

## Delocalization and fragmentation of collective modes in doped ${}^4\text{He}$ drops

E. S. Hernández

*Departamento de Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires,  
1428 Buenos Aires, Argentina*

M. Barranco

*Departament d'Estructura i Constituents de la Matèria, Facultat de Física, Universitat de Barcelona,  
E-08028 Barcelona, Spain*

(Received 15 September 1994; revised manuscript received 30 November 1994)

We have investigated the fragmentation of collective modes in doped  ${}^4\text{He}$  drops in the framework of a finite-range density-functional theory, as well as the delocalization of the impurity inside the cluster. Our results indicate that the impurity is gradually delocalized inside the drop as the size of the latter increases. As an example, results are shown in the case of  $\text{Xe-}{}^4\text{He}_N$  systems up to  $N=112$ .

In a recent paper<sup>1</sup> we have presented a systematic study of the response of doped  ${}^4\text{He}$  drops within the frame of finite-range density-functional theory (FRDFT). Although, generally speaking, the results for pure  ${}^4\text{He}$  drops are comparable with either those obtained from standard zero-range density functionals<sup>2</sup> or with variational or diffusion Monte Carlo calculations,<sup>3</sup> the major interest of FRDFT resides in the ability of such functionals to describe inhomogeneity details such as the surface tension<sup>4</sup> and dynamical consequences of nonvanishing momentum transfer like the dispersion relation of zero sound in liquid  ${}^3\text{He}$ .<sup>5,6</sup> In this respect, FRDFT overcomes one of the most important criticisms on the applicability of density functionals to quantum liquids<sup>3</sup> associated with the underlying contact interaction.<sup>7</sup> Prior computations of the structure of doped  ${}^4\text{He}$  drops have been carried by Barnett and Whaley employing variational<sup>8</sup> and both variational and diffusion<sup>9</sup> Monte Carlo methods and by Dalfovo<sup>10</sup> resorting to the finite-range density functional of Ref. 4.

In Ref. 1, we have observed several consequences of contaminating  ${}^4\text{He}$  clusters with rare gas (Xe) impurities. In particular, it was noticed that the collective  $l=2$  energy is a decreasing function of the atom number in the drop. The  $N=300$  cluster is already unstable against a quadrupole excitation, and no further discussion of this issue was there pursued. Very recently, Chin and Krotschek<sup>11</sup> have investigated the onset of multipolar instabilities in doped droplets using an optimized variational approach. In particular, they have pointed out that the collapse of the dipole mode for a given cluster size is a signature of the delocalization of the foreign atom which, in the calculations of Refs. 1, 8, 10, and 11 is fixed at the center of the cluster. As discussed in Ref. 11, there are two possible scenarios for the appearance of these instabilities: (1) The center of the cluster is a relative energy minimum for any given particle number, but for large enough  $N$  this minimum is very shallow, so that the impurity becomes delocalized inside the drop. This

scenario would show up as a gradual convergence of the dipole energy towards zero.<sup>11</sup> (2) The center of the cluster is a relative energy maximum beyond a given value of  $N$ . In this case, the spherical symmetric state becomes unstable and the dipole energy should cross zero at the  $N$  value corresponding to the limit of stability. The findings of Ref. 11 seem to be consistent with this second scenario.

The purpose of this paper is to investigate the extent to which the FRDFT of Ref. 1 can cope with impurity delocalization and destabilizing effects in  ${}^4\text{He}$  droplets, and if possible, to ascertain which of the above scenarios is likely to occur within FRDFT. For this sake, we have computed the  $l$ -mode strength corresponding to the density functional

$$E[\rho] = \int d\vec{r} \mathcal{E}(\rho) = \int d\vec{r} \left\{ \frac{\hbar^2}{2m} \sum_i |\nabla \phi_i(\vec{r})|^2 + \frac{c}{2} \rho(\vec{r}) [\bar{\rho}(\vec{r})]^{\gamma+1} + \frac{1}{2} \rho(\vec{r}) \int d\vec{r}' \rho(\vec{r}') V(|\vec{r} - \vec{r}'|) \right\}, \quad (1)$$

where  $\bar{\rho}(\vec{r})$  is the coarse-grained density given by

$$\bar{\rho}(\vec{r}) = \int d\vec{r}' \rho(\vec{r}') \mathcal{W}(|\vec{r} - \vec{r}'|) \quad (2)$$

and  $\mathcal{W}(|\vec{r}|)$  is

$$\mathcal{W}(|\vec{r}|) = \begin{cases} \frac{3}{4\pi h^3} & \text{if } |\vec{r}| < h, \\ 0 & \text{otherwise.} \end{cases} \quad (3)$$

The finite-range interaction is a soft-core Lennard-Jones (LJ) potential

$$V(r) = \begin{cases} 4\epsilon_{\text{LJ}} \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], & r \geq \sigma, \\ b_{\text{LJ}} \left[ 1 - \left(\frac{r}{\sigma}\right)^8 \right], & r \leq \sigma, \end{cases} \quad (4)$$

with

$$b_{LJ} = \frac{33}{8} \left[ \frac{8}{9} \epsilon_{LJ} + \frac{b}{4\pi\sigma^3} \right]. \quad (5)$$

The parameter values are given in Ref. 1.

