# Superfluidity of $^4$He nanoclusters in confinement

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The structure and superfluid response of nanoscale size $^4$He clusters enclosed in spherical cavities are studied by computer simulations. The curved surface causes the formation of well-defined concentric shells, thus imparting to the system a very different structure from that of freestanding clusters. On a strongly attractive substrate, superfluidity is only observed at a low density, in the single layer coating the inner surface of the cavity. If the substrate is very weak (e.g., Li), on the other hand, a superfluid two-shell structure can form, whose physical properties interpolate between two and three dimensions. It is shown how experimental signatures of this physical behavior can be detected through measurements of the momentum distribution.

## I. INTRODUCTION

Clusters of $^4$He comprising several tens of atoms (i.e., of characteristic size of a few nanometers) are perhaps the simplest quantum few-body system; their investigation, both theoretical and experimental, has been pursued for a few decades now. Early theoretical studies yielded considerable information on their structure [1–4], Bose condensation [5,6], excitations [7,8], and predicted superfluid behavior [9] at temperatures of the order of 1 K.

Probing their physical properties experimentally is obviously a difficult proposition, as pristine $^4$He clusters are very weakly bound and easily fragmented, e.g., on impact with a scatterer. Thus, although some experiments were carried out, in which low-energy $^4$He atoms were scattered off $^4$He clusters [10], most of what is now known about their physics, chiefly their superfluid properties, has come from spectroscopic studies of a single linear molecule (e.g., OCS) embedded in them [11–13].

Despite the remarkable microscopic insight afforded by this approach, the presence of the embedded impurity, whose linear size is typically that of a few $^4$He atoms, is expected to alter drastically the structure of a cluster of such a small size. Specifically, a significant fraction of the $^4$He atoms is predicted to bind to the foreign molecule, while the rest are arranged in shells around it [14]. This is very different from the featureless structure of a pristine $^4$He cluster [9]. The question therefore remains open whether one could probe experimentally the superfluid properties of a finite assembly of $^4$He atoms in a way that does not make use of a foreign impurity and preserves at least the full rotational invariance of the cluster.

Aside from possible experiments on freestanding clusters, with the aforementioned difficulties that they entail, one possibility that does not seem to have been given much consideration so far is that of studying $^4$He clusters enclosed in nanometer-size cavities, e.g., those of a suitably chosen porous material. For example, one could think of adsorbing $^4$He inside zeolites, whose pore diameter is typically of the order of a nanometer and, therefore, may accommodate clusters of a few atoms [15]. One could therefore think of investigating the physics of the clusters, e.g., by performing neutron scattering

experiments on the system, on the assumption that the bulk of the signal should come from helium confined inside the (relatively regularly shaped) cages. Obviously, the presence of a confining surface is likely to affect significantly the structure and physical behavior of the cluster, compared to those of a free one. For example, one may expect superfluidity to be suppressed, with crystallization originating at the surface of the cavity and then extending to adsorbed layers.

While a classical hard-sphere fluid in spherical confinement has been the subject of much theoretical investigation [16–19], surprisingly little is known about the effect of this type of confinement on the superfluid transition of $^4$He. A number of studies of superfluidity of $^4$He in narrow cylindrical channels have been carried out [20–23], typically aimed at modeling $^4$He in porous media or in the confines of carbon nanotubes [24,25]. Theoretical studies of adsorption of $^4$He on spherical substrates have mostly focused on layering on the outer surface of macromolecules such as fullerenes [26–30]; however, the superfluid properties of $^4$He clusters confined inside spherical cavities of nanoscale size remain largely unexplored. A recent theoretical study of parahydrogen clusters confined inside spherical cavities of nanoscale size has yielded surprising evidence of an enhanced superfluid response, with respect to free clusters [31], showing that the curved surface can affect the behavior of the system in nontrivial ways.

In this work, we carried out a theoretical study of structural and superfluid properties of clusters of $^4$He confined inside a spherical cavity of 2-nm diameter. Specifically, we performed equilibrium quantum Monte Carlo simulation of a reasonably realistic model of the system at low temperatures (down to $T = 0.5$ K). We considered the two limiting cases of strong and weak substrate, in order to differentiate geometrical effects from those arising from the specific nature of the adsorbing medium. Our purpose is twofold: first, we aim to gain some further insight into the effect of nanoscale confinement on the physical properties of $^4$He clusters; second, we wish to furnish some definite theoretical predictions, helping in the design and interpretation of experiments on $^4$He adsorbed inside porous media whose open volume consists primarily of (quasi)spherical cavities of the characteristic size of a few nanometers.

