Condensation of helium in interstitial sites of carbon nanotubes bundles

B. Marcone, E. Orlandini, F. Toigo, and F. Ancilotto
Dipartimento di Fisica "G. Galilei," Università di Padova, via Marzolo 8, I-35131 Padova, Italy
and DEMOCRITOS National Simulation Center, Trieste, Italy

(Received 27 April 2006; revised manuscript received 15 June 2006; published 21 August 2006)

Helium atoms are believed to be strongly bound within the interstitial channels in bundles of carbon nanotubes. In a recent paper [F. Ancilotto *et al.*, Phys. Rev. B **70**, 165422 (2004)] inhomogeneity in the size distribution of nanotube radii was shown to make a system of ^{4}He atoms in such an environment effectively a four-dimensional Bose gas, thus permitting a Bose-Einstein condensation (BEC) of the adsorbed atoms into the minimum energy state. This surprising result was obtained for a model of noninteracting atoms in a continuum distribution of (virtually) infinite interstitial channels. Here we investigate how the singular thermal properties of the ideal system and the occurrence of BEC are affected by a more realistic modeling of a bundle of nanotubes where (i) the number of nanotubes is finite and where (ii) ^{4}He atoms adsorbed within the same interstitial channel interact among themselves. Also in this case we observe an anomalous heat capacity close to the ideal condensation temperature, suggesting the persistence of the condensation transition for interacting ^{4}He atoms, which might be experimentally observed.

DOI: 10.1103/PhysRevB.74.085415 PACS number(s): 68.43.−h, 67.40.−w, 64.70.−p, 67.70.+n

I. INTRODUCTION

The macroscopic condensation of bosons in their ground-state [Bose-Einstein condensation, (BEC)],[1] first proposed on the basis of a noninteracting particles model, is believed to be at the heart of superfluidity in ^{4}He, which is a system consisting of relatively strongly interacting atoms.[2] More recently, BEC has been observed to occur in ultracold gases consisting of alkali or H atoms and in systems of excitons at low temperature T.[3–5]

In a recent paper it was shown that a system of bosons (either H_2 or ^{4}He) confined within the interstitial channels (ICs) of a bundle of carbon nanotubes may exhibit BEC (Refs. 12 and 13) provided that the distribution of the three neighboring tubes (with radii R_1, R_2, R_3) defining an IC site is nonuniform. On the contrary, a uniform bundle, being the collection of identical one-dimensional (1D) systems, cannot sustain BEC.[14,15]

The experimental evidence concerning the relative binding energy of either H_2 or ^{4}He in the ICs and in the grooves on the outside surface of carbon nanotube bundle[6–10] is still controversial, although some experimental evidence seems to support particle localization within the ICs.[8,11] In the following, we will assume that adsorption in the ICs is the preferred mechanism, leaving to further studies the investigation of the consequences of simultaneous adsorption also on the groove sites on the bundle's surface on the BEC transition described here.

Let us briefly review the main results of Ref. 12. We consider noninteracting atoms in a bundle of nanotubes with all their axis aligned along the z axis. The energy of a single-particle state confined within the i-th IC, surrounded by three nanotubes with radii $R_1(i)$, $R_2(i)$, $R_3(i)$, can be written as the sum of the energy for the free (longitudinal) motion parallel to the axis of the tubes and of the lowest eigenvalue $\epsilon_i \equiv \epsilon[R_1(i),R_2(i),R_3(i)]$ of the Schrödinger equation relative to the (transverse) motion in the x-y plane, i.e.,

$$E_i(p) = \epsilon_i + \frac{p^2}{2m}. \tag{1}$$

If necessary, small effects on the longitudinal motion due to the corrugation of the atom-surface potential can easily be incorporated by using a suitable effective mass approximation.[16,17] At the very low temperatures of interest here (tens of mK), we can safely neglect excitations of particles in higher states of transverse motion, since for a given channel the transverse energy levels are separated by energies of order 100 K.

