

Lattice dilation near a single hydrogen molecule in an interstitial channel within a nanotube bundle

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(Received 16 July 2003; revised manuscript received 10 October 2003; published 14 May 2004)

We explore the ground state of a single hydrogen molecule within an interstitial channel (IC) of a bundle of carbon nanotubes. A previous (variational) study found that when many molecules are present, comprising a dense fluid, the nanotube lattice is slightly dilated, with a 1% relative increase of lattice constant. Although small, that dilation doubled the binding energy per molecule inside the IC's. Here, in the case of a single particle, the result is an even smaller dilation, localized near the particle, and a much smaller increase of the binding energy.

DOI: 10.1103/PhysRevB.69.195408

PACS number(s): 61.46.+w, 68.43.-h, 68.65.-k

I. INTRODUCTION

The nature of adsorbed phases within a bundle of carbon nanotubes has been explored recently with many techniques.^{1–13,15} The varied motivations for this effort include interest in both basic scientific questions (e.g., novel phases of matter) and possible applications (gas storage, separation, and sensing). Most of the theoretical and simulation research has assumed that the nanotubes are neither deformed nor displaced by the adsorbate. Such assumptions are convenient and might appear to be well justified by the small interaction between the gas and tubes relative to the large cohesive energy of the tubes. However, our recent studies^{13,15} found that the behavior of He, Ne, and H₂ gases within interstitial channels (IC's) contradicts that assumption. In particular, the ground state of the system corresponds to a slight expansion of the lattice of nanotubes in order to accommodate the gas (which is a moderately high density fluid at zero line pressure). The resulting expanded lattice provides a much larger binding energy for the particles because the interstitial potential of the gas is extremely sensitive to the tubes' separation. For example, in the case of H₂, the binding energy per molecule doubles when a 1% increase of lattice constant occurs.¹⁶ While the exact numbers found in that calculation are sensitive to the details of the potential, which is only approximately known, a large effect of dilation is expected to be present for all such potentials that have been proposed to describe these particles within IC's. The reason is that the particles experience strong forces in this environment, implying strong reaction forces acting on the neighboring tubes. Such a dilation will effect the energetics, structure, and dynamics of interstitial hydrogen.¹⁴

One interesting concomitant of this dilation was suggested in the previous study. The fact that the binding energy per molecule, $|E_N|/N$, of many molecules in a dilated lattice is much greater than that of a single molecule in an undilated lattice, $|E_1^0|$, suggests that there exists a strongly attractive, effective interparticle attraction, mediated by the lattice. Here, the superscript 0 refers to the value in the absence of any dilation. If true, this “mediation hypothesis” implies that the molecules will condense to form an anisotropic liquid at and below a high critical temperature T_c , an estimate of

which is provided by the increase in binding energy due to the dilation: $(|E_N| - |E_N^0|)/N \approx 300$ K for H₂. An analogy occurs in the BCS model of superconductivity, in which case the dynamical lattice deformation (phonons) mediates an electron-electron attraction, which drives the transition. The mediation hypothesis hinges on the implicit assumption that the strong binding found for the many-particle system is not present in the analogous one-body problem (including dilation). The heuristic idea underlying the hypothesis is simple and plausible: a single particle cannot deform its environment significantly, so only small dilation occurs in its vicinity. If several particles aggregate in the IC, instead, they can share the benefit of the lattice deformation without much additional cost in lattice energy. Thus, the large increase in binding is a cooperative, many-body effect and a high value of T_c is expected.

The present paper is one contribution toward developing and testing this hypothesis. We compute the energy of a single H₂ molecule in the presence of a deformed environment. The procedure employs a Born-Oppenheimer type of approximation, fixing the environment with a given deformation and finding the hydrogen eigenenergy in that environment. This is also analogous to the small-polaron theory employed to treat electrons in alkali halide crystals.¹⁷ It may therefore be appropriate to term the entity consisting of the hydrogen molecule and its surrounding dilation a “dilaton.” The net energy (tube lattice energy + H₂ energy) is minimized with respect to possible deformations. We evaluate the ground-state energy of the dilaton by solving the Schrödinger equation in the presence of an anisotropic lattice distortion, centered on the mean position of the impurity. We obtain a result that is consistent with the mediation hypothesis: the binding energy of a single molecule in the deformed lattice, $|E_1|$, is only slightly greater than that in the undeformed lattice, $|E_1^0|$. This means that the enhanced binding of the large N system¹³ is necessarily a consequence of the effective interaction between two or more dilatons. Hence, the hypothetical transition should indeed exhibit a high critical temperature.

