans the three components, and a sum over $\nu$ is assumed. From this expression one finds for the back-flow part of the residual interaction

$$V_{ph}^{(bf)}(1, 2) = -\frac{\hbar^2}{4m^2} \left( \frac{\delta^2 E^{(bf)}[\rho, J]}{\delta J_\nu(r_2) \delta J_\nu(r_1)} \right)_{g.s.} (\vec{\nabla}_1 - \vec{\nabla}_1)(\vec{\nabla}_2 - \vec{\nabla}_2),$$

(22)

where the parenthesis is in fact independent of $\nu$ and the gradients act only on the single-particle wave functions. This last expression shows explicitly how the current-dependent term yields a velocity-dependent residual interaction. Indeed, Eq. (22) is quite similar to the Skyrme residual interaction in nuclear physics, and we will use a similar technique to calculate the associated RPA response. Summarizing, we have two contributions to the residual interaction

$$V_{ph} = V_{ph}^{(0)} + V_{ph}^{(bf)},$$

(23)

where $V_{ph}^{(0)}$ is the residual interaction, obtained with Eq. (19), associated to the functional without current terms, while $V_{ph}^{(bf)}$ is the contribution from these current terms.

C. Results

In this section we present the results obtained for $R(\omega)$ in the formalism presented above. We use the technique developed in Ref. [23,24] and already applied to $^4$He droplets in the context of a contact (zero-range) effective interaction in Ref. [22]. The present formalism generalizes that of [22] by including both finite range and back-flow effects. We expect these to be important for the droplet response at high transferred momentum $q$, while for low $q$ we expect to recover a surface-mode systematics similar to that of Ref. [22]. The present functional reproduces by construction the dispersion of the elementary excitations in bulk liquid $^4$He [2], i.e., the phonon-roton curve up to $q \approx 2.3$ Å$^{-1}$. Consequently, it is particularly appropriate for the study of the response of droplets in this region of $q$’s.

1. Low $q$ results

Fig. 6 shows the imaginary part of $R(\omega)$ for the low $q$ limit of the monopole and quadrupole external fields, which are $Q = \sum_i r_i^2$ and $Q = \sum_i r_i^2 Y_{20}$, respectively, for the droplet with $N=112$ atoms. The monopole corresponds to a breathing mode, while the quadrupole is a surface vibration [22]. It is clearly seen how a very intense peak appears in the RPA result (continuous line), corresponding to a collective oscillation of the $^4$He atoms. The independent-particle result (dashed line), obtained by neglecting in Eq. (14) the particle-hole interaction, is in both cases more fragmented, revealing that the RPA correlations play a crucial role in the dynamics of the system.

The effect of the current dependent part of the residual interaction, $V_{ph}^{(bf)}$, on the monopole and quadrupole excitations in this range of $q$ is completely negligible. We have explicitly checked that the monopole result in Fig. 6 is not affected at all by $V_{ph}^{(bf)}$. This is consistent with the fact that in bulk liquid the lowest excitation for $q \to 0$ is the phonon-mode, which is not affected by backflow-like correlations. As concern the $L \neq 0$ modes of
the clusters, Chin and Krotscheck have recently shown that, at low \( q \), they approach the dispersion of ripplons on the free surface. The latter, again, is found to be practically unaffected by backflow correlations.

The static induced densities \( \delta \rho^{(0)}(r) \) for the same cluster are plotted in Fig. 7. This figure proves the behaviour mentioned before: the monopole induced density has a node and penetrates the interior of the cluster, while the quadrupole is almost completely localized at the droplet surface. An interesting result shown by this figure is the appearance of small oscillations in \( \delta \rho^{(0)} \), in the inner part, both for the monopole and the quadrupole. This behaviour is connected to the oscillations displayed by the droplet equilibrium density and is due to the repulsive core of the effective interaction (see also Ref. [25]). In fact, with the use of a contact interaction the small oscillations disappear both in \( \rho \) and \( \delta \rho \). Similar oscillations have also been found using other microscopic methods, like Monte Carlo calculations.