A numerical analysis[12] shows that, in a heterogeneous bundle of nanotubes with a uniform quasicontinuum distribution of tubes radii, two distinct behaviors characterizes $g_t(E)$, the density of single-particle states (DOS) for transverse motion. At low energies (i.e., lower than ~20 mK for ^{4}He) $g_t(E) \sim (E-E_{\min})^{1/2}$, $E_{\min} \equiv \min(\epsilon_i)$ being the lowest eigenvalue for transverse motion, while at higher energies $g_t(E)$ decreases with energy and is well fit by the expression $g_t(E) \sim (E-E_{\min})^{-1/2}$. The total DOS, $g(E)$, is the convolution of $g_t(E)$ with the one-dimensional DOS for quasifree motion along the IC axis. As a result, at very low energies ($T < \sim 20$ mK) $g(E)$ exhibits the behavior $\propto (E-E_{\min})$ of a system of non-interacting particles in four dimensions, whereas at somewhat higher energies it becomes almost independent of energy, exhibiting a behavior characteristic of a 2D system. At energies above 1 K the 1D behavior is eventually recovered.

As a consequence of the 4D behavior of the total DOS at low temperature, Bose atoms adsorbed in a bundle of carbon nanotubes with a nonhomogenous, quasicontinuum distribution of tubes' radii, may undergo a Bose-Einstein condensation into the interstitial channel with the lowest transverse energy $E_{\min}$. On the contrary, the density of states for atoms in a perfectly uniform set of ICs is that of a 1D system, excluding the possibility of BEC.

A signature of BEC in a nonhomogeneous system is observable, in principle, as a singular behavior of the heat capacity at the transition temperature T_c.[12] This phenomenon might be difficult to achieve in practice due to the very long times required for equilibration (which entails the rearrange-

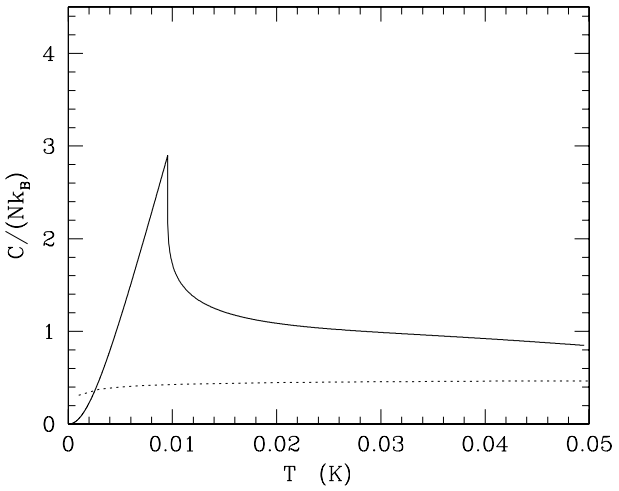

FIG. 1. Heat capacity of noninteracting ^{4}He atoms in a continuum (heterogeneous) distribution of ICs (from Ref. 12) as a function of temperature. The dotted line shows the heat capacity of 1D ^{4}He at the same linear density.

ment of particles from the ICs with higher transverse energies to those with lower energies, as the temperature is lowered) and the extremely low temperatures predicted for the transition (a few tens of mK for ^{4}He).

It has been pointed out in a recent publication by Calbi *et al.*[18] that additional adsorption sites with quite large binding energy may appear under particular circumstances at the end of carbon nanotube bundles, which can be separated by quite high energy barriers from the adsorption states in the interior of the ICs. When present, these states may act as "plugs" inhibiting the intake of gases within the bundles, thus dramatically reducing the adsorption kinetics. This effect is particularly important in the case of H_2.[18] However, the existence of such states and the magnitude of the associated energy barriers are shown to be extremely sensitive both to the value of the radii of the adjacent nanotubes forming the IC, and also to the length parameter characterizing the gas-carbon interaction (represented for simplicity in Ref. 18 by some characteristic Lennard-Jones diameter σ_{gc}). In the case of ^{4}He adsorption in the ICs system investigated here, the tube radii have typical values above $\sim$8 Å,[12] while the Lennard-Jones diameter is $\sigma_{gc} \sim 2.98$ Å. As a result of both these circumstances the outer adsorption states predicted by Calbi *et al.* disappear completely (see Fig. 3 in Ref. 18), allowing in principle the flow of ^{4}He atoms from one IC to the other, which is the fundamental mechanism permitting the BEC transition described here to be observable in experiments. In the case of H_2, however, the blocking of the ICs due to the presence of the outer states would probably imply extremely long times for exchange of H_2 molecules between ICs, making the BEC for such system virtually unobservable in experiments.