The organization of this paper is the following. In Sec. II, we describe the calculation of the elastic energy E_{latt} of the deformed nanotube lattice. We compute the potential energy

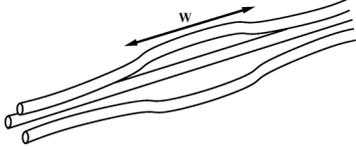


FIG. 1. Schematic depiction of the nanotube bulge. For clarity, neighboring tubes that surround the three tubes involved in the bulge are not shown in this figure (see Fig. 2).

V and the H_2 energy E_1 inside the channel in Sec. III. Then, we find the ground state of the system (lattice + molecule) by minimizing the total energy $E = E_{latt} + E_1$ with respect to possible lattice distortions. Section IV summarizes our results and comments on its implications for the N -body problem.

II. NANOTUBE BULGE ENERGY

Within a nanotube bundle, the interstitial channel between three parallel nanotubes will bulge beyond its equilibrium size to accommodate a molecule in the channel. Because of the rigidity of the tubes, the bulge will swell gradually along the channel axis and then contract again with some long length scale w (Fig. 1). The deformation will involve long wavelength acoustic modes of the nanotubes; it is energetically prohibitive for the unit cells of the tubes to undergo short wavelength, optical deformations. It is therefore appropriate to model the nanotube unit cells as rigid cylinders of length $c = 2.5 \text{ \AA}$, so that each nanotube consists of a chain of cylinders secured end to end by spring forces.¹⁸ The forces within each chain of cylinders, as well as the forces between chains, can be obtained from the Born–von Karman force constants of Ref. 18, provided that nanotubes are assumed to be of the (10,10) variety.

Our ansatz for the shape of the bulge assumes that the three central nanotubes get pushed symmetrically outward a distance $d(z)$ by the molecule (Fig. 2). We adopt a Lorentzian form to describe the magnitude of the displacement away from equilibrium,

$$d(z) = \frac{h}{1 + (z/w)^2}. \quad (1)$$

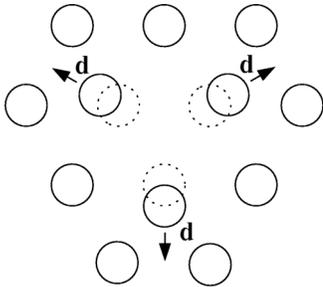


FIG. 2. Transverse view (at a given z) of the deformed IC when the tubes have been pushed a distance $d(z)$ from their equilibrium positions.

Here, h gives the maximum outward displacement of a unit cell while w characterizes the extension of the bulge along the channel axis.

An internal energy $E_{internal}$ is required for the tubes to bend, which is determined by the frequency of transverse acoustic modes v_{TA}/c . Within the model of Ref. 18 adopted here, it has the value

$$E_{internal} = 3 \sum_{l=-\infty}^{\infty} \frac{1}{2} M \frac{v_{TA}^2}{c^2} [d(l+1) - d(l)]^2. \quad (2)$$

Here, $v_{TA} \approx 2 \times 10^6 \text{ cm/s}$ is the velocity of the transverse acoustic modes that cause a tube to flex like a snake, while $M = 8 \times 10^{-22} \text{ g}$ is the mass of one nanotube unit cell, which contains 40 atoms.¹⁸ An intertube energy E_3 arises as the three tubes forming the channel spread apart. Since they are members of a nanotube rope, the three tubes will push on nine neighboring tubes, contributing an additional intertube energy E_9 , while the neighboring nine tubes themselves are assumed to remain in place. Utilizing the Lorentzian form (1) in the energy function of Ref. 18, one computes the deformation energy of the tubes as a function of the channel bulge shape,

