Instability scenarios for doped He^4 clusters

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In the frame of finite range density functional (FRDF) theory, we review the systematics of energetic features of ^{4}He$_N$ clusters doped with atomic or molecular impurities, as well as the instability scenario of their collective motions. It is shown that for drops up to $N = 500$, the predictions of FRDF theory are coincident with those arising from microscopic many-body calculations that employ variational or diffusion Monte Carlo methods. For larger drops, the present description predicts a smooth approach to zero of the collective energies, a scenario that appears to support the most recent experimental data and microscopic calculations that demonstrate that the impurity is located within the bulk of the drop. © *1997 American Institute of Physics.* [S0021-9606(97)50727-6]

I. INTRODUCTION

Helium clusters doped with rare gas or sulfur hexafluoride molecules have been a subject of both experimental and theoretical study for the past few years. Starting from the pioneering experiment by Scheidemann *et al.*,[1] in which Ne impurities were dissolved in helium droplets, spectroscopic tools have been extensively employed to investigate structural and excitation properties of these systems.[2–5]

Among the various questions arising from the first experiments, an interesting one concerns the location of the impurity with respect of the center of mass of the droplet.[2,3] This point is an important one in view of the relationship between the position of the foreign molecule and the destabilization of the collective motions that can be supported by the cluster, an issue that has been traced to the vanishing of the dipole excitation energy when the number of atoms in the drop exceeds a critical value. In this respect, two possible scenarios have been suggested:[6] (1) as the cluster mass increases, the energy minimum broadens and the impurity is allowed a larger zero point motion around the center of mass; and (2) at a given critical size of the system, the energy minimum disappears, giving rise to a maximum. In the latter case, the impurity would be expelled from the center towards the periphery of the drop. Earlier experimental evidence involving SF$_6$ impurities appeared to support the second scenario,[2,3] this seemed to be confirmed by optimized variational calculations carried out by Chin and Krotschek[6] in the frame of hypernetted chain/Euler Lagrange theory (HNC/EL). These authors showed that for helium drops doped with rare gas or SF$_6$ molecules, the energy of the dipole oscillation approached zero at a rather abrupt rate, for an atom number between 54 and 90 according to the impurity under consideration.

By contrast, variational and diffusion monte Carlo calculations (VMC/DMC)[7] provide microscopic density profiles for the doped droplets and for the SF$_6$ impurity where the latter appears unambiguously located within the bulk of the drop. Furthermore, calculations based on density functionals[8,9] have also clearly selected scenario (1) for Xe impurities, in view of the fact that the collective dipole energy approaches zero in a smooth fashion. The most recent experiments carried out upon helium clusters doped with sulfur hexafluoride have definitely solved the controversy, and it is now certain that the foreign molecule is in the bulk of the cluster, at least for particle numbers lower than $N \approx 4000$ (Refs. 4 and 5). In addition, the best accurate VMC/DMC results appearing in the literature[10] provide density profiles for SF$_6$–He$_{39}$ and SF$_6$–He$_{40}$ drops, together with density plots for the impurity that confirm its location near the cluster center. This is in contrast to the findings in Ref. 11, where the SF$_6$ probability density appeared to be peaked at the surface of the droplet; as shown in Ref. 10, this discrepancy was due to insufficient numerical accuracy in the density profiles computed in Ref. 11. Since microscopic calculations cannot deal with the largest drop sizes available in experiments, it is the purpose of the present work to prove that scenario (1) persists for atom numbers above those permitted in VMC/DMC computations and for clusters doped with various rare gases, as well as with SF$_6$ molecules. The requested calculations are possible within the frame of finite range density functional theory (FRDF), since the number of particles in the droplet poses no serious computational restriction.

In Sec. II we indicate a few essentials of the density functional formalism and the parameterization employed here. The results are presented and discussed in Sec. III, and the summary and conclusions are the subject of Sec. IV.

