Condensation of Helium in Nanotube Bundles

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Helium atoms are strongly attracted to the interstitial channels within a bundle of carbon nanotubes. The strong corrugation of the axial potential within a channel can produce a lattice gas system wherein the weak mutual attraction between atoms in neighboring channels induces a transition to an anisotropic condensed phase. At low temperatures, the specific heat of the adsorbate phase (with fewer than 2% of the atoms) greatly exceeds that of the host.

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While once of only academic interest [1,2], helium in one-dimensional (1D) or quasi-one-dimensional systems has received increased attention recently since the realization that such systems can be created in the laboratory. Helium is very strongly bound within the narrow interstitial channels between tubes within the triangular lattice of a bundle of carbon nanotubes [3–5]. Within such a channel, the transverse degrees of freedom are frozen out even at relatively high temperatures of ~30 K. The binding energy per atom, ~370 K, is the highest known for He, over twice as large as on the basal plane of graphite [6]. It exceeds the ground state binding energy of bulk liquid ^{4}He by nearly 50 times [7].

Here we describe how the He/nanotube-bundle system can produce an experimental realization of a lattice gas wherein the weak coupling between He atoms in neighboring channels induces a finite-temperature transition into a weakly bound anisotropic condensed state. This qualitatively new phase of He has strong 1D character, highly localized He atoms, and kinetics dominated by atomic tunneling between lattice sites.

We assume that the He-He interaction is unaffected by the substrate, an approximation that omits screening by both phonons and electrons. On planar graphite, electrodynamic screening reduces the well depth of the He-He pair potential by ~10% [8]. The smaller He-C separation in the interstitial channels should yield a somewhat larger effect; its omission then implies a moderate overestimate in the binding energies described below.

The external potential felt by a He atom in the interstitial channel has a large corrugation. Modeling this interaction with a C-He pair potential [4], the band structure of an isolated ^{4}He atom within an interstitial channel of a (18,0) [9] tube lattice yields a purely 1D dispersion with a very large enhancement of the lowest-band effective mass: $m^*/m \approx 18$, with a bandwidth of ~0.18 K. The lowest band has a binding energy of 370 K. Measured along the channel's central axis, the potential barrier for axial motion is ~20 K. (This barrier acts in concert with the variable transverse width of the potential; the effects of the corrugation are most directly revealed through m^*.) For a regular tube lattice, the interchannel tunneling is negligible. Figure 1 shows ground state isoprobability surfaces for ^{4}He at $k = 0$ in the single-particle band structure. The coupling between sites is sufficiently weak that single-particle atomic tunneling dominates even at moderately high temperatures. Because of the heterogeneity of currently accessible nanotube systems (i.e., mixtures of tubes with different wrapping angles and diameters), this result should be treated qualitatively, as a demonstration that the states are well localized axially within the interstitial channel. Such a small bandwidth implies well-confined single-particle wave functions which, in this particular geometry, occupy a regular lattice with a separation of 4.2 Å between sites. The bandwidth could be controlled by changing the

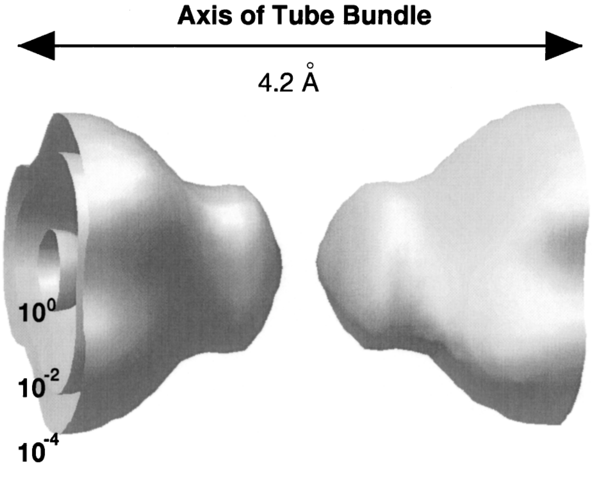

FIG. 1. Isoprobability surfaces for the $k = 0$ state in the lowest band for helium within the interstitial channel of a lattice of (18,0) nanotubes. The dimples arise from the three nanotubes which bound the channel. The isosurfaces correspond to probability densities of 10^0, 10^{-2}, and 10^{-4} Å^{-3}. The axial lattice constant is 4.2 Å and a single unit cell (and single adsorption site) is shown. The lowest-band states are well confined to distinct lattice sites.