$$E_{latt}(h, w) = E_{internal} + E_3 + E_9. \quad (3)$$

III. HYDROGEN DILATON ENERGY

As in most studies of hydrogen near nanotubes, we ignore the internal degrees of freedom of the molecule and focus on the motion of its center of mass. This assumption has been examined in a recent study in our group,¹⁹ which found a substantial barrier to rotation, a conclusion consistent with one experiment, but not another.^{20,21} If the anisotropy is indeed large, the energetic motivation for dilation will be increased in both the single molecule and the many-molecule calculations of dilation. We do not expect, however, any change in the qualitative conclusions concerning the key output of this paper: the difference between the undilated and dilated energies.

We compute the ground-state energy $E_1(h, w)$ of the molecule in the deformed channel $E_1(h, w)$ by solving the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(r, z) \right] \psi(r, z) = E_1 \psi(r, z) \quad (4)$$

using the diffusion method. Here, $V(r, z)$ is the potential energy due to the deformed tubes. Since the deformation of the tubes is expected to vary over a long distance, we evaluate the potential using a local approximation (confirmed *a posteriori*) in which the potential is that of a uniform system having the local value of the function $d(z)$: $V(r, z) \equiv U_{d(z)}(r)$, where r is the radial distance from the center of the channel. The potential energy $U_{d(z)}(r)$ is obtained by summing the contribution from the three tubes surrounding the channel and according to the nanotube potential model described in Ref. 9. It is important to note that we are using the same potential we considered in Ref. 13 for describing the uniform dilation so that our results can be compared in a

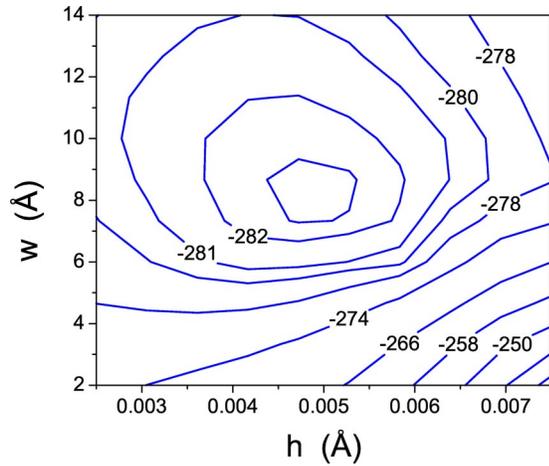


FIG. 3. (Color online) Ground-state energy $E_{latt} + E_1$ (in K) as a function of the deformation parameters h and w . A minimum $E = -282.5$ K occurs for $w = 8$ Å and $h = 0.005$ Å.

meaningful way. Semiempirical model potentials like this one have been used extensively in the literature of physical adsorption, in nanotubes, and in other surfaces (see, for example, Refs. 1, 5, and 7), and they can be relied upon to produce reasonable qualitative results. In this way, we obtain the total energy as

$$E(h, w) = E_{latt}(h, w) + E_1(h, w). \quad (5)$$

The ground state of the system is obtained by minimizing this expression with respect to the deformation parameters h and w . Figure 3 shows the function $E(h, w)$ and the presence of a minimum $E_{min} = -282.5$ K at $h = 0.005$ Å and $w = 8$ Å. This represents a binding energy increase of 1 K with respect to the case of non-deformed tubes. The deformation is extremely small in the transverse direction ($h/a \approx 0.0003$, where $a = 17$ Å is the unperturbed lattice constant) and it extends over a much larger distance (≈ 16 Å) along the axis of the channel. This value of h/a is much smaller than that found for the ground state in the uniformly dilated case (w going to ∞) of many molecules¹³: $h/a \approx 0.0056$.