As expected, confinement drastically alters the structure of the clusters, in comparison to freestanding ones, imparting clusters a well-defined shell-like structure; nevertheless,

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superfluidity is resilient and still observable within such tight confines at temperatures of order 1 K, under relatively broad conditions. The character of the superfluid response changes considerably depending on the strength of the substrate. On a strong substrate, a quasi-two-dimensional (quasi-2D) superfluid film coats the surface and undergoes crystallization as the density increases, and no re-entrant superfluid phase is seen as a second layer (i.e., a concentric shell) forms. On a sufficiently weak substrate, on the other hand, the system forms two concentric superfluid shells, reminiscent of what was seen for parahydrogen in Ref. [31]. Signatures of such different physics can be detected in the single-particle momentum distribution, probed by neutron scattering, a technique which has offered a great deal of insight into the physics of $^4$He and other quantum fluids (like parahydrogen) in the confines of porous media [32–35].

In the next section, we introduce the mathematical model of the system and provide some basic details of the simulation technique utilized. We then illustrate our results and outline our conclusion in Secs. III and IV.

## II. MODEL AND METHODOLOGY

Our system of interest is an ensemble of $N$ $^4$He atoms, regarded as point particles of spin 0, enclosed in a spherical cavity. The quantum-mechanical many-body Hamiltonian is

$$\hat{H} = -\lambda \sum_{i=1}^{N} \nabla_i^2 + \sum_{i<j} V(r_{ij}) + \sum_i U(r_i). \qquad (1)$$

Here, $\lambda = \hbar^2/2m$, $m$ being the mass of a $^4$He atom, $\mathbf{r}_i$ is the positions of the $i$th atom, measured with respect to the center of the cavity (set as the origin), $r_{ij} \equiv |\mathbf{r}_i - \mathbf{r}_j|$, $V$ describes the interaction of a pair of atoms, and $U$ describes the confinement of each atom inside the cavity. For $V$ we used the accepted Aziz potential [36], whereas for $U$ we used the expression [37]

$$V(r) = 2D\left\{ \frac{b^9 F(x)}{(1-x^2)^9} - \frac{6b^3}{(1-x^2)^3} \right\}, \qquad (2)$$

where $x \equiv r/R$, $F(x) = 5 + 45x^2 + 63x^4 + 15x^6$, $b \equiv (a/R)$, and $a$ and $D$ are two parameters that are adjusted to reproduce the main $^4$He adsorption features of specific substrates.

Equation (2) is merely the extension to the case of a spherical cavity of the so-called "3-9" potential, describing the interaction of a particle with an infinite, planar substrate. $D$ is the depth of the attractive well of the potential experienced by a $^4$He atom in the vicinity of the substrate, whereas $a$ is essentially the distance of closest approach of a $^4$He atom to the substrate.

As a model of $^4$He in the confines of, e.g., the cages of zeolites, Eq. (1) clearly contains simplifications, chiefly the fact that the cavity is regarded as perfectly spherical and smooth. However, it allows us to address the physical question that we wish to pose here, namely, the effect of confinement on the superfluid response of a $^4$He cluster. Equivalent, or even simpler, models (e.g., cavities with hard walls) have been utilized to study the structure of $^4$He and classical fluids in confinement [18,21].

We obtained results for a cavity of radius $R = 10$ Å, but with two distinct choices of the parameters $D$ and $a$ in Eq. (2), corresponding to very different adsorption properties. The first choice, henceforth labeled with Li, has $D = 17.87$ K and $a = 3.76$ Å; these values are apt to describe the interaction of a $^4$He atom with a Li substrate, one of the most weakly attractive known, on which $^4$He is predicted to form a superfluid monolayer at low temperatures [38].

The second choice, namely, $D = 100$ K and $a = 2.05$ Å, is roughly in the ballpark of what one would expect for $^4$He atoms near a silica substrate [39]; thus, we henceforth refer to the scenario described by this parameter set as glass. The considerably deeper well, together with the much shorter range of the repulsive core, render the "glass" much more attractive to $^4$He atoms than the Li cavity. Obviously, in neither case do we aim to reproduce accurately any realistic interaction (which would require more elaborate functional forms anyway). Rather, our aim is to investigate opposite ends of the adsorption continuum.

