Interstitial He and Ne in Nanotube Bundles

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We explore the properties of atoms confined to the interstitial regions within a carbon nanotube bundle. We find that He and Ne atoms are of ideal size for physisorption interactions, so that their binding energies are much greater there than on planar surfaces of any known material. Hence high density phases exist at even small vapor pressure. There can result extraordinary anisotropic liquids or crystalline phases, depending on the magnitude of the corrugation within the interstitial channels.

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The bulk synthesis of carbon nanotubes has led to several investigations of molecular sorption within these tubes. Tubes readily imbibe those materials with low liquid-vapor surface tensions, in agreement with a qualitative argument based on the ratio of the cohesive energy to the adhesive energy. One might expect, therefore, that inert gases would be strong absorbers within these tubes; this belief was confirmed in both recent calculations and experiments. Here we explore adsorption in the linear interstitial channels (IC’s) between close-packed nanotubes within a bundle or rope. Small atoms, such as He and Ne, fit well in these IC’s. Since this environment has a large number of nearby C atoms at an optimal distance, the binding is stronger than in any other known charge-neutral system. The present paper describes our initial model calculations which establish this fact. After considering the energetics of individual atoms, we describe a variety of unique collective phenomena which may occur.
Using the pairwise summation of atomic interactions with C, we have computed the potential energies of He and Ne within the IC’s (which we assume to be infinitely long and perfect); \( \epsilon \) is the well depth of the pair potential (16.2 K for He and 32.1 K for Ne). The study has been done as a function of separation \( d \) between the axes of adjacent channels. Fig. 1 shows the resulting potential for the experimental separation \( d = 9.8 \) Å (tube radius 6.9 Å). Fig. 2 reveals that this value of \( d \) provides nearly the greatest possible attraction for both Ne and He atoms; the potential on the IC axis is approximately a factor of two greater than the well depth within a tube of the same radius and is \( \sim150\% \) greater than the well depth on a graphite surface. Note that graphite provides the most attractive potential of any planar surface known. These comparisons imply that the uptake of these gases within the IC’s ought to be significant and easily measured. We may compute the sorption using a variety of alternative models, several of which we discuss here.

One possible assumption is to neglect the corrugation of the potential along the \( z \) axis, i.e. the axial direction of the IC’s, and to angularly average the transverse potential. We then solve the single particle Schrödinger equa-
Fig. 2. Minimum of the potential energy for He (solid line) as a function of IC separation $d$, as well as the ground state energy (filled circles). Shown for comparison is the analogous result for He adsorption within a tube (dashed line and open circles). The case of Ne appears in the inset. Typically, $d \sim 10 \text{Å}$.

In order to make quantitative predictions about the sorption in the IC’s, we present here several simplified model calculations. A more thorough investigation is in progress. We believe that the finding of significant sorption will not be affected by refinements of the calculations.

At sufficiently low density (and not too low $T$), we assume that the adsorbate is an ideal classical 1d gas; hence, the resulting chemical potential satisfies $\mu = E_\perp + k_B T \ln(\rho \lambda)$. Here $\rho$ is the 1d density within an IC, $E_\perp$ is the transverse ground state energy and $\lambda$ is the de Broglie thermal wavelength. From this relation and the analogous expression for the coexisting vapor (of density $n$ and pressure $P$), we find that $\rho = n \lambda^2 \exp(-E_\perp/k_B T)$. This relation implies for He that an extraordinarily low pressure, $P \approx 10^{-34}$ atm, yields a 1d gas with spacing 5 Å at $T = 4.2$ K. One requires a pressure 20 orders of magnitude higher to achieve the same interparticle spacing on a graphite surface!
Quantum and interaction effects enhance interest in this problem. Hence we have addressed the extreme case of 1d He at $T = 0$. We have determined the equation of state of this system numerically, using the Diffusion Monte Carlo method with the Aziz interatomic potential. Fig. 3 shows our results. While such a 1d system undergoes no finite temperature transition, we have explored the effects of interactions between atoms in neighboring IC’s. Using a variational approach we have demonstrated the existence of a self-bound liquid at a density around $0.05 \, \text{Å}^{-1}$, with a binding energy per particle (and transition temperature) $\simeq$ tens of mK. We believe that it is a remarkable superfluid without Bose-Einstein condensation (as found also in 2d He at low $T$).

From the data in Fig. 3, we find that the chemical potential of the 1d system increases rapidly above a density $0.25 \, \text{Å}^{-1}$ (rising from $\sim 50$ K to over $300$ K at $0.35 \, \text{Å}^{-1}$) due to both zero-point energy and the repulsive interactions. At density $< 0.25 \, \text{Å}^{-1}$, however, the net chemical potential, including the IC single particle energy $E_\perp$, lies below the single particle chemical potential on graphite. Hence we predict that a high density interstitial fluid would form at low $\mu$ in the IC’s before any significant gas would adsorb on a graphite surface at low $T$.

We next examine the assumption that the atomic motion along the channels is that of a free particle. The corrugation of the potential on a graphite surface is known to be a $\sim 15\%$ effect, leading to band mass $m^* \sim 1.05 \, m$. 

![Figure 3](image-url)
In the very confined environment of the IC, the energy scale associated to corrugation is now magnified so that band structure effects are considerable. This problem merits a fully three dimensional calculation, which we have not yet performed. Rather, we have solved a 2d Schrödinger equation for a series of fixed positions $z$ along the IC axis; the resulting eigenvalue $E_\perp$ becomes an input into a 1d band structure calculation. We observe in Fig. 4 that this effective potential corresponds to a highly localized system. This property is manifested in the energy level and wave function shown, which are computed with a simplified harmonic approximation. The system of many atoms moving in such a potential has remarkable properties. The atoms may be so strongly localized that the system realizes the (usually artificial) lattice gas model. The ground state would then be a unique quantum crystal which can be characterized in a diffraction, thermodynamic, or NMR experiment. We shall report on its properties in a future publication.

The corrugations treated here are extrema within the available possibilities. Uniform aligned tubes yield the maximum possible corrugation. We are currently evaluating alternative geometries to see whether the intriguing fluid, derived with the smooth potential model, may also be realized by appropriate choice of geometry.

We summarize our results as follows. Calculations indicate that He and Ne are well suited to squeeze into the interstitial channels between C
nanotubes. The binding there is so strong that a high density fluid is reached
at vapor pressures so low that negligible adsorption occurs on basal plane
graphite. When cooperative effects between atoms in neighboring tubes are
included, we find exotic anisotropic condensed phases to occur. These are
being investigated currently.

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were considered \((d = 9.95 \text{ Å})\), i.e. radial lines from \(z = 0\) to the axis of each
tube intersect the center of a hexagon.