The atomic orbitals arise from a Hartree calculation where, in addition to the mean field, a central Xe-He potential has been incorporated.<sup>12</sup> The Xe impurity is assumed to be a classical object standing at the center of the cluster. The collective modes of the doped drop are calculated in the random-phase approximation (RPA).<sup>1,2</sup>

The results for the energy of the lowest-lying  $l = 1, 2,$  and  $3$  are shown in Fig. 1 as a function of the number of helium atoms, whose chemical potential is also displayed.<sup>13</sup> For  $N$  larger than 124 the dipole excitation is so small that we have not been able to find a stable solution of the RPA equations. Higher multiplicities survive longer as the particle number increases; even considering, say,  $N = 112$ —last point depicted in Fig. 1—as a stability cutoff for the present calculations, this number is substantially larger—about a 50%—than the one encountered by Chin and Krotscheck<sup>11</sup> for Xe-doped helium drops. It is important to remark that the shape of the dipole energy as a function of  $N$  is also different from the variational one, since the prediction of FRDFT presents no inflection; this fact then seems to support scenario (1). The transition densities corresponding to this dipole excitation are depicted in Fig. 2 for the  $N = 40, 70,$  and  $112$  clusters (dashed lines) together with the corresponding particle densities (solid lines). In agreement with Ref. 11, the height of the particle density peak becomes larger as  $N$  grows. In addition to corroborating the surface character of these oscillations, we can appreciate the increasing delocalization evidenced in both the outwards drift and the broadening of the peak in the transition density.

An interesting feature of the present calculations is that *all* collective modes are fragmented in small clusters.

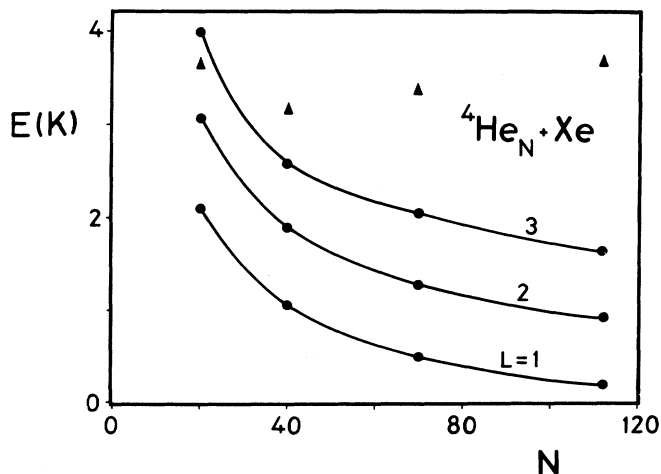


FIG. 1. Collective energies of the lowest lying  $l = 1, 2,$  and  $3$  modes of  $\text{Xe-}^4\text{He}_N$  drops as a functions of the atom number. The absolute value of the chemical potential of the drops is indicated by triangles.

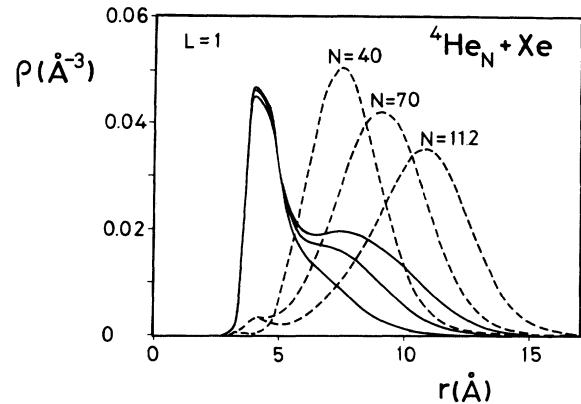


FIG. 2. Particle density (solid lines) and transition density (dashed lines) (in arbitrary scale) of the first dipole collective state of  $\text{Xe-}^4\text{He}_N$  clusters for  $N = 40, 70,$  and  $112$ .