We studied the low-temperature physical properties of the system described by Eqs. (1) and (2) by means of first-principle computer simulations based on the worm algorithm in the continuous-space path integral representation [40,41]. Specifically, we used a variant of the method which allows one to perform calculations in the canonical ensemble (i.e., fixed $N$) [42,43]. Because this well-established computational methodology is thoroughly described elsewhere, we do not review it here. The most important aspects to be emphasized here are that it enables one to compute thermodynamic properties of Bose systems at finite temperature, directly from the microscopic Hamiltonian, in particular, energetic, structural, and superfluid properties of the confined $^4$He fluid, in practice with no approximation. Technical details of the simulation are standard, and we refer the interested reader to Ref. [41]. All of the results reported here were obtained with a value of the imaginary time step $\tau = 1/640\,\mathrm{K}^{-1}$, with a high-temperature approximation for the many-particle propagator accurate up to order $\tau^4$.

## III. RESULTS

### A. Energetics

We begin the illustration of the results of the simulations by discussing the computed energetics. We obtain ground-state estimates by extrapolating low-temperature results to $T = 0$. In practice, we find that energy values, as well as radial density profiles, remain unchanged on the scales of the figures shown here, below $T \lesssim 1$ K.

Figure 1 displays the energy per $^4$He atom (in K) as a function of the number of atoms in the cavity. Both curves feature minima at specific numbers of atoms, which correspond to the minimum filling of the cavity. Polynomial fits to the data shown in Fig. 1 (which, for a glass cavity include energy estimates up to $N = 110$, not shown for clarity in the figure) yield a minimum for a Li (glass) cavity at approximately $N = 22$ ($N = 38$) $^4$He atoms, at an energy close to $-26.3$ K ($-101.5$ K), which can be compared to the value $-9.6$ K ($-65$ K) yielded by the corresponding 3-9 potential for a flat substrate [38,44]. Stronger atomic binding arises from
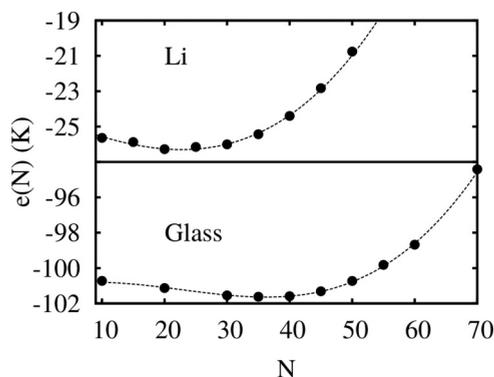
FIG. 1. Energy per $^4$He atom $e$ (in K) versus number $N$ in the $T \to 0$ limit, inside Li (top) and glass (bottom) cavities of radius 10 Å. Dashed lines are polynomial fits to the data. Statistical errors are atmost equal to the symbol size.



FIG. 3. (Color online) Radial density profiles at $T = 1$ K for a cluster of 45 $^4$He atoms inside a Li cavity (squares) and a glass cavity (circles). The origin is at the center of the cavity. Also shown is the result for a free $^4$He cluster (diamonds), computed with respect to its center of mass. Statistical errors are at most equal to the symbol size.

the curved confinement, and it is interesting to note that the enhancement is proportionally greater for the weaker substrate.

The same fits show that the chemical potential, obtained as $\mu(N) = e(N) + N(de(N)/dN)$, becomes comparable to that of bulk superfluid $^4$He ($\sim -7.2$ K) for $N \approx 45$ for a Li cavity and $N \approx 85$ for glass. This estimate is relevant to possible experiments in which a porous matrix in which $^4$He is adsorbed is held in thermal contact with a bath of superfluid $^4$He. Inside a glass substrate, under these physical conditions, we estimate the kinetic energy per $^4$He atom to be $38.0 \pm 0.5$ K. This value is in the same ballpark as the most recent experimental estimates [45] of the mean atomic kinetic energy of $^4$He adsorbed in cylindrical nanopores of diameter 24 Å, but the very large ($\sim$20%) uncertainty quoted therein renders such a comparison scarcely meaningful. In general, one might expect the kinetic energy to be mostly affected by the characteristic size of the confining medium, and not so much by its specific geometry. For a cluster of 45 atoms inside a Li cavity, we find the kinetic energy per $^4$He atom to be $21.33 \pm 0.03$ K at $T = 1$ K.