We show in Fig. 1 the main result of Ref. 12, showing the singular character of the heat capacity for ^{4}He at the transition temperature T_c. Note that in the displayed range of energies, the heat capacity value tends towards its 2D limit, $C/NK_B=1$, due to the peculiar character of the total DOS described above. At higher energies (>1 K) the 1D behavior is eventually recovered, with $C/NK_B=1/2$. For comparison, we show in the same figure the heat capacity of ^{4}He at the same density in one dimension, i.e. in a perfectly uniform set of ICs.

The results reported in Ref. 12 have been obtained (i) by assuming a continuum distribution of a virtually infinite number of ICs, with varying radii uniformly distributed in a given range, such that one may treat adsorption statistically, and (ii) by neglecting the mutual interactions between the particles adsorbed in the same IC. The first assumption is not realistic, since nanotube bundles actually contain a finite number of tubes (from a few tens to few hundreds), while the second assumption might break down for sufficiently low temperatures, when the condensation into the lowest energy IC could make the interparticle interactions important.

We want therefore to establish here whether the prediction of such condensation transition would survive under a more realistic modeling of the system, or the different environment would either preempt the BEC or alter the nature of the BEC itself, as it happens in 3D ^{4}He, where interactions reduce the fraction of condensate atoms (and lead to the new phenomenon of superfluidity). The focus of the present work is thus to relax the two just mentioned assumptions and to study a more realistic model where ^{4}He is adsorbed within the ICs in a bundle made of a finite number of nanotubes. We will also take into account explicitly the interparticle interactions, although in an approximate way based on a mean-field approach, as described below.

II. RESULTS AND DISCUSSION

The energy of ^{4}He atoms confined within the ICs of a nanotube bundles is written as

$$E = \sum_{k,i} \left[\frac{\hbar^2 k^2}{2m} + \epsilon_i \right] N_{k,i} + \sum_i \epsilon_{int}(\rho_i) N_i. \tag{2}$$

Here $N_{k,i}$ is the number of atoms in the i-th IC with wave number k, $N_i=\Sigma_k N_{k,i}$, and $\rho_i=N_i/L$ is the linear density within the $i-$th IC. L is the (finite) length of the IC. The total number of ^{4}He atoms is then $N=\Sigma_i N_i$, while N_{IC} is the total number of ICs in the sample. Note that since we consider a finite number of ICs and infinite-wall boundary conditions over the allowed momenta of the particles inside each tube, the energy spectrum described by Eq. (2) turns out to be discrete. We neglect here dilation-induced effects on the binding energies of the adsorbed atoms, associated with a moderate swelling of the bundle as the atoms fill the ICs, as predicted in Ref. 19.

We treat interactions between ^{4}He atoms in the spirit of a mean-field approach, by using a density-dependent single-particle energy term [$\epsilon_{\rm int}(\rho)$ in Eq. (2)]. We use for the latter the interaction energy per ^{4}He atom reported in Ref. 20, where the ground state energy of fully interacting ^{4}He atoms adsorbed in a single IC formed by three carbon nanotubes with the same radii is obtained from diffusion Monte Carlo calculations.

The condensation transition discussed in this paper and in Ref. 12 is a direct consequence of inhomogeneities in the

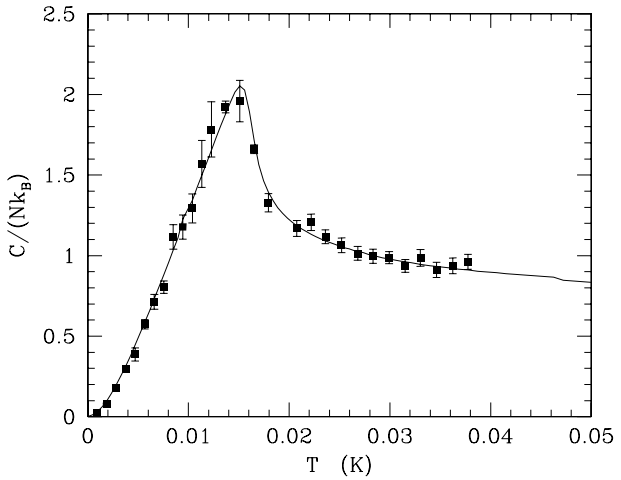

FIG. 2. Heat capacity of $N=6000$ noninteracting ^{4}He atoms adsorbed in $N_{IC}=840$ ICs of a bundle of nanotubes. Points: MC calculations; solid line: exact result [Eq. (3) in the text].