II. THE DENSITY FUNCTIONAL FORMALISM

The FRDF formalism has been presented in Refs. 8 and 9 and will be briefly summarized below for the sake of completeness. We consider that the total energy of an ensemble of N helium atoms can be expressed as

$$E[\rho] = \int d\mathbf{r}\, \mathscr{E}(\rho)$$

$$= \int d\mathbf{r} \left\{ \frac{\hbar^2}{2m}(\nabla\sqrt{\rho(\mathbf{r})})^2 + \frac{c}{2}\rho(\mathbf{r})[\widetilde{\rho}(\mathbf{r})]^{\gamma+1} \right.$$

$$\left. + \frac{1}{2}\rho(\mathbf{r})\int d\mathbf{r}'\, \rho(\mathbf{r}')V(|\mathbf{r}-\mathbf{r}'|) \right\}, \tag{1}$$

where $\widetilde{\rho}(\mathbf{r})$ is an averaged density given by

$$\widetilde{\rho}(\mathbf{r}) = \int d\mathbf{r}'\, \rho(\mathbf{r}')\mathscr{W}(|\mathbf{r}-\mathbf{r}'|), \tag{2}$$

and $\mathscr{W}(|\mathbf{r}|)$ is

$$\mathscr{W}(|\mathbf{r}|) = \begin{cases} \dfrac{3}{4\pi h^3} & \text{if}\,|\mathbf{r}|<h, \\[2mm] 0 & \text{otherwise.} \end{cases} \tag{3}$$

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

$$V(r) = \begin{cases} 4\epsilon_{\text{LJ}}\left[\left(\dfrac{\sigma}{r}\right)^{12} - \left(\dfrac{\sigma}{r}\right)^6\right] & r\geqslant\sigma \\[3mm] b_{\text{LJ}}\left[1-\left(\dfrac{r}{\sigma}\right)^8\right] & r\leqslant\sigma, \end{cases} \tag{4}$$

where the core strength b_{LJ} is given by

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

The parameter values are the same as in Refs. 8 and 9, namely

$\epsilon_{\text{LJ}} = 10.22$ K,

$\sigma = 2.556$ Å,

$h = 2.377$ Å,

$b = -888.81$ K Å^3,

$c = 1.04554\times10^7$ K Å$^{3(\gamma+1)}$,

$\gamma = 2.8$.

The atomic orbitals are obtained by means of a Hartree calculation that provides single-particle (s-p) energies ε_n and wave functions ϕ_n for a finite system of N bosons at zero temperature. We treat the impurity particle as an object with infinite mass located at the coordinate origin. The potentials for rare gas impurities are taken from Ref. 12, and for the spherically averaged SF$_6$–He potential we use that of Ref. 13. As in previous works, we compute the collective modes of the doped cluster according to the random-phase approximation (RPA),[8,9,14] which consists of looking for solutions of the integral equation for the propagator G^{RPA},

$$G^{\text{RPA}}(\mathbf{r}_1,\mathbf{r}_2,\omega) = G^0(\mathbf{r}_1,\mathbf{r}_2,\omega) + \int d\mathbf{r}_3\, d\mathbf{r}_4\, G^0(\mathbf{r}_1,\mathbf{r}_3,\omega)$$

$$\times V^{\text{ph}}(\mathbf{r}_3,\mathbf{r}_4)G^{\text{RPA}}(\mathbf{r}_4,\mathbf{r}_2,\omega). \tag{6}$$

Here V^{ph} is the residual particle-hole interaction and $G^0(\mathbf{r}_1,\mathbf{r}_2,\omega)$ is the Hartree Green's function whose expression is

$$G^0(\mathbf{r}_1,\mathbf{r}_2,\omega) = N\sum_n \left\{ \frac{\phi_0^*(\mathbf{r}_1)\phi_0(\mathbf{r}_2)\phi_n^*(\mathbf{r}_2)\phi_n(\mathbf{r}_1)}{\hbar\omega - E_{n0} + \iota\epsilon} \right.$$

$$\left. - \frac{\phi_0^*(\mathbf{r}_2)\phi_0(\mathbf{r}_1)\phi_n^*(\mathbf{r}_1)\phi_n(\mathbf{r}_2)}{\hbar\omega + E_{n0} + \iota\epsilon} \right\}, \tag{7}$$

where ϵ is a small energy parameter in charge of securing the adiabaticity conditions of linear response theory, $\phi_0(\mathbf{r})$ is the s-p wave function of the Bose condensate, $E_{n0} = \varepsilon_n - \varepsilon_0$ is the transition energy from state ϕ_n into the condensate, and the sum runs over all excited Hartree states.