### B. Structure

Figure 2 shows radial density profiles $n(r)$, computed with respect to the center of the cavity, for a cluster of 25 atoms
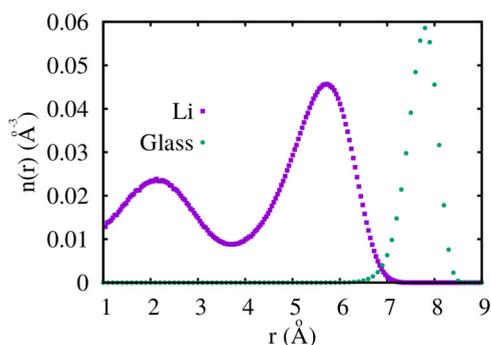


FIG. 2. (Color online) Radial density profiles at $T = 1$ K for a cluster of 25 $^4$He atoms inside a Li cavity (squares) and for 35 $^4$He atoms inside a glass cavity (circles). The origin is at the center of the cavity. Statistical errors are at most equal to the symbol size.
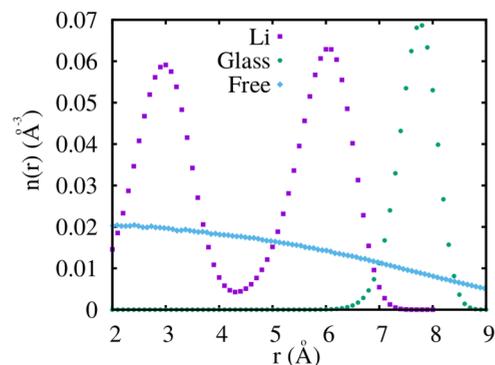
inside the Li cavity (squares) and for one of 35 atoms inside the glass cavity (circles), i.e., in both cases close to the equilibrium filling. Clearly, the arrangement of the particles in the two cases is very different, reflecting the different strengths of the adsorption potentials. Inside the more attractive glass cavity, $^4$He forms a single thin film (a spherical shell) coating the surface, whose effective 2D density at the minimum ($N = 38$) can be estimated to be $\sim 0.05$ Å$^{-2}$, based on the position of the peak of $n(r)$. This value is only slightly higher than the $^4$He 2D equilibrium density [46]. The structure of the adsorbed film comprises a single shell, and this remains the case for $N \lesssim 80$, at which point the second shell begins to appear. This corresponds to a surface coverage of approximately $0.100$ Å$^{-2}$ where second layer promotion begins to occur, quantitatively consistently with what is observed on a flat substrate [44].

Inside a Li cavity, on the other hand, two largely overlapping, floppy concentric shells form, as atoms experience a repulsive core extending over 3 Å away from the surface. Thus, even though $^4$He does form a monolayer on a flat Li substrate [38], inside a nanometer-radius spherical cavity the energetically favored arrangement is droplet-like. This result mimics what is observed for parahydrogen clusters in the same setup, on a weakly attractive substrate [31]. Figure 3 shows density profiles for systems comprising $N = 45$ $^4$He atoms inside the two cavities, at $T = 1$ K. The change is minimal on a glass substrate, as the $^4$He film coating the surface of the cavity becomes compressed, whereas the two shells inside the Li cavity become noticeably more rigid, especially the inner one, and a clearer demarcation between them emerges, although substantial atomic overlap in the region between the two shells remains. The structure of these clusters is clearly very different from that of a free cluster, as illustrated in Fig. 3. A free $^4$He cluster is very loosely bound, is featureless, and extends out all the way to approximately 12 Å from its center of mass [47]. The absence of structure for the free cluster is in agreement with previous finite-temperature simulations [9]. The interesting issue, of course, is how confinement, which modifies their shape so significantly, affects the superfluid properties of these clusters and whether one might be able to probe them experimentally.
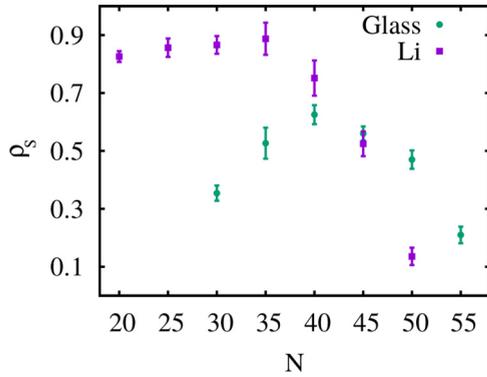
FIG. 4. (Color online) Superfluid fraction at $T = 1$ K of clusters of varying numbers of $^4$He atoms enclosed inside a Li (squares) and a glass (circles) cavity of radius $R = 10$ Å. Where not explicitly shown, statistical errors are at most equal to the symbol size.