radii distribution of the nanotubes forming the ICs, which results in a range of different values for the lowest eigenvalue for the transverse motion, ϵ_i. The details of the distribution for such energy levels are however not crucial, as discussed in Ref. 12, for the occurrence of the BEC. For this reason, rather than calculating the energy levels describing the transverse motion ϵ_i from a random finite sample of ICs, we decide to choose from a distribution of transverse states (corresponding to a range of nanotube radii $8<R<10$ Å) that reproduces the total DOS for an infinite sample, as computed in Ref. 12. This will allow us to compare the results of the present work with those presented in Ref. 12, and in particular to emphasize from this comparison the effect of having either a finite number of ICs in the bundle or an interaction between the ^{4}He atoms belonging to the same IC.

The thermal properties of the system described by Eq. (2) are estimated by Monte Carlo simulations in the canonical ensemble, with $N=6000$, $N_{IC}=840$ (corresponding roughly to $N_{IC}/2$ nanotubes in the bundle) and $L=1$ μm. With these values the total density of ^{4}He atom is such that the predicted transition temperature for the ideal system (i.e., infinite number of ICs and neglecting the interparticle interactions) would be $T_c \sim 10$ mK.[12]

To test the efficiency of our sampling algorithm, we have preliminarily performed Monte Carlo simulations for the noninteracting case [i.e., $\epsilon_{int}=0$ in Eq. (2)]. In particular we have checked that our results compare well with the exact calculation of the specific heat for the same sample of ICs. Indeed the heat capacity for the non interacting system can be directly calculated as

$$C = \partial/\partial T \sum_{k,i} E_{k,i}/(e^{(E_{k,i}-\mu)/K_B T}-1), \tag{3}$$

where the chemical potential is evaluated at a given T by imposing the condition of a fixed total number of atoms, i.e. by solving the equation $N=\Sigma_{k,i}(e^{(E_{k,i}-\mu)/K_B T}-1)^{-1}$.

The calculated heat capacity as a function of temperature for the noninteracting system is shown in Fig. 2, where we compare the results of MC calculations [computed as usual from the energy fluctuations $C=(\langle E^2\rangle-\langle E\rangle^2)/K_B T^2$] with the exact result from Eq. (3). As expected, the sharp features of the infinite system as shown in Fig. 1 are no longer present: the heat capacity shows instead a broader and lower peak at a transition temperature which is slightly higher than the one of Fig. 1.

We next consider the effect of the interaction between He atoms that belong to the same IC. As we said in the previous section the interaction has been treated in the mean field approximation. In particular we consider a binding energy per atom $\epsilon_{int}(\rho)$ (as obtained in Ref. 20 from diffusion Monte Carlo calculations) that is zero at $\rho=0$ (being referred to the adsorption energy of a single ^{4}He atom in the IC), is minimum at $\rho_0 \sim 0.08$ Å^{-1} with $\epsilon_{int}(\rho_0)\sim -10$ mK, and it rapidly grows towards positive values as the density is increased, due to the repulsive He-He interaction. Since the minimum energy $\epsilon_{int}(\rho_0)$ is large both with respect to the minimum spacing between transverse energies ϵ_i in different ICs (at least for relatively low values of ϵ_i) and between adjacent levels of the kinetic energy, the ^{4}He atoms in a given IC will tend to achieve a density close to the optimal value ρ_0. Since our calculations are done at constant number of particles, as a consequence of the condensation fewer ICs will be occupied as the temperature is lowered (those with the lowest binding energies), leaving the others ICs almost empty. In a typical configuration during a MC run at low T a fraction of ICs will thus be occupied by $N_0 \sim \rho_0 L$ atoms and fluctuations, which determine the thermal behavior, will mainly occur around this value. In particular, as we have checked numerically, the total energy landscape shows many deep local minima in the space of the occupation numbers of the various ICs, n_i, which are quite flat around their optimal values n_i^* (each in turn very close to N_0). At low T, small fluctuations of the occupation numbers around these values are then favored, because of the flatness of the energy minima, while big fluctuations are highly suppressed because of their deepness.