The dependence of the collective energy with the number of atoms in the cluster is shown in Fig. 8. The comparison with independent particle predictions shows that the role of RPA correlations increases with \( N \). The deviations of the RPA predictions from the Liquid Drop Model (LDM) results (long-dashed line, see [22]) are due to finite-size effects and are important up to \( N \approx 100 \) for surface vibrations and up to \( N \approx 500 \) for compression modes. The energies are in nice agreement with those of Ref. [22], confirming the expectation that the response at \( q \to 0 \) is not affected by the long range part of the atom-atom interaction. In the following section we show how this is completely different for the high \( q \) region of the response.

2. High \( q \) results

In this section we will focus on the \( L = 0 \) response. In this case, the hole and particle states which contribute to the Green’s function have spherical symmetry and this allows us to take only the radial part of the \( \frac{\nabla}{\nabla} \) in \( V^{(bf)}_{ph} \), as a consequence, only the monopole term in the multipole expansion of the second functional derivative of Eq. (22) is needed. The situation is different for higher multipoles, since then the residual interaction \( V^{(bf)}_{ph} \) involves different multipoles of the second functional derivative of Eq. (22). This greatly complicates the numerical calculation and we leave this case for a future investigation. In this work we concentrate on the monopole response to show the influence of the current term in the high-\( q \) response of droplets.

Figure 9 shows the contour lines of the surface \( \text{Im}[\mathcal{R}(q, \omega)] \) for the \( N = 112 \) droplet. One clearly appreciates that the zone of higher response strength, where the peaks are located, resembles the dispersion curve of the bulk \(^4\text{He} \) elementary excitations. The existence of a roton minimum is clearly seen around \( q = 2 \) \( \text{Å}^{-1} \). However, the energy of this excitation is quite affected by the current term \( V^{(bf)}_{ph} \). The upper panel is the result when \( V^{(bf)}_{ph} \) is not included and provides a minimum energy at \( \approx 15 \) K. When this current term is included the minimum energy moves to \( \approx 9 \) K. Fig. 10 shows how this picture changes for different cluster sizes. For \( N = 20 \) the number of atoms is not enough to develop the roton minimum while for \( N = 728 \) the result follows quite closely the bulk one. Similar behaviour has been found using other microscopic methods; being based on Feynman-like wave functions, those
calculations yield a roton minimum at approximately twice the experimental roton gap in bulk liquid.

V. CONCLUSIONS

We have presented static and dynamic calculations for pure $^4$He droplets using a new density functional theory developed by the Orsay-Trento collaboration [2]. The density functional is written in such a way that relevant properties of the uniform liquid (equation of state, static response function, phonon-roton dispersion) are accurately reproduced. The theory is suitable to study properties of non uniform states of liquid helium.

The static density profile and the energy of helium droplets have been calculated as a function of the number of atoms. We have found small density oscillations associated with regular deviations of the evaporation energy from the smooth liquid drop behaviour. We have discussed these oscillations in connection with the structure of the static response function, as suggested by a previous model of Regge and Rasetti [4]. Our results compare well with recent ab initio Monte Carlo calculations.

We have also calculated the energy and transition densities of monopole and quadrupole excited states. The transition densities at $q \to 0$ display small oscillations similar to those of the ground state density. As in the case of the zero-range interaction, the solution of the RPA equations reveals the importance of the finite size effects and the long range correlations in the determination of the excitation energies of the compression and surface modes. In particular, the deviation from the LDM results are important up to $N \approx 500$ for compression modes and up to $N \approx 100$ for surface vibrations.

The analysis of the monopole mode at high momentum transfer shows the existence of a roton minimum around $q \approx 2 \text{ Å}^{-1}$ for clusters with a number of atoms $N \geq 20$. As in the uniform liquid, the backflow correlations, which are included phenomenologically in the theory, yield a sizeable decrease in the energy of this minimum, from $\approx 15$ K to $\approx 9$ K.

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APPENDIX A: RPA IN THE CONTINUUM

The sum in Eq. (13) can be written in a more compact way, using the particle Green’s function $g_p$ corresponding to the particle Hamiltonian $H_p$, in coordinate space:

$$g_p(r_1, r_2; \omega) = \frac{1}{H_p - \omega} | r_2 >,$$

as

$$G^{(0)}(r, r'; \omega) = - N \varphi_0^*(r) \varphi_0(r') \left( g(r, r'; \varepsilon_0 + \omega + i\eta) + g(r, r'; \varepsilon_0 - \omega - i\eta) \right).$$
The particle Hamiltonian $H_p$ is defined from Eq. (9)

$$H_p = -\frac{\hbar^2}{2m} \nabla^2 + U[\rho, \mathbf{r}], \quad \text{(A3)}$$

with $\rho$ the ground state density.