FIG. 5. (Color online) Superfluid fraction $\rho_S(T)$ versus temperature for a cluster of $N = 45$ $^4$He atoms enclosed inside a Li (squares) and a glass (circles) cavity of radius $R = 10$ Å. Also shown is the result for a free $^4$He cluster (diamond), computed with respect to its center of mass. Where not explicitly shown, statistical errors are at most equal to the symbol size.

### C. Superfluidity

Figure 4 shows the superfluid fraction $\rho_S$ computed using the well-known "area" estimator [9] at temperature $T = 1$ K for clusters of varying numbers of atoms, from $N = 20$, at the lower limit of thermodynamic stability for a Li cavity, to $N = 55$. We also computed the same quantity for free $^4$He clusters comprising $N = 45$ and 55 atoms, both yielding approximately 82%, i.e., essentially the same value reported by Sindzingre *et al.* [9] for $N = 64$ at this temperature.

The superfluid response is quantitatively different inside the two cavities. Specifically, on the weakly adsorbing Li substrate the two-shell structure that forms (Figs. 2 and 3) displays a superfluid fraction in excess of 80%, remarkably constant (within statistical uncertainties) for $20 \leqslant N \lesssim 40$, declining rapidly above $N = 40$, and becoming negligible for $N \gtrsim 50$, where the cluster acquires a solid-like structure, with the appearance of atoms at the center of the cavity. Inside a glass cavity, the single film coating the surface has a finite superfluid response at the equilibrium coverage, quantitatively similar to that inside a Li cavity, for the same number of atoms. As the number of atoms is increased, the film is compressed and the superfluid response weakens, becoming negligible for $N \gtrsim 55$, which corresponds to a 2D coverage around $0.072$ Å$^{-2}$, in quantitative agreement with the location of the $T = 0$ melting density in two dimensions [48]. Indeed, even inside a glass cavity of such a narrow diameter the physics of the adsorbed $^4$He is largely 2D.

No re-entrant superfluidity at higher densities is seen in either cavity; on the glass substrate, this means that inner shells are not superfluid, at least not at the lowest temperature considered here, namely, $T = 0.5$ K. This suggests that a glassy confining medium of the characteristic size considered here may be too tight for superfluidity to be observed, at least in an experiment in which a porous glass filled with helium is in equilibrium with bulk superfluid.

Naturally, there is an objective limit to how closely the simple, spherical model of confinement considered here can reproduce results of experiments aimed at investigating superfluid properties of helium inside porous media, whose microscopic structure is typically one of interconnected cylindrical
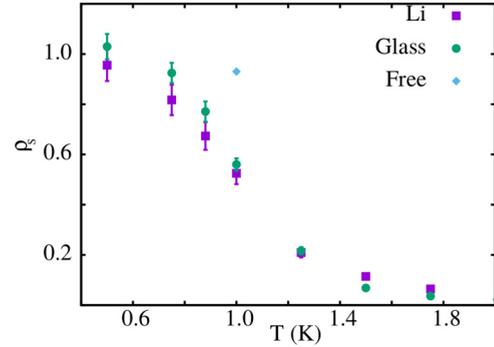
channels. However, this result is consistent with experimental evidence indicating that a characteristic confining length of the order of 25 Å may correspond to the lower limit of existence of superfluidity of $^4$He in porous media [49].

Figure 5 shows our computed values of the superfluid fraction $\rho_S(T)$ as a function of the temperature, for a cluster comprising $N = 45$ $^4$He atoms, enclosed in the two spherical cavities considered here. Also shown for comparison is the corresponding value for a free $^4$He cluster [47]. Although the superfluid signal is weaker than that which one would observe in a finite cluster, nonetheless it remains robust, comparable values of the superfluid fraction being observed only at a fraction of a kelvin lower temperature. Within the statistical uncertainties of the calculation, the estimates obtained for this specific cluster are indistinguishable, This is peculiar, considering that the structures of the two clusters are very different, as shown in Fig. 3. On a glass substrate, the character of the superfluid transition can be expected to be largely 2D; in the Li cavity, on the other hand, there are two shells, with a rather clear demarcation between the two, even though, as remarked above, some finite atomic overlap exists.