To illustrate this fact, we consider the various transition densities for the  $N = 20$  droplet, which can be essentially regarded as a single-layered shell surrounding the impurity at a distance close to the minimum of the Xe-He interaction potential. It is worthwhile noticing that neither the finite-range density functional of Ref. 4 nor the present one yields enough binding in an ideal system consisting of a pure  $^4\text{He}$  planar surface distribution for densities above  $0.01 \text{ atom}/\text{\AA}^2$ . This was already observed by Clements *et al.*<sup>14</sup> who presented such a model calculation for the density functional of Ref. 4. In spite of this drawback, it is clear that for the restricted geometry of the single-atom orbitals in the spherical shell, the presence of the impurity at its center makes room to a bound  $\text{Xe-}^4\text{He}_{20}$  cluster. It is also convenient to remark

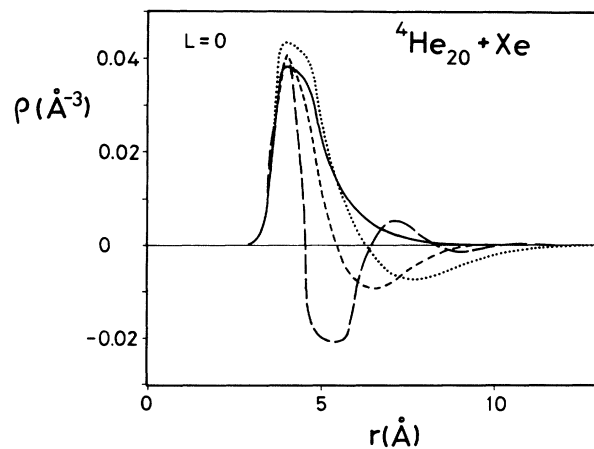


FIG. 3. Transition density in arbitrary scale of the first three monopole collective states of  $\text{Xe-}^4\text{He}_{20}$ . The solid line corresponds to the particle density in the cluster, and the dotted and short- and long-dashed lines to the first, second, and third excitations, respectively.

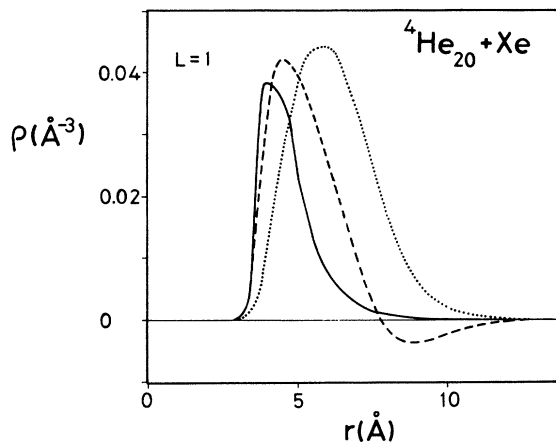


FIG. 4. Same as Fig. 3 for the first and second dipole excitations.

that the chemical potential of a Xe impurity predicted by this density functional approaches a limiting value of  $\sim -240$  K for  $N = 112$ , quite similar to the figure obtained by Chin and Krotschek through an optimized variational calculation.<sup>11</sup>

The fact that for such a small drop the clear distinction between bulk and surface almost disappears gives rise to the features depicted in Figs. 3–5. In these figures we show, in addition to the doped cluster density given in solid lines, the transition density for the more intense collective modes with  $l = 0, 1$ , and  $2$ , respectively. The profiles for  $l = 3$  are quite similar to those for  $l = 2$ . The location and strength, characterized by the exhausted percentage of the energy-weighted sum rule (EWSR),<sup>1</sup> of the corresponding peaks are displayed in Table I. The situation for the monopole mode (Fig. 3) is simple to understand; while the lowest-lying mode compresses the whole mass of the droplet to the expense of a dip at the surface, as the energy of the collective oscillation increases, the appearance of nodes in the outer

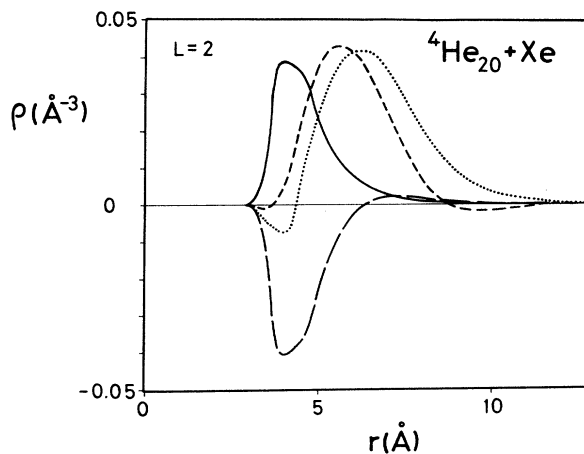


FIG. 5. Same as Figs. 3 and 4 for the three lowest-lying quadrupole modes.

TABLE I. Collective energies (K) and relative strengths of the lowest lying  $l = 0, 1$ , and  $2$  modes for  ${}^4\text{He}_{20}$ .