The RPA transition density $\delta\rho(\mathbf{r})$, namely that induced by an external field $V^{\text{ext}}(\mathbf{r})$ acting upon every boson, is written in terms of G^{RPA} as

$$\delta\rho(\mathbf{r},\omega) = \int d\mathbf{r}'\, G^{\text{RPA}}(\mathbf{r},\mathbf{r}',\omega)V^{\text{ext}}(\mathbf{r}'), \tag{8}$$

and the response function or dynamical susceptibility $\chi(\omega)$ is

$$\chi(\omega) = \int d\mathbf{r}\, \delta\rho(\mathbf{r},\omega)V^{\text{ext}}(\mathbf{r}). \tag{9}$$

III. CALCULATIONS AND RESULTS

As it is well known, the poles of $\chi(\omega)$ correspond to the elementary excitations of the system, and the imaginary part of the dynamical susceptibility is proportional to the strength function $S(\hbar\omega)$, whose peaks locate the above poles. The numerical calculation thus consists of (1) solving the Hartree problem, which supplies the density profile of the condensate and the wave functions of s-p states; (2) solving the discretized integral Eq. (6); (3) computing $\chi(\omega)$ and $S(\hbar\omega)$ in a wide energy range and searching for the peaks that carry a measurable strength, in other words, those that supply a sizable fraction of the energy weighted sum rule (EWSR) (see Ref. 8 for details). The transition densities are calculated for a given collective state introducing the RPA propagator at the corresponding value of $\hbar\omega$.

In previous calculations we obtained numerical results for saturation properties of a set of clusters doped with Xe atoms[8] and investigated the instability scenario of these clusters for the dipole, quadrupole, and octupole energies as functions of the number of particles.[9] Later trials with larger computing facilities have demonstrated that the Hartree minima of doped clusters may be sensitive to algorithmic parameters such as the size of the box, the spatial mesh size, or the quality of the continuum wave functions. Improvements of the original calculations, based on a careful search of stability against changes in these parameters, have somehow modified the energetics of the Xe-doped clusters and the values of the collective energies. These improved results are contained in Figs. 1 to 5, as well as in Table I.

In Fig. 1, the energy per particle of the helium atoms is shown as a function of N for drops with Ne, Ar, Kr, Xe, and SF$_6$ impurities. The crosses on the curve for SF$_6$ correspond
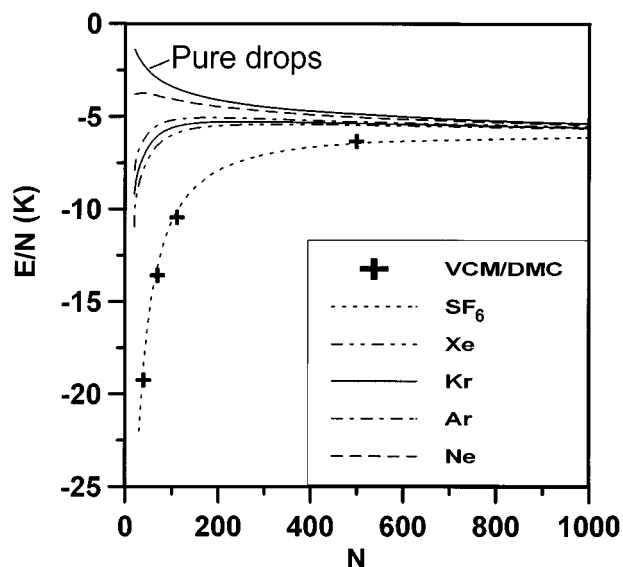
FIG. 1. Energy per helium atom in K of pure and doped clusters as a function of the number of ^{4}He particles.

FIG. 3. Collective energies in K of the dipole mode of doped ^{4}He$_N$ clusters as a function of the number of helium atoms.

to the values provided by the VMC/DMC calculations in Ref. 7. It is seen that for any of these molecules, the large mass limit approaches a common value which, for an infinite number of particles, is the saturation energy of bulk ^{4}He, $\varepsilon_0 = -7.15$ K. A similar behavior can be attributed to the helium chemical potential, namely the energy of the $1s$ s-p state, depicted in Fig. 2.