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nanotube diameter [10] or through external pressure, possibly inducing a quantum phase transition. Note that this single-particle calculation is consistent with recent experimental results that the He binding energy in tube bundles can exceed that for a flat graphitic substrate [5].

For this lattice of localized He sites, the natural description is a lattice gas model (in contact with an external reservoir of particles) wherein the relevant degrees of freedom are the site occupations, 0 or 1 [11]. The intersite hopping energy (i.e., ~0.1 K) is significantly lower than the potential energy of interaction between atoms on neighboring sites in a channel (~0.5 K), suggesting that the lattice gas model is appropriate to a lowest approximation. For other configurations of nanotubes which have larger intersite separations, the ratio of the hopping energy (which drops exponentially with separation) to the potential energy of interaction (which drops as a power law) is likely to be even smaller. Multiple occupancy is excluded by the hard-core repulsive interaction between atoms (estimated to impose an energetic cost of ~50 K). Intrasite excitations also involve high energy scales (~50 K), which are irrelevant at low T. A preliminary description of the phase behavior can be obtained from results previously obtained [12,13] for an anisotropic simple cubic Ising model with an interaction strength J_z between neighboring spins along the z axis (i.e., within the same channel) and a transverse interaction $J_t = cJ_z$. For the He-nanotube system, c is very small. When $c < 0.1$, the transition temperature is well approximated by the asymptotic formula [12,13]

$$\frac{T_c}{J_z} = \frac{2}{\ln(1/c) - \ln[\ln(1/c)]}. \tag{1}$$

Here we have $J_z = |V(a)|/4$, where $V(a)$ is the equilibrium interatomic interaction at the intersite separation and the factor of $1/4$ arises from the familiar transformation from the Ising model to the lattice gas. For He with an intrachannel site spacing of $a = 4.2$ Å, $J_z = 0.5$ K. As the present lattice is honeycomb rather than simple cubic and as second neighbors are not included in Eq. (1), the transverse interaction strength J_t should be renormalized by roughly a factor of $3 \times 3/4$, which includes a factor of ~3 for the second neighbors in adjacent channels and a factor of $3/4$ for the reduced coordination of the lattice. This approximation is supported by numerical calculations on the honeycomb lattice (see below). For He with interchannel spacing $d = 9.8$ Å, we obtain $J_t \approx 7$ mK, and $c \approx 0.015$. Equation (1) then yields $T_c \approx 0.7J_z$. The transition temperature for condensation in this lattice-gas model is then $T_c \sim 0.36$ K, somewhat below the ground-state binding energy of 2 K. Reducing c by even a factor of 5 would change T_c by less than 25%, illustrating the insensitivity of T_c to the transverse interaction. Variation in T_c through changes in $|V(d)|$ will be minor so long as this lattice-gas model remains valid.

We obtain more detailed information from Metropolis Monte Carlo canonical ensemble simulations of atomic motion on the honeycomb lattice. The lattice measures $10 \times 10 \times 100$ unit cells (10×10 in the plane of a honeycomb) with two sites per cell. The highly elongated cell accounts for the much longer-ranged correlations along a bundle axis. We include interactions of an atom with nearest neighbors within a channel and with three neighbors in each of the three neighboring channels. At each temperature and coverage we compute approximately 500 000 Monte Carlo steps per atom. The heat capacity is obtained from the energy fluctuation formula $C = (\Delta E)^2/kT^2$ and checked by also computing dE/dT. (The former is shown in Fig. 2.) We obtain the temperature-coverage curve as a function of temperature from grand canonical ensemble simulations of a $10 \times 10 \times 200$ system using 5000 Monte Carlo steps per site (50 000 steps near the critical point). Although this system falls in the three-dimensional Ising model class, the quasi-1D character manifests itself in the specific heat above the transition. For small c, the specific heat above the transition [13] closely follows the one-dimensional result [2]:

$$C(T)/k_B N = \left[\frac{J_z}{k_B T}\,\mathrm{sech}\left(\frac{J_z}{k_B T}\right)\right]^2. \tag{2}$$

The one-dimensional specific heat has a maximum of 0.44 near $T/J_z = 0.83$, slightly above the transition. We take this temperature as a convenient reference point for comparison to other systems. For $d = 9.8$ Å and $a = 4.2$ Å, the resulting adsorbed particle density implies