As a consequence, MC runs performed at low T and starting from a configuration close to the one where the ICs are optimally populated, one observes that the system does not change significantly during the MC evolution, i.e. the occupation numbers of each tube remain essentially the same as in the initial configuration. If instead one starts from a configuration with a random occupation of the ICs, the system almost never samples the minimum around the optimally populated state, but rather, reaches one of the metastable states described above. Thus in order to reach the true equilibrium at low T, one has either to start from an initial configuration close to the GS, or to use other, more efficient, schemes for the MC sampling (collective Monte Carlo moves, annealing, etc.).

One comment is in order concerning the He-He interaction energy term $\epsilon_{int}(\rho)$ that we borrowed from the diffusion Monte Carlo results of Ref. 20. Such energy has been computed for a "regular" IC, i.e., an IC bounded by three carbon nanotubes with the same radii.[20] In principle, however, differences in the radii of the nanotube forming the IC (as those considered here) can modify the interaction energy of ^{4}He

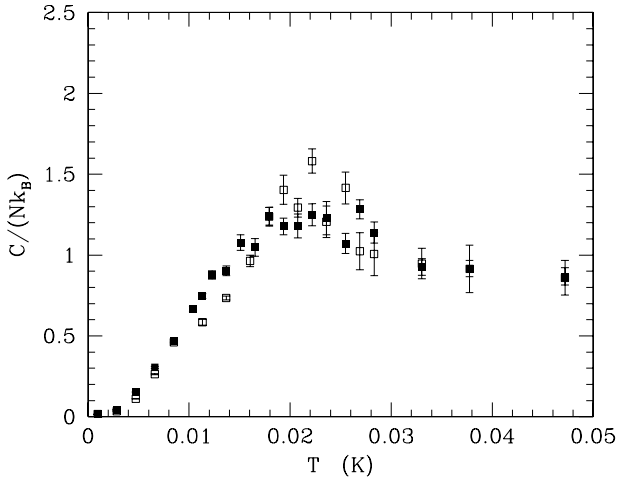

FIG. 3. Calculated temperature dependence of the heat capacity for a system of N interacting ^{4}He atoms adsorbed in N_{IC} ICs. Filled squares: $N=6000$ and $N_{\mathrm{IC}}=840$. Empty squares: $N=2000$ and $N_{\mathrm{Ic}}=280$.

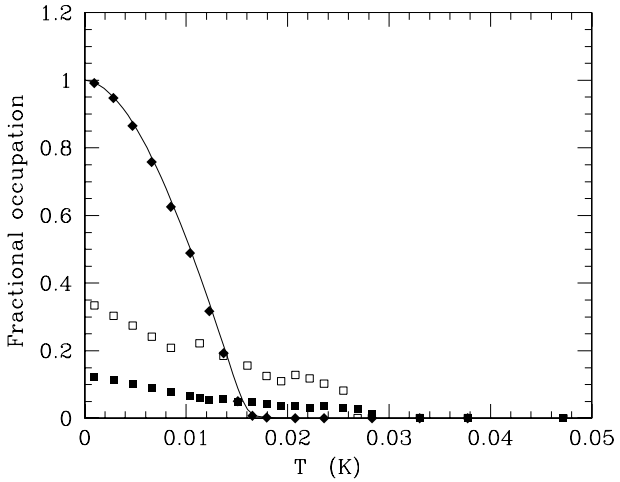

FIG. 4. Fraction of atoms condensed into the lowest-energy IC as a function of temperature for the noninteracting (diamonds) and interacting (squares) case. The solid line shows the exact result for the noninteracting system. Filled squares: $N=6000$ and $N_{\mathrm{IC}}=840$. Empty squares: $N=2000$ and $N_{\mathrm{IC}}=280$.

atoms adsorbed in the IC because of the (small) changes in the available volume between the three nanotubes forming the IC. Although we do not expect significant changes in the interaction energy due to this effect, one should keep in mind the approximation underlying our choice.