One might be inclined to think that in the less attractive Li cavity the superfluid response is essentially that of two almost independent 2D shells, or radii $\sim$3 and $\sim$6 Å. However, it should be noted that the numbers of particles in the two shells are 9 and 36, respectively, i.e., the effective 2D density is approximately $0.08$ Å$^{-2}$ for both, i.e., well into the crystalline region of the bulk phase diagram [48]. Moreover, the rapid decrease in the superfluid response for $N > 45$ coincides with the sharp reduction in the overlap between the two shells, signaling that quantum-mechanical exchanges of atoms in different shells play a vital role in underlying the superfluid response of these clusters. We computed the local superfluid density [50] and consistently found it to be homogeneous throughout the cluster, i.e., not concentrated mostly in some parts of it (e.g., one of the two shells). This physical behavior closely resembles that observed in simulations for parahydrogen clusters trapped inside nanoscale spherical cavities [31].
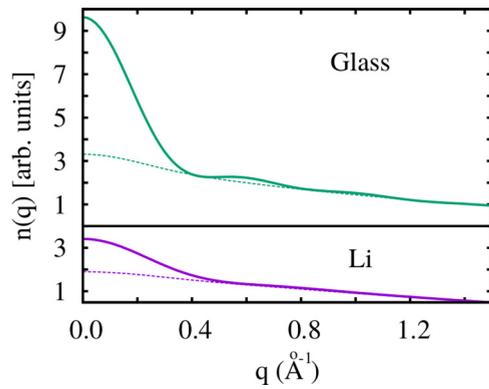
## IV. CONCLUSIONS

The purpose of this study was to gain insight into the physical behavior of nanoscale $^4$He clusters inside a spherical cavity, with particular attention to the superfluid properties. The idea is to provide a possible, alternate avenue to the exploration of clusters, one that does not involve the use of a foreign probe embedded in the cluster. Obviously, the presence of the confining surface has a significant effect on the structure of the clusters, but the main result of this work is that superfluidity can still be observed at temperatures comparable to those at which its onset is predicted for free clusters.

We have focused on spherical cavities of radius 1 nm, because they can accommodate clusters of a few tens of atoms, which is an interesting size because of the strong competition between surface and bulk energetics. We have shown that in a cavity carved inside a medium like silica, which exerts a strong attraction on $^4$He atoms, superfluidity can only occur in the form of a film coating the surface of the cavity, at equilibrium density. In an experiment in which the system is in thermal contact with a bath of superfluid $^4$He, our calculations show that cavities will be filled with frozen $^4$He, i.e., no superfluid signal will be seen, at least down to $T = 0.5$ K. On the other hand, in a weakly attractive cavity, especially one like that studied here in which the repulsive core of the interaction between atoms and cavity wall extends as far out as a third of the radius of the cavity itself, then one can expect the $^4$He fluid inside the cavity to display a significant superfluid response.

Clearly, the mathematical model contains important simplifications, notably the assumption that the cavity may be regarded as perfectly spherical and smooth. The expected minimum distance from the surface (over 3 Å) at which atoms sit in the case of a Li substrate seems to justify, at least in part, the neglect of corrugation and surface defects, an assumption routinely made in numerical studies of adsorption of He or parahydrogen on alkali substrates [38]. In the case of a strongly attractive substrate such as glass, this assumption is clearly far more questionable. It is our hope that this work will provide at least some general aid in the design of experiments aimed at probing the superfluid response of nanoscale clusters of helium or other quantum fluids (e.g., parahydrogen) in confinement.

FIG. 6. (Color online) Spherically averaged momentum distribution $n(q)$ computed for a cluster of $N = 45$ $^4$He atoms enclosed inside a Li (bottom) and a glass (top) cavity of radius $R = 10$ Å. Dashed lines refer to data at temperature $T = 2$ K; solid lines, at $T = 0.5$ K.

