The structure of large $^3$He-$^4$He mixed drops around a dopant molecule

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(May 23, 2018)

We have investigated how helium atoms are distributed within a mixed $^3$He$_{N_3}$-$^4$He$_{N_4}$ large drop with $N_3 \gg N_4$. For drops doped with a SF$_6$ molecule or a Xe atom, we have found that the number of $^3$He atoms within the volume containing the first two solvation shells increases when $N_4$ decreases in a way such that these dopants may be in a superfluid environment for $N_4 \geq 60$, which gradually disappears as $N_4$ decreases. The result is in qualitative agreement with recent experimental data.

PACS 36.40.-c 67.60.-g 67.40.-w 67.55.-s

In a recent experiment, Grebenev et al [1] have carried out the equivalent of the Andronikashvili experiment [2] in a microscopic system, namely a mixed $^3$He-$^4$He drop consisting of about $10^4$ atoms doped with an oxygen carbon sulfide (OCS) molecule. By analyzing the infrared spectrum of OCS, Grebenev et al (see also Ref. [3]) conclude that the molecule freely rotates when a number of $^4$He atoms large enough coats the impurity, preventing the $^3$He atoms, which are in the normal phase at a temperature of the order of 150 mK [4], from getting too close to the OCS molecule. That number is of the order of 60, in excellent agreement with path integral [5] and variational [6] Monte Carlo calculations. It is remarkable that the presence of the impurity, which causes the $^3$He density to rise up to several times the saturation value, is not destroying its superfluid character, and that in spite of the high densities reached, the first solvation shell remains liquid [7]. An indication of this fluidlike behavior is that the peak density in the first solvation shell continues to increase as the second shell grows [8].

Even if the interpretation of the microscopic Andronikashvili experiment is on a firm basis, a remaining major question is how $^3$He is distributed around the $^4$He-plus-impurity complex, and in general, how liquid $^3$He is dissolved into $^4$He droplets at very low temperatures. These are the questions we want to address in this work.

At zero temperature, it is known that the maximum solubility of $^3$He in the bulk of $^4$He is $\sim 6.6\%$ [1]. For liquid $^4$He systems having a free surface, it is also known that a large amount of $^3$He is accumulated on the free surface occupying Andreev states [1][2] before it starts being dissolved into the bulk. In the case of drops made of up to several thousands of atoms, the surface region constitutes a sizeable part of the system [3], and the surface has a large capacity of storing $^3$He atoms before they get inside the drop [4]. Due to the wide free surface of both isotopes [3][16] and to the low surface tension of the $^3$He-$^4$He liquid interface [7], one expects that this region plays a prominent role when it constitutes a large part of the system or, as in the present case, when it is close to the foreing atom or molecule.

The structure and energetics of mixed, doped or not, helium droplets has been addressed using a finite-range density functional [14]. That work was carried out before the experiments reported in Ref. [4], and the emphasis was put on improving the density functional to better describe the thermodynamical properties of the liquid mixture, and to study rather small mixed droplets with $N_4 \gg N_3$. Our main goal here is to apply the density functional method to droplets whose characteristics are closer to those of the experiments, with the restriction of spherical symmetry for the He-impurity potential for the sake of simplicity. We have considered Xe and SF$_6$ as dopants, using for the later a spherically averaged interaction potential. The Xe-He potential is weaker than the SF$_6$-He one. In this respect, our results for that atomic impurity should better represent the experimental ones for OCS even if this linear molecule produces deformations in the helium drop that we have not considered here. The density functional and the treatment of the impurity are thoroughly described in Ref. [14].

The large number of $^3$He atoms in the droplets we are describing ($N_3 > 1000$) allows us to employ an Extended Thomas-Fermi method to describe the fermionic component of the mixture. We have used for the $^3$He kinetic energy density the expression given in Ref. [15], which contains up to second order density gradient corrections to the standard $\rho^3/3\rho$ expression, where $\rho_3$ and $\rho_4$ will denote the particle density of each isotope.

We have checked that this density functional reproduces accurately the Hartree-Fock results [12] obtained for the largest drops there studied (see also Refs. [16][17]).

Figure 3 displays the situation in which a $^4$He$_{728}$ drop, whose size is large enough to clearly distinguish in it a surface and a bulk region, is coated with an increasing number of $^3$He atoms, and the limiting situation of the same drop immersed into liquid $^3$He. The evolution with $N_4$ of the $^4$He concentration inside the $^4$He drop, defined as $x_3 \equiv \rho_3/\rho_4 [\rho_3 + \rho_4]_{\text{bulk}}$, is shown in the insert. Several interesting features of this figure are worth to comment. First of all, a fairly large amount of $^3$He is needed before it is appreciably dissolved in the bulk: for $N_3 = 1000$, $\rho_3$ near the origin is $\sim 1.4 \times 10^{-8} \text{Å}^{-3}$. The solubility is appreciably reduced by finite size effects. Indeed, one can see from the insert that the limiting solubility into the $N_4 = 728$ drop is $\sim 2.5\%$, as compared to the 6.6 % value in
the liquid mixture. It is also worth to see that for large
$N_3$ droplets, the bulk solubility is slightly higher than the
limiting solubility, indicating that finite size effects still
appear in rather large drops. Another manifestation of a
finite size effect is that the average $^3$He density is above
the saturation value even for the larger drops, showing
that the existence of the outer $^3$He surface still causes a
visible density compression.