Figure 3 displays the instability scenario for the dipole collective energies as a function of N, with the same impurities as above. We realize that the collective energy decreases monotonically in all cases; these energies do not compare with those reported in Ref. 6, since the latter present an oscillation and go abruptly to zero at a few tens of particles. For a given small drop, the collective dipole energy is
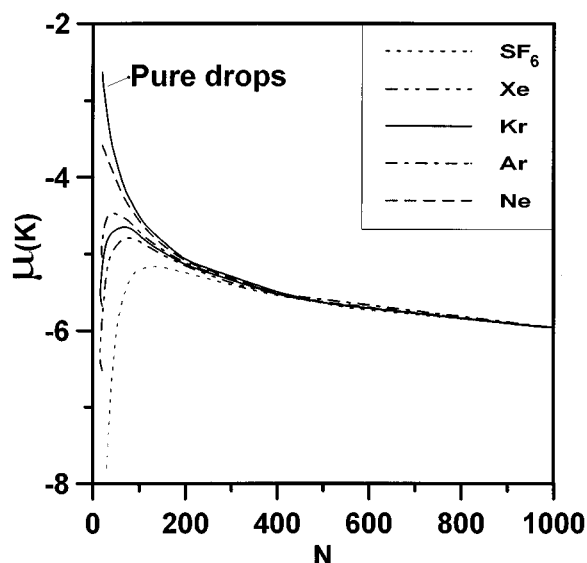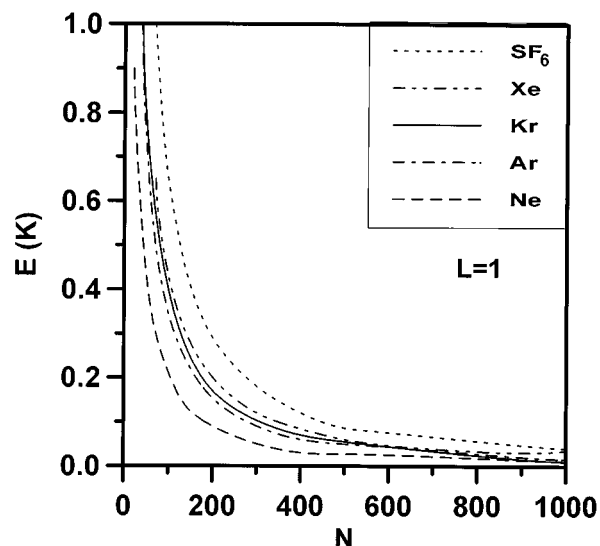
very sensitive to the size of the impurity, being larger for the heavier molecules. This relative ordering coincides with that reported in Ref. 6. For sufficiently large particle numbers, the dipole energy approaches zero, thus being insensitive to the nature of the molecule; the different curves merge into a single one. It is clear that the present scenario, which can be identified as type (1) according to the characterization given in the Introduction, strongly departs from the type (2) scenario encountered in Ref. 6.

We have plotted in Fig. 4 the energy of the collective mode for $L = 1,2,3$ against N for clusters doped with SF$_6$ molecules. We realize that the collective energy is a smooth monotonically vanishing function of the number of atoms, regardless of the multipolarity of the excitation. In addition,
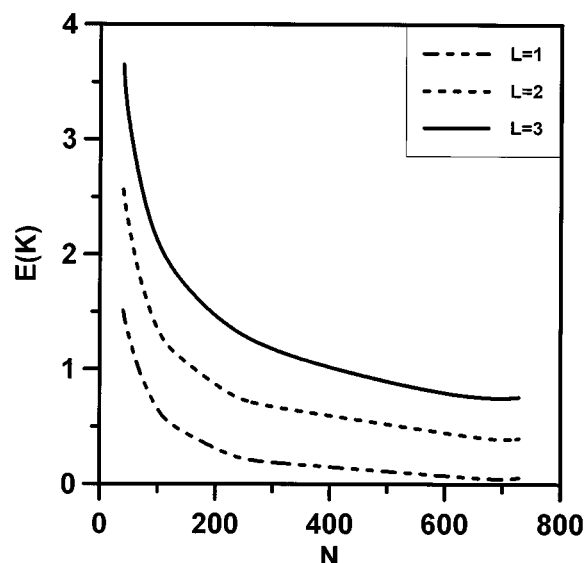

FIG. 2. Helium chemical potential in K in pure and doped clusters for the same impurities as in Fig. 1.

FIG. 4. Collective energies in K of the dipole, quadrupole, and octupole modes of SF$_6$–^{4}He$_N$ drops as a function of N.