### D. Momentum distribution

As mentioned in Sec. I, one of the main reasons for studying the physics of $^4$He clusters in confinement is that one might be able to access their superfluid response more easily and directly than by performing spectroscopy of molecular probes embedded in free clusters. For example, one may measure the momentum distribution, typically by scattering neutrons off a sample of $^4$He adsorbed inside some suitably chosen porous medium. On the assumption that the bulk of the signal should come from $^4$He inside the cavities, one may look for the appearance at low temperatures of a peak at zero momentum [51], which signals the onset of Bose-Einsten condensation, intimately connected to superfluidity.

Figure 6 shows the spherically average single-particle momentum distribution $n(q)$ computed for a cluster of 45 $^4$He atoms inside the two cavities that we considered in this work, at the two temperatures $T = 2$ K and $T = 0.5$ K. The appearance of a peak at short momenta as the temperature is lowered below ∼1 K, i.e., when the clusters turn superfluid, is clear. The peak is not sharp as it would be in bulk superfluid but, rather, broadened by the fact that the system is confined over a length of ∼1 nm. In contrast, no such peak develops if crystallization occurs inside the cavities. There is a quantitative difference between the signal observed in the glass cavity, inside which superfluidity is essentially 2D (as mentioned above), and in the Li one. The peak inside the glass cavity is stronger, and $n(q)$ is slightly more structured and falls off more slowly at high $q$ than inside the Li cavity, due to the localization of atoms in the vicinity of the cavity surface.

[1] V. R. Pandharipande, J. G. Zabolitsky, S. C. Pieper, R. B. Wiringa, and U. Helmbrecht, Phys. Rev. Lett. **50**, 1676 (1983).

[2] V. R. Pandharipande, S. C. Pieper, and R. B. Wiringa, Phys. Rev. B **34**, 4571 (1986).

[3] S. A. Chin and E. Krotscheck, Phys. Rev. Lett. **65**, 2658 (1990).

[4] M. V. Rama Krishna and K. B. Whaley, J. Chem. Phys. **93**, 746 (1990).

[5] S. Stringari and J. Treiner, J. Chem. Phys. **87**, 5021 (1987).

[6] D. S. Lewart, V. R. Pandharipande, and S. C. Pieper, Phys. Rev. B **37**, 4950 (1988).

[7] M. V. Rama Krishna and K. B. Whaley, Phys. Rev. Lett. **64**, 1126 (1990).

[8] S. A. Chin and E. Krotscheck, Phys. Rev. Lett. **74**, 1143 (1995).

[9] P. Sindzingre, M. L. Klein, and D. M. Ceperley, Phys. Rev. Lett. **63**, 1601 (1989).

[10] D. Eichenauer, A. Scheidemann, and J. P. Toennies, Z. Phys. D **8**, 295 (1988), and references therein.

[11] S. Grebenev, J. P. Toennies, and A. F. Vilesov, Science **279**, 2083 (1998).

[12] J. Tang, Y. J. Xu, A. R. W. McKellar, and W. Jäger, Science **297**, 2030 (2002).

[13] Y. Xu, W. Jäger, J. Tang, and A. R. W. McKellar, Phys. Rev. Lett. **91**, 163401 (2003).

[14] See, for instance, J. Tang, A. R. W. McKellar, F. Mezzacapo, and S. Moroni, Phys. Rev. Lett. **92**, 145503 (2004).

[15] It should be noted that fabrication techniques with the potential of significantly extending the diameter of the cages are being developed. See, for instance, W. Roth *et al.*, Nature Chem. **5**, 628 (2013).

[16] A. K. Macpherson, Y. P. Carignan, and T. Vladimiroff, J. Chem. Phys. **87**, 1768 (1987).

[17] G. B. Woods, A. Z. Panagiotopoulos, and J. S. Rowlinson, Mol. Phys. **63**, 49 (1988).

[18] S.-T. Chui, Phys. Rev. B **43**, 11523 (1991).

[19] A. González, J. A. White, F. L. Romàn, S. Velasco, and R. Evans, Phys. Rev. Lett. **79**, 2466 (1997).

[20] M. Boninsegni, A. B. Kuklov, L. Pollet, N. V. Prokof'ev, B. V. Svistunov, and M. Troyer, Phys. Rev. Lett. **99**, 035301 (2007).

[21] A. Del Maestro, M. Boninsegni, and I. R. Affleck, Phys. Rev. Lett. **106**, 105303 (2011).

