

## Dilation-Induced Phases of Gases Absorbed within a Bundle of Carbon Nanotubes

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A study is presented of the effects of gas (especially H<sub>2</sub>) absorption within the interstitial channels of a bundle of carbon nanotubes. The ground state of the system is determined by minimizing the total energy, which includes the molecules' interaction with the tubes, the intertube interaction, and the molecules' mutual interaction (which is screened by the tubes). The consequences of swelling include a reduced threshold pressure for gas uptake and a 2.7% increase in the tubes' breathing mode frequency.

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Considerable attention has focused in recent years on the absorption of H<sub>2</sub> (and other gases) in various forms of carbon, especially high surface area materials, because of the potential such materials present for efficient storage, isotope separation, and other applications. Numerous techniques of interfacial science are being applied to study the remarkable properties of this system. In the case of carbon nanotubes (NT), the unusual geometry presents the possibility of novel phase transitions. Theoretical work has explored a variety of transitions and proposed ways to observe them experimentally [1–3].

In this paper we propose such an unusual transition for hydrogen and other gases, associated with the dilation of a lattice of nanotubes. The most striking feature of a single nanotube is its quasi-one dimensional (1D) character, which makes contact with a growing body of 1D theory. This geometry stimulated Gordillo, Boronat, and Casulleras [2] to study a system of H<sub>2</sub> molecules in 1D and quasi-1D [in which case the molecules' small amplitude motion perpendicular to the tube's axial ( $z$ ) direction was taken into account]. They found density-dependent transitions at temperature  $T = 0$  to a liquid phase and then to a novel 1D solid phase. These results are qualitatively similar to those found by Boninsegni and co-workers [1,4] for <sup>4</sup>He in both 1D and within an ordered lattice (bundle) of parallel NTs. If we consider such a bundle, then the interactions between molecules in adjacent interstitial channels (IC) allow a fully 3D transition to occur. However, the large spacing ( $\sim 10$  Å) between adjacent channels