The probability density $|\psi|^2$ and the external potential V for the minimum energy configuration are plotted in Fig. 4. The molecule's localization in the transverse direction is very similar to that found in the undiluted case, with a root-mean-square transverse displacement $\sqrt{\langle r^2 \rangle} \approx 0.2$ Å. The localization in the direction parallel to the axis has a much larger spread of the wave function, $\sqrt{\langle z^2 \rangle} \approx 1.6$ Å. Note that the longitudinal spread of the wave function is much smaller than the spread of the deformation that is responsible for the localization. This is evident in Fig. 4: the equipotential lines in Fig. 4(a) show more anisotropy than the constant probability lines of Fig. 4(b). The line shapes are consistent with a simple model calculation in which one assumes an anisotropic harmonic oscillator potential with radial and axial frequencies in the ratio $\omega_r/\omega_z = 150$.

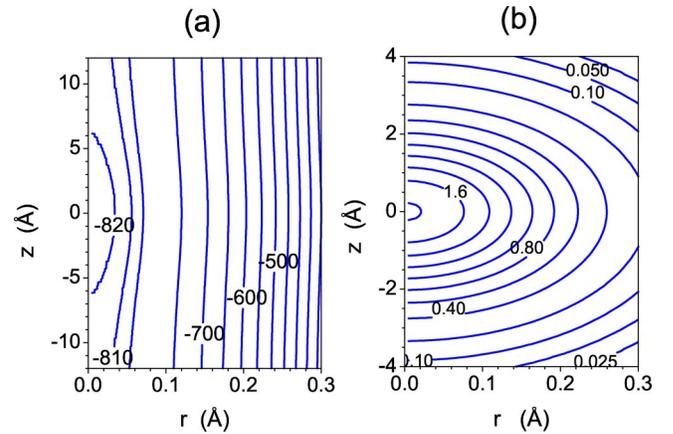


FIG. 4. (Color online) Dilation properties for the lowest energy case. (a) External potential energy (in K) due to the deformed tubes as a function of the radial distance r and the distance z along the axis of the channel. From left to right, the first three isopotential contours correspond to -820 K, -810 K, and -800 K, followed by contours of increasing energy every 50 K. (b) Probability density (normalized in units of Å^{-3}) of a hydrogen molecule for the same case as (a). From 1.8 Å^{-3} to 0.2 Å^{-3} , the contours are 0.2 Å^{-3} apart. Note the differing scales on the ordinates of the two parts.

IV. SUMMARY

We have investigated the ground-state properties of the hydrogen dilaton, consisting of a localized molecular wave function plus the accompanying lattice deformation. As assumed from the start, the rigidity of the tubes implies that the longitudinal extent of the deformation is large compared to the other length scales in the problem. The ground-state energy obtained by minimizing the total energy is just 1 K below the ground-state energy of a molecule interacting with the rigid nanotube lattice; this value is the net result of a 10 K increase in lattice energy and an 11 K decrease in energy of the molecule due to the deformation. While the exact values of these energies are sensitive to the assumptions in the potential-energy calculation, their small magnitude (compared to the binding energy of the many-body system) should be a robust conclusion of our study. This leaves open the question posed in the Introduction: how does one account for the huge cohesive energy found in our previous study of the many-body system?

That large cohesive energy (about 200 K) is necessarily a consequence of interdilaton couplings: two body, three body, etc. One may speculate, for example, about whether a dilaton dimer, consisting of two molecules plus their deformation, has a much lower energy than two isolated dilatons. This might well be the case because a second molecule can exploit the rather extended deformation we have found for a single molecule. This argument would imply that the binding energy of the dimer is at least 10 K because the dimer need not produce a deformation that is longer than that shown in Fig. 4 for one molecule.

We intend in future work to explore this dimer problem by a technique similar to that used here, which is essentially

a variational, strong-coupling method. If we find greatly enhanced cohesion in that problem, it will imply that the two-dilaton interaction is strongly attractive, with a resulting high-temperature critical transition. In addition, the future work directed toward understanding the problem of an anisotropic liquid phase will have to determine the interaction effects of two atoms' lattice deformations when the atoms reside in different IC's.

ACKNOWLEDGMENTS

We are grateful to William Saam and Gerry Mahan for many helpful discussions. A.M. acknowledges support under the NSF NIRT Program Grant No. DMR-0103068 as well as support by the Packard Foundation. M.M.C and M.W.C. acknowledge support from the NSF Grant Nos. DMR-0208520 and NIRT-0303916.

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