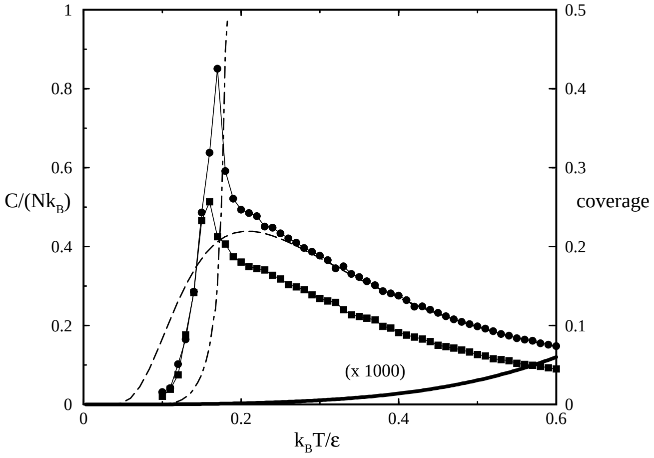

FIG. 2. The heat capacity per site at coverages of 0.2 (squares) and 0.5 (circles) as functions of the temperature k_BT/ϵ, where $\epsilon \equiv V(a)$ is the in-column nearest-neighbor coupling. Lines are guides for the eye. The specific heat at the critical site coverage diverges at $T_c \approx 0.36$ K and asymptotes to the one dimensional specific heat (dashed curve) at high temperatures. The dash-dotted line gives the coverage as a function of the transition temperature, referring to the right-hand axis. The lowest (solid) curve shows a theoretical result [14] for the specific heat of the nanotube substrate (×1000).

a specific heat of ~4 mJ/gK (normalized to the mass of the carbon host) at $T \approx 0.83 J_z$. This contribution to the specific heat greatly exceeds the background specific heat of the host material. For example, measurements on a sample of single-walled carbon nanotubes yield a specific heat of $C \sim 0.2$ mJ/gK at 1 K which is decreasing with decreasing temperature [14]. The specific heat of graphite is at least 3 orders of magnitude smaller in this temperature range [15]. Note also that experimental measurements of the specific heat of single-walled nanotube bundles significantly exceed theoretical estimates for the contributions from the nanotube substrate [14]; the low-energy degrees of freedom of adsorbed gases might account for this discrepancy.

In these He/nanotube-bundle systems, the lattice-gas model describes a transition between high-temperature gas and a low-temperature solid. The model predicts phase behavior topologically identical to that found in the familiar isotropic case. Since the phase diagram has particle-hole symmetry, the critical density has mean site occupancy of 1/2. The high-temperature limit is a random occupation of the sites, while the low-temperature limit is a coexistence of a dense phase of fully occupied sites and a vapor phase. Just above T_c, the system has a large intrachannel correlation length with 1D islands of densely occupied sites. At T_c, the transverse correlation length diverges and neighboring islands acquire long-range correlation. At densities other than 1/2 the system will undergo a first order transition (at a density-dependent temperature) to a low-temperature domain of coexistence between a dilute phase and a dense phase.

How can one separate the effects of axial confinement from the effects of the weak interchannel interactions in determining the transition temperature of condensation? To shed light on this question, we compare our results above to an analogous system of interacting channels wherein the intrachannel potential is smooth. Since the lattice-gas model is not valid in this limit, we describe the He-He interactions within a single channel within a diffusion Monte Carlo calculation, treating the interchannel interaction within the Hartree approximation. A previous analysis of a single isolated channel [4,16] yielded a very weakly bound state (~2 mK per atom) of remarkably low density (~0.04 Å^{-1}). Here we introduce the interchannel interactions through a variational wave function which is a product of identical states of density ρ in every interstitial channel. The energy shift Δ due to the interchannel interaction between channels separated by distance d is