One may ask whether the scenario emerging from our Monte Carlo simulations, i.e., the presence of long-lived metastable states, is conserved in real systems, or not. This will depend in a crucial way from the very nature of the dynamic processes which are responsible for the particle exchange within tubes, but also on the time scale over which the system is observed. If a collective diffusion from IC to IC is possible (through the open ends of the bundle), then the system should be able to reach the true equilibrium state in a reasonable time, even at low T.

The results of our MC calculations for the interacting system are shown in Fig. 3, for two different numbers of ICs in the bundle. The heat capacity curves still show an anomalous behavior close to the "transition" temperature, although the rather sharp peak present for the noninteracting system is now smeared out, leaving a bump in the heat capacity well above the ideal value $C/NK_B=1/2$. This behavior could be observed experimentally, although direct observation might be hampered by very long equilibration times as suggested by the Monte Carlo simulations. In Fig. 4 we show the fraction of ^{4}He atoms that condense into the lowest energy IC, as a function of temperature. It is clear that, both for the noninteracting and the interacting cases, a critical temperature exists below which such fraction shows a rather sudden increase from zero to a maximum value at $T=0$. The differences between the noninteracting and interacting cases are in the value of the critical temperature and of the condensed fraction at $T=0$. In particular the interacting cases are characterized by a maximum fraction of condensate lower than 1 and an higher transition temperature with respect to the noninteracting case.

We note that the increase in the transition temperature for the interacting system is just the opposite of what happens in the case of bulk liquid ^{4}He, where the transition temperature for BEC in the interacting liquid is lower than that for the ideal Bose gas. We remark that the nature of the BEC transition investigated here has a totally different origin than that occurring in bulk liquid ^{4}He, i.e. it is not a condensation in the momentum space, but rather it has a mixed nature, where also condensation in real space occurs (i.e., adsorption of a large fraction of ^{4}He atoms within the lowest energy IC). It is thus not surprising to find a different behavior of the critical temperature as the interactions between particles is taken into account. We do not have any explanation for the observed increase in the critical temperature, and we consider it as an interesting empirical observation, deserving further investigations in future work.

The reduced fraction of condensate atoms with respect to the noninteracting case is apparently similar to what happens to liquid ^{4}He where the strong interparticle interactions result in a reduced fraction of the atoms condensed into the groundstate. However, one should keep in mind that the condensate fraction is defined here as the ratio between the occupation of the lowest energy IC and the total number of ^{4}He atoms. Since our calculations are performed at a constant number of particles, the condensate fraction at $T=0$ for the interacting system is expected to depends on the total density of ^{4}He and also on the details of the transverse energy levels distribution (this is clearly visible in Fig. 4, where the two sets of points for the interacting systems have been computed with the same ^{4}He density, but different set of transverse energy levels). For this reason no particular significance should be attached to the actual value found in our calculations for this fraction. Rather, we consider the behavior of the condensate fraction with the temperature as a useful indicator signaling the onset of condensation.

In order to better characterize the effect of the He-He interactions in modifying the thermal behavior of the ideal system, we have used a different recipe to model the interparticle interactions of ^{4}He atoms adsorbed in the same IC

[represented by the density-dependent term $\epsilon_{\text{int}}(\rho)$ in Eq. (2)], i.e., we used the ground-state energy of 1D ^{4}He as computed with diffusion Monte Carlo method.[21] In 1D the ground-state of interacting ^{4}He atoms turns out to be a very weakly bound liquid, with a binding energy per particle of about 1.7 mK (to be compared with the 10 mK for the 3D case). As a result of the reduced He-He interactions within an IC, the heat capacity curve turns out to be much more similar to the noninteracting case of Fig. 2.