For spherical droplets each of the functions in Eq. (14) can be expanded in multipoles as

$$G(\mathbf{r}, \mathbf{r}') = \sum_{LM} G_L(r, r') Y_{LM}^*(\hat{r}) Y_{LM}(\hat{r}') \quad \text{(A4)}$$

and, as a result, Eq. (14) also separates for different multipoles. In a symbolic notation

$$G_L = G^{(0)}_L + G^{(0)}_L V_{ph,L} G_L \quad \text{(A5)}$$

The particle Green’s function for each partial wave $g_L$ is most easily calculated by means of the scattering solutions to the effective radial Hamiltonian $H_{p,L}$ at energy $\omega$:

$$H_{p,L} u_L(r) = \omega u_L \quad \text{(A6)}$$

It is

$$g_L(r, r'; \omega) = \frac{2m}{\hbar^2} \frac{u_L(r_< w_L(r_>)}{rr'W(u_L, w_L)} \quad \text{(A7)}$$

where $u$ and $w$ are, respectively, the regular and irregular at the origin radial solutions of (A6), and $W(u_L, w_L)$ is their Wronskian. In this way we can obtain $G^{(0)}$ without having to impose any truncation of the continuum.
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FIGURES

FIG. 1. Density profile of $^4$He droplets for $10 \leq N \leq 60$, normalized to the bulk value.

FIG. 2. Static response function of liquid helium (above) and free surface profile (below). Circles: experimental data [15]; lines: density functional calculations with functional of Ref. [4] (dotted), Ref. [3] (dashed) and the one of Eq. (2) (solid).

FIG. 3. Density profile of two droplets. Solid line: present work; solid circles: DMC calculations of Ref. [14]; empty circles: DMC calculations of Ref. [13]; dashed line: HNC calculations of Ref. [18].

FIG. 4. Energy per particle versus $N$. Solid line: present work; dotted line: Ref. [4]; dashed line: results with functional of Ref. [3]; empty circles: Ref. [13]; solid circles: Ref. [14].

FIG. 5. Evaporation energy. Solid line: present work; dashed line: liquid drop formula. Dot-dashed line: deviation from the liquid drop formula (axis on the right).

FIG. 6. Imaginary part of the response function at zero momentum transfer ($q = 0$) of the droplet with $N = 112$ atoms. Part (a) corresponds to the monopole case for which the external field is $Q = \sum_i r_i^2$, and (b) to the quadrupole, with $Q = \sum_i r_i^2 Y_{20}(\hat{r}_i)$. See text.

FIG. 7. Induced densities for the droplet $N = 112$ in the static limit, $\omega = 0$, corresponding to the results of Fig. 3. We used arbitrary vertical scale. The dashed line shows the ground state density of the same droplet with the labeled vertical scale. See text.

FIG. 8. Energy of the collective peak at $q = 0$ as a function of size for the quadrupole and monopole. The short-dashed line shows, for comparison, the results of Ref. [22]. The long-dashed line corresponds to the LDM prediction.

FIG. 9. Contour lines of the surface $\text{Im}[\mathcal{R}(q, \omega)]$ for the monopole excitation of the droplet $N = 112$. Part (a) is without including the current-dependent term $V^{(bf)}_{ph}$ while (b) corresponds to the complete functional. See text.

FIG. 10. Same as Fig. 9b, with the complete functional, for the droplets with $N = 20$ (a) and $N = 728$ (b).
TABLES

TABLE I. Values of the parameters used in $V_J(r)$, see Eq. (7).

| $\gamma_{11}$ | $\gamma_{21}$ | $\gamma_{12}$ | $\gamma_{22}$ | $\alpha_1$ | $\alpha_2$ |
|----------------|----------------|----------------|----------------|------------|------------|
| -19.7544       | -0.2395        | 12.5616 Å$^{-2}$ | 0.0312 Å$^{-2}$ | 1.023 Å$^{-2}$ | 0.14912 Å$^{-2}$ |