$$\Delta = \rho \int_0^\infty dx\, V(r')\,, \tag{3}$$

where $r' = \sqrt{x^2 + d^2}$. A straightforward numerical integration of (3), using the Aziz interatomic potential for He [17] and including the three nearest and the six next-nearest neighbor channels yields $\Delta/\rho = -0.228$ K Å. Because of the rapid decay of V with distance, inclusion of more distant channels produces no appreciable change. Figure 3 shows how the interchannel interaction increases the binding energy (2 → 16 mK) and the equilibrium density (0.035 → 0.080 Å^{-1}) of the condensed state above that in the single-channel picture. Classical statistical mechanics implies a proportionality between the ground state cohesive energy and the critical temperature of a given system. Although this law of corresponding states fails for quantum systems, a specific class of systems (i.e., a definite de Boer quantum parameter [18]), typically has a strong correlation between the critical temperature and the ground-state cohesive energy. For example, ^{4}He in 3D has a binding energy per particle of 7.17 K and a critical temperature 5.2 K. In 2D, these values are 0.87 and 0.85 K, respectively [19]. The smooth channel model should then condense at ~10 mK. The variational approximation underestimates T_c, whereas the neglect of fluctuations in this nearly one-dimensional system overestimates T_c. The delocalized smooth channel approximation yields a much lower transition temperature (~10 mK) than the localized case (~0.3 K). This result then provides important insight into the origin of the relatively high transition temperature in the more realistic lattice-gas system: In the smooth channel, the kinetic energy maintains a large (~15 Å) distance between He atoms within a channel, which reduces their interaction energy by 30-fold. The corrugation in the external axial potential forces a much smaller He-He separation and thereby produces a much higher transition temperature due to the larger intrachannel interaction [20]. Although the *inter*channel interaction is necessary to induce the phase transition, the much stronger *intra*channel interaction, which determines the spacing of the localized sites, sets the scale of T_c.

In experimentally produced nanotube bundles the distribution of nanotube diameters is rather sharp, but present evidence suggests a heterogeneous distribution of

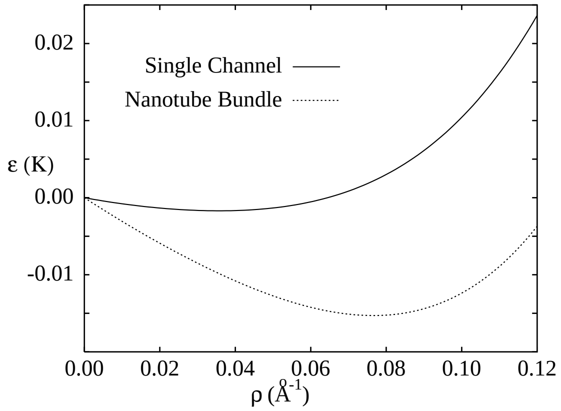

FIG. 3. Energy ϵ per ^{4}He atom in an isolated smooth 1D channel (solid line), compared to the energy per atom for a hexagonal lattice of smooth channels at the same interchannel separation as for a carbon nanotube bundle (dashed line).

wrapping angles for the individual tubes. The consequent variations in the binding and axial separation of adsorption sites can strongly affect the critical phenomena near the transition and the nature of the condensed phase [21], but should cause comparatively minor variations in the transition temperature of condensation. As T_c is linearly proportional to J_z and only weakly dependent on J_t in this regime, the main effect on T_c will arise from variations in the intrachannel intersite separation. Should the spatial extent of axial localization be substantially longer in some bundle geometries, then double occupancy could become important as well. Note that the excited-state properties of these systems are also extremely interesting, as they represent highly correlated low-dimensional hard-core quantum systems within either periodic or qausiperiodic external potentials.

In summary, we demonstrate that He within the interstitial channels of carbon nanotube bundles can condense into an anisotropic phase wherein the strong axial confinement induced by the external potential greatly enhances the density and, hence, the transition temperature to the low-temperature solid. This qualitatively new phase of He is distinguished by strong He localization, a pronounced 1D character to thermodynamic quantities such as the specific heat, and single-particle atomic tunneling between sites. This contrasts sharply with the He/planar-graphite system wherein the He single-particle bandwidth is an order of magnitude higher [22]. At low temperatures the specific heat of the helium absorbates, which comprise less than 2% atomic fraction of the He/nanotube-bundle system, greatly exceeds that of the much stiffer background material. This intriguing interstitial-channel condensation should also be observable for other small atoms, for example, H_2 [23] and Ne [4]. Preferential adsorption to the interstitial sites can be guaranteed by choosing small adsorbates which energetically prefer the tighter coordination of the interstitial channel over the interior of a tube (or by simply using nanotubes with closed ends); adsorption to the outer bundle surface must be treated separately. For ^{3}He, we expect the ordering behavior to be similar to that of ^{4}He, since atomic exchange is negligibly small. This situation is reminiscent of the epitaxial ordering transition of ^{3}He and ^{4}He on the graphite basal plane. In that case, exchange is much higher than here, yet transition temperatures of the isotopes differ by less than 1% [24,25].

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