III. CONCLUSIONS

In summary, by means of Monte Carlo calculations we have investigated the behavior of interacting ^{4}He atoms adsorbed in the interstitial channels of a more realistic model of a carbon nanotubes bundle than that studied previously. We find that the signature of a recently proposed BEC transition for non interacting ^{4}He atoms persists also for the interacting case. The effect of the interaction consists in smearing out the singular character of the transition and to shift the transition temperature towards higher values. Such broad signature could be observed in principle in experiments of ^{4}He adsorption in a bundle of an heterogeneous sample of carbon nanotubes. A similar effect is predicted to occur for other Bose particles, e.g., H_2 molecules adsorbed in the ICs of a nanotube bundle.[12] However, for such a system the blocking of the ICs due to the presence of strongly binding outer states separated by large energy barriers from the adsorption states inside the ICs, as predicted by Calbi *et al.*,[18] would probably imply extremely long times for exchange of H_2 molecules between ICs, making the BEC for such system virtually unobservable in experiments.

ACKNOWLEDGMENTS

We are grateful to M. W. Cole for helpful discussions.

[1] S. G. Brush, *Statistical Physics and the Atomic Theory of Matter* (Princeton University Press, Princeton, 1983).
[2] F. London, Nature (London) **141**, 643 (1938).
[3] E. A. Cornell and C. E. Wieman, Rev. Mod. Phys. **74**, 875 (2002).
[4] T. J. Greytak, D. Kleppner, D. G. Fried, T. C. Killian, L. Willmann, D. Landhuis, and S. C. Moss, Physica B **280**, 20 (2000).
[5] S. A. Moskalenko and D. W. Snoke, *Bose-Einstein Condensation of excitons and Biexcitons and Coherent Nonlinear Optics with Excitons* (Cambridge University Press, Cambridge, 2000).
[6] M. Muris, N. Dupont-Pavlovsky, M. Bienfait, and P. Zeppenfeld, Surf. Sci. **492**, 67 (2001).
[7] A. D. Migone and S. Talapatra, J. Nanosci. Nanotechnol. **2**, 467 (2002); T. Wilson and O. E. Vilches, Physica B **329**, 278 (2003); M. Muris, M. Bienfait, P. Zeppenfeld, N. Dupont-Pavlovsky, M. Johnson, O. E. Vilches, and T. Wilson, Appl. Phys. A: Mater. Sci. Process. **74**, S1293 (2002).
[8] T. Wilson, A. Tyburski, M. R. DePies, O. E. Vilches, D. Becquet, and M. Bienfait, J. Low Temp. Phys. **126**, 403 (2002).
[9] Y. H. Kahng, R. B. Hallock, E. Dujardin, and T. W. Ebbesen, J. Low Temp. Phys. **126**, 223 (2002).
[10] M. M. Calbi, S. M. Gatica, M. J. Bojan, G. Stan, and M. W. Cole, Rev. Mod. Phys. **73**, 857 (2001).
[11] J. C. Lasjaunias, K. Biljakovic, J. L. Sauvajol, and P. Monceau, Phys. Rev. Lett. **91**, 025901 (2003).
[12] F. Ancilotto, M. M. Calbi, S. M. Gatica, and M. W. Cole, Phys. Rev. B **70**, 165422 (2004).
[13] F. Ancilotto, S. M. Gatica, and M. W. Cole, J. Low Temp. Phys. **138**, 201 (2005).
[14] The distribution of tube sizes present in actual samples leads to predictions that are quite different from those based on the monodisperse models, in better agreement with experimental data than the naive models' (of all equal tube radii) predictions (Ref. 15).
[15] W. Shi and J. K. Johnson, Phys. Rev. Lett. **91**, 015504 (2003).
[16] M. Boninsegni, S.-Y Lee and V. H. Crespi, Phys. Rev. Lett. **86**, 3360 (2001).
[17] Band-structure effects due to the corrugation of the He-tube potential in an IC has been investigated in A. Siber and H. Buljan, Phys. Rev. B **66**, 075415 (2002).
[18] M. M. Calbi and J. L. Riccardo, Phys. Rev. Lett. **94**, 246103 (2005).
[19] M. M. Calbi, F. Toigo, and M. W. Cole, Phys. Rev. Lett. **86**, 5062 (2001).
[20] J. Boronat, M. C. Gordillo, and J. Casulleras, J. Low Temp. Phys. **126**, 199 (2002).
[21] M. Boninsegni and S. Moroni, J. Low Temp. Phys. **118**, 1 (2000).