Due to the high incompressibility of helium, the bulk
density of $^4$He decreases when $^3$He is dissolved, and the
rms radius of the $^4$He drop manifests a peculiar $N_3$ be-
havior. It decreases when $N_3$ increases up to a few hundreds
due to the initial compression of the outermost $^4$He sur-
face, and then steady increases as $^3$He is pushed off the
center by intruder $^3$He atoms. This is a very tiny effect
anyway. For example, we have found that the rms radius of
the $^4$He$_{728}$ drop is 15.70 Å. It decreases when $^3$He is
added, reaching a minimum value of 15.64 Å for $N_3 \sim
250$, and then it steadily increases up to 16.11 Å for $N_3
= 10000$. The rms radius of the $^4$He$_{728}$ drop immersed
into liquid $^3$He is 16.14 Å.

When a SF$_6$ molecule is captured by a helium drop, it
moves into the bulk producing a drastic rearrangement
of the drop density around it [21, 23, 24]. For large $^4$He
droplets, it is especially noteworthy the appearance of
two high density solvation shells with a density-depleted
region in between. It is then natural to ask about the pos-

sition of catalysis (Fig. 4), where we have plotted the number of
$N_3$ atoms in the first solvation shell (extending up to $\sim
5.5 \, \text{Å}$) is sensibly the same for the three selected $N_4$
values. It is also worth to look at the ratios $N_3/(N_4+N_4)$
within the second solvation shell which extends from $\sim
5.5$ to $\sim 8.5 \, \text{Å}$. In the SF$_6$ case, they are $\sim 8\%$ for $N_4=100$, $\sim 29\%$ for $N_4=60$, and
$\sim 65\%$ for $N_4=35$. Considering the content of the two
shells, these ratios are $\sim 5\%$, $\sim 19\%$, and $\sim 41\%$ which

We first observe that the first solvation shell [19] can host
$\sim 23$ $^4$He atoms in the case of SF$_6$, as a dopant, and $\sim
15$ atoms in the case of Xe [21, 23, 24]. According to Refs.
[23, 24], these numbers are too small for the $^4$He drop
being superfluid. It is thus crucial to know how the second
solvation shell is built, especially what is its composition.
Too many $^3$He atoms in that shell might shrink or even
wash out the superfluid environment around the dopant.

The density functional method cannot tell whether a
given configuration is superfluid or not, but it can give a
quantitative answer to its local composition because it is
able to reproduce available microscopic density profiles
[23, 24]. We present examples of such compositions in
Figs. 3 and 4.

Figure 3 shows the density profiles for $^4$He$_{N_3}+^3$He$_{1000}
+ \text{SF}_6$ and $^4$He$_{N_4}+^3$He$_{1000}+\text{Xe}$ with $N_4=35, 60$
and 100. We have carried out calculations for two different
dopants to see what is the influence of the He-impurity
potential on the results. It turns out that a weaker at-
tractive potential favors the mixing of both isotopes in
the whole allowed volume (the Xe-He and SF$_6$-He poten-
tials are plotted in Ref. [22], for instance). However, this
is in part a first glance effect, since the number of $^3$He
atoms in the first solvation shell around Xe is less than
one (see Fig. 3). Rather, the relevance of Fig. 3 lies in
that it shows how $^3$He is filling the second solvation shell
as $N_4$ decreases.

A more quantitative look at this phenomenon is pre-
sented in Fig. 4, where we have plotted the number of
atoms of each isotope as a function of the radial distance
to the center of the drop. Notice that for a given im-
purity, the number of $^4$He atoms in the first solvation
shell (extending up to $\sim 5.5 \, \text{Å}$) is sensibly the same for
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We are indebted to Peter Toennies and Andrej Vilesov
for useful discussions. This work has been performed un-
der grants PB95-1249 and PB95-0271-C02-01 from CI-
CYT, Spain and Program 1996SGR-00043 from General-
itat of Catalunya.

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FIG. 1. Density profiles of $^4$He$_{728}$ + $^3$He$_{N_3}$ droplets for $N_3$ values from 1000 to 10000 in $\Delta N_3 = 1000$ steps. To ease the figure, only the $^4$He densities corresponding to a few $N_3$ cases have been plotted. Also shown is the density profile of a $^4$He$_{728}$ drop immersed into liquid $^3$He (dotted lines). Insert: bulk $^3$He concentrations. The connecting solid line is to guide the eye. Also shown is the value corresponding to $^4$He$_{728}$ in liquid $^3$He (dotted line).

FIG. 2. Density profiles of $^4$He$_{728}$ + $^3$He$_{N_3}$ + SF$_6$ droplets for for $N_3$ values from 4000 to 10000 in $\Delta N_3 = 1000$ steps.

FIG. 3. Bottom panel: Density profiles of $^4$He$_{N_4}$ + $^3$He$_{1000}$ + SF$_6$ droplets for $N_4$ = 35, 60 and 100. Top panel: Density profiles of $^4$He$_{N_4}$ + $^3$He$_{1000}$ + Xe droplets for the same $N_4$ values.
$\rho(\text{Å}^{-3})$ vs. $r(\text{Å})$

$^4\text{He}_{728} + ^3\text{He}_{N_3} + \text{SF}_6$