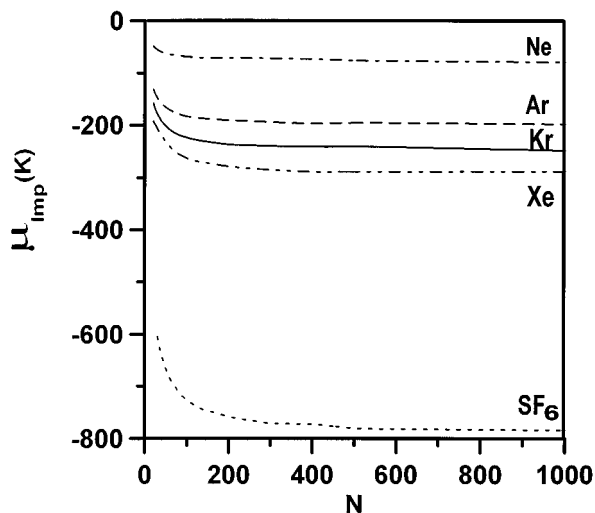FIG. 5. The solvation energy in K of the impurity as a function of the number of helium atoms in the cluster.
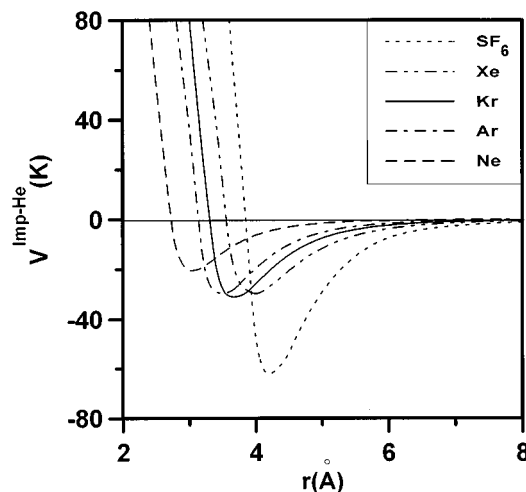

FIG. 6. Impurity potentials employed in this work. For the rare gas atoms the potentials have been taken from Ref. 12, while for SF$_6$ the potential is the isotropic one of Ref. 13. Energies are given in K and radii in Å.

it is worthwhile noticing that the collective state represented here is the only existing one—i.e., with a sizable strength—for these multipolarities. By contrast, the monopole mode appears rather fragmented in the smaller drops. However, the strength is increasingly concentrated in a single state as the number of helium atoms becomes larger. This is illustrated in Table I, where we display the monopole energies and corresponding contribution to the EWSR for droplets doped with Xe and SF$_6$ impurities. From these data, we can appreciate that neither the energy nor the intensity of a given monopolar peak is very sensitive to the details of the impurity potential.

To complete the energetics of doped helium droplets, the solvation energy of the foreign particle is depicted in Fig. 5 as a function of N. The values obtained here are a rough 20% lower than those shown in Ref. 6 for $N<100$; the

asymptotic limits for very large particle numbers coincide with those obtained by Dalfovo,[15] for the heavier rare gases. For Ne and SF$_6$ impurities, the present asymptotic values are, respectively, 40% and 25% lower than those in Ref. 15. Although the deviations between the current FRDF calculations and those previous ones[15] can be ascribed to the differences in the density functional involved, the main features of the energetics can be related to the shape of the isotropic impurity potentials depicted in Fig. 6, where we clearly appreciate that both the core width and the well depth increase as the mass of the impurity enlarges. It is then easy to understand that heavier particles provide stronger binding and demand higher energies to start a collective displacement of the helium atoms around their center of mass; in addition, the close appearance of the energetic features of drops containing Xe, Ar, or Kr impurities (cf. Figs. 1–3 and Fig. 5) can be traced to the similar well depth and spatial range of the corresponding potentials.

In Ref. 7, it has been shown that for small and medium size clusters investigated there ($N=39,69,111,499$), the SF$_6$ molecule remains solvated within a helium shell of about 23 atoms. It was also suggested that this shell may delocalize in the largest drops. To test the predictability of the present FRDF as compared with microscopic VMC/DMC calculations, in Fig. 7(a) we display density profiles for SF$_6$–^{4}He$_N$ drops with $N=39$, 69, 111, and 499. The present profiles are similar to those for the same atom numbers in Ref. 7; some differences to be commented on concern the size of the main peak, a rough 10%–15% higher in the present calculations, together with the fact that the maximum height remains almost invariant for these atom numbers, for which integration of the common peak density gives around 23 particles. By contrast, in Ref. 7 this maximum decreases for the larger drops. Moreover, in our computation the secondary peak becomes higher for increasing cluster size—indeed, for $N=728$ this maximum is 12% above the one for $N=20$—while the profiles in the above mentioned paper