$l$	$\hbar\omega$ (K)	EWSR (%)
0	4.4	38
	7.1	54
	17.5	8
1	2.1	70
	5.0	10
2	3.1	54
	5.5	12
	10.2	12

region of the cluster pushes the already existing ones from the surface towards the center. As a consequence, inside the droplet bulk, neighboring layers support a counterphase oscillation.

The dipole oscillations in Fig. 4 are somehow more interesting; while the peak at the lowest energy corresponds to a motion of the surface, the second excitation exhibits a motion of the inner edge of the shell in counterphase with respect to the outer edge. This is a consequence of the peculiar shape of this cluster, whose thin width is comparable to the He-He interaction range, thus allowing a strong coupling between both sides of the spherical atomic layer. Considering the quadrupole mode, we see in Fig. 5 that the location of the induced density is progressively displaced from the surface to the bulk with increasing collective energy, the highest mode here displayed possessing a transition density quite close to that of the lowest monopole excitation in Fig. 3.

In conclusion, we have shown that FRDFT is also able to display the dipole instabilities of center-doped He drops, a phenomenon overlooked in our previous work<sup>1</sup> that has been interpreted in Ref. 11 as a signature of the impurity seeking a noncentral location inside the drop. We have indeed checked that for alkali-metal impurities, which have a positive solvation energy when the impurity is located at the center of the drop (see Ref. 10, for example), the response equation has no stable solution even for  $\text{Na-}{}^4\text{He}_{20}$  and  $l = 3$ . For small  $\text{Xe} + {}^4\text{He}_N$  drops, the strength is very fragmented, and the whole drop is involved in building up high-energy modes. We have found that for these collective excitations the innermost and outermost density surfaces oscillate out of phase. Besides some qualitative differences with variational calculations in small drops that can be attributed to the poor description of two-dimensional pure He systems by current finite-range density functionals,<sup>1,4</sup> our results show up as a quite distinct scenario with respect to that of Ref. 11: The Xe impurity, rather than having the tendency to be localized off center [scenario (2)], moves almost freely inside the drop [scenario (1)] for large enough systems. From the experimental point of view, there are evidences in favor of scenario (1) for large  ${}^4\text{He}$  clusters doped with  $\text{SF}_6$ .<sup>15</sup> To confirm or discard that possibility, new experimental data are called for.

We are indebted to Professor E. Krotschek for useful correspondence. M.B. thanks the Departamento de Física at the Universidad de Buenos Aires for its warm hospitality during the development of this work, which

has been partially supported by the Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina (Grant No. PID 334520092), and DGICYT, Spain (Grant No. PB92-0761).

- 
- <sup>1</sup> M. Barranco and E. S. Hernández, *Phys. Rev. B* **49**, 12078 (1994).  
<sup>2</sup> M. Casas and S. Stringari, *J. Low Temp. Phys.* **79**, 135 (1990).  
<sup>3</sup> S. A. Chin and E. Krotschek, *Phys. Rev. B* **45**, 852 (1992).  
<sup>4</sup> J. Dupont-Roc, M. Himbert, N. Pavloff, and J. Treiner, *J. Low Temp. Phys.* **81**, 31 (1990).  
<sup>5</sup> C. García-Recio, J. Navarro, N. van Giai, and L. L. Salcedo, *Ann. Phys. (N.Y.)* **214**, 293 (1992).  
<sup>6</sup> M. Barranco, D. M. Jezek, E. S. Hernández, J. Navarro, and Ll. Serra, *Z. Phys. D* **28**, 257 (1993).  
<sup>7</sup> S. Stringari and J. Treiner, *J. Chem. Phys.* **87**, 5021 (1987).  
<sup>8</sup> R. N. Barnett and K. B. Whaley, *J. Chem. Phys.* **96**, 2953 (1992).  
<sup>9</sup> R. N. Barnett and K. B. Whaley, *J. Chem. Phys.* **99**, 9730 (1993).  
<sup>10</sup> F. Dalfovo, *Z. Phys. D* **29**, 61 (1994).  
<sup>11</sup> S. A. Chin and E. Krotschek (unpublished).  
<sup>12</sup> K. T. Tang and J. P. Toennies, *Z. Phys. D* **1**, 91 (1986).  
<sup>13</sup> The large value of the chemical potential of Xe-<sup>4</sup>He<sub>20</sub> is due to the fact that almost all atoms in the drop ( $\sim 17$ ) are in the Xe-He attractive potential well. That confers on this drop a special stability.  
<sup>14</sup> B. E. Clements, H. Forbert, E. Krotschek, and M Saarela, *J. Low Temp. Phys.* **95**, 849 (1994).  
<sup>15</sup> A. Scheidemann, B. Schilling, and J. Peter Toennies, *J. Phys. Chem.* **97**, 2128 (1993).