[22] L. Pollet and A. B. Kuklov, Phys. Rev. Lett. **113**, 045301 (2014).

[23] L. Vranješ Markić and H. R. Glyde, Phys. Rev. B **92**, 064510 (2015).

[24] M. Boninsegni, S.-Y. Lee, and V. H. Crespi, Phys. Rev. Lett. **86**, 3360 (2001).

[25] G. Stan, S. Gatica, M. Boninsegni, S. Curtarolo, and M. W. Cole, Am. J. Phys. **67**, 1170 (1999), and references therein.

[26] E. S. Hernández, M. W. Cole, and M. Boninsegni, Phys. Rev. B **68**, 125418 (2003).

[27] L. Szybisz and I. Urrutia, J. Low Temp. Phys. **134**, 1079 (2004).

[28] S. Park and Y. Kwon, Phys. Rev. E **89**, 042118 (2014).

[29] E. S. Hernandéz and L. Szybisz, J. Low Temp. Phys. **176**, 101 (2014).

[30] S. Park, B. Kim, and Y. Kwon, J. Chem. Phys. **143**, 104311 (2015).

[31] T. Omiyinka and M. Boninsegni, Phys. Rev. B **90**, 064511 (2014).

[32] P. E. Sokol, R. T. Azuah, M. R. Gibbs, and S. M. Bennington, J. Low Temp. Phys. **103**, 23 (1996).

[33] F. Albergamo, J. Bossy, H. R. Glyde, and A.-J. Dianoux, Phys. Rev. B **67**, 224506 (2003).

[34] F. Albergamo, J. Bossy, J. V. Pearce, H. Schober, and H. R. Glyde, Phys. Rev. B **76**, 064503 (2007).

[35] J. Bossy, T. Hansen, and H. R. Glyde, Phys. Rev. B **81**, 184507 (2010).

[36] R. A. Aziz, V. P. S. Nain, J. S. Carley, W. L. Taylor, and G. T. McConville, J. Chem. Phys. **70**, 4330 (1979).

[37] H.-Y. Kim, S. M. Gatica, and M. W. Cole, J. Phys. Chem. A **111**, 12439 (2007).

[38] M. Boninsegni, M. W. Cole, and F. Toigo, Phys. Rev. Lett. **83**, 2002 (1999).

[39] The values $D = 100$ K and $a = 2.05$ Å have been utilized in some studies to characterize the interaction of a helium atom with a glass substrate. See, for instance, L. Pricaupenko and J. Treiner, Phys. Rev. Lett. **74**, 430 (1995).

[40] M. Boninsegni, N. Prokof'ev, and B. Svistunov, Phys. Rev. Lett. **96**, 070601 (2006).

[41] M. Boninsegni, N. V. Prokof'ev, and B. V. Svistunov, Phys. Rev. E **74**, 036701 (2006).

[42] F. Mezzacapo and M. Boninsegni, Phys. Rev. Lett. **97**, 045301 (2006).

[43] F. Mezzacapo and M. Boninsegni, Phys. Rev. A **75**, 033201 (2007).

[44] M. Boninsegni, J. Low Temp. Phys. **159**, 441 (2010).

[45] C. Andreani, C. Pantalei, and R. Senesi, Phys. Rev. B **75**, 064515 (2007).

[46] P. A. Whitlock, G. V. Chester, and M. H. Kalos, Phys. Rev. B **38**, 2418 (1988).

[47] The calculation for the specific free $^4$He clusters mentioned in this work was carried out separately. Because such a small cluster is very loosely bound, an artificial confining potential was utilized, of the form $V(r) = \tan(\pi r/2R)$, with $R = 20$ Å and $R = 25$ Å, yielding consistent results.

[48] M.-C. Gordillo and D. M. Ceperley, Phys. Rev. B **58**, 6447 (1998).

[49] K. Yamamoto, H. Nakashima, Y. Shibayama, and K. Shirahama, Phys. Rev. Lett. **93**, 075302 (2004).

[50] See, for instance, F. Mezzacapo and M. Boninsegni, Phys. Rev. Lett. **100**, 145301 (2008).

[51] See, for instance, R. T. Azuah, W. G. Stirling, H. R. Glyde, M. Boninsegni, P. E. Sokol, and S. M. Bennington, Phys. Rev. B **56**, 14620 (1997).