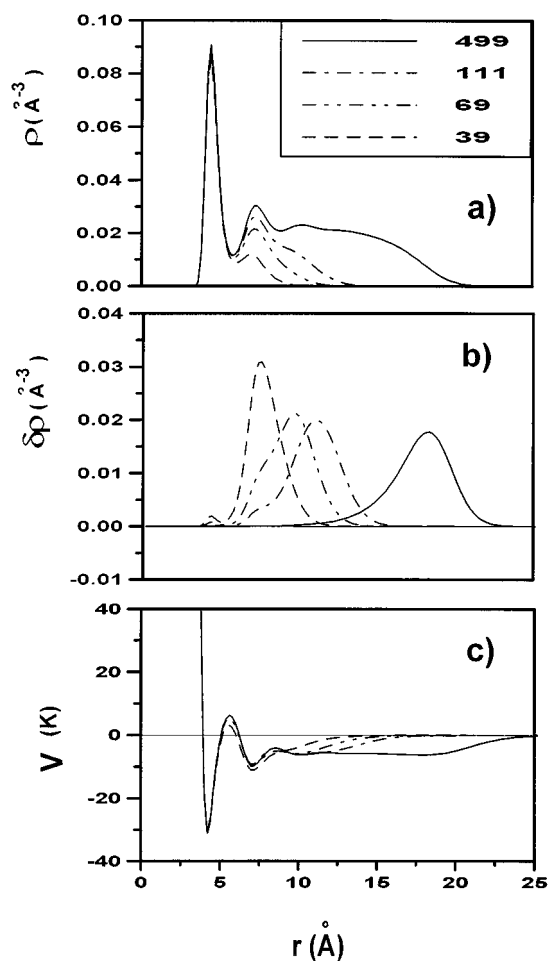TABLE I. Energies in K of the collective monopole states, and their contribution to the energy weighted sum rule for helium clusters with Xe and SF$_6$ impurities.

N	Xe		SF$_6$	
	$\hbar\omega_0$	% EWSR	$\hbar\omega_0$	% EWSR
40	4.33	46	5.76	41
	5.83	15	7.78	16
	7.48	14	10.01	23
70	3.86	64	4.41	56
	5.67	17	6.27	14
	7.55	13	8.19	12
112	3.66	65	3.94	59
	5.45	17	5.75	17
	7.03	12	7.38	13
240	3.41	80	3.47	75
	5.26	13	5.36	15
	6.47	5	6.60	7
728	2.81	94	2.89	94
	4.66	5	4.78	5
	7.37	1		

FIG. 7. (a) Helium particle density in Å^{-3} of SF_6–^4He_N clusters with N = 39, 69, 111, and 499 as a function of the radial distance in Å; (b) transition density (in arbitrary scale) of the dipole collective state of the same drops, and (c) the corresponding one-body Hartree potential.

present a crossing, i.e., the second maxima of $^4He_{499}$ and of $^4He_{69}$ coincide.

Finally, the transition densities for the dipole mode of the same drops are shown in Fig. 7(b), while Fig. 7(c) displays the corresponding one-body Hartree potentials.

IV. SUMMARY

In this work we have shown that FRDF calculations of the energetics and structural properties of doped helium clusters yield results in agreement with those arising from microscopic VMC/DMC computations. In contrast to these powerful treatments of the many-body problem, density functional methods are not, in principle, limited by the size of the system under study. This permits us to carry a systematic investigation of the scenario concerning stability of the collective motion as a function of the number of atoms in the drop. We have thus shown that up to a thousand particles, FRDF calculations definitely support configurations where the impurity lies in the bulk of the helium cluster. While the energetics of the smaller drops and their collective states are sensitive to the nature of the foreign molecule, due to the vanishing of the collective energy, for clusters above a few hundreds of atoms the details of the different impurity potentials are of little relevance. As one would expect, as the number of helium atoms increases, the behavior of the doped system resembles that of the pure drops in a unique fashion, regardless of the particular impurity.

Concerning the stability scenario of doped helium clusters, it is important to remark that the vanishing of the collective dipole energy is an indication of the lack of excitations involving displacements of the helium center of mass with respect to the impurity. It is clear now that the earlier controversy between predictions of the location of the impurity, based on methods of many-body theory,[6,7,11] has been elucidated by the most recent experimental findings;[5] the reason for the discrepancy between the results in Refs. 7 and 11 has been clearly exposed in Ref. 10, where it has been shown that numerical convergence was not reached in the work of Ref. 11. The present FRDF calculations, whose quality can be appreciated from the agreement with the VMC/DMC descriptions of the energetics and structure of helium clusters up to 500 atoms, indicate that a clear delocalization effect sets in as the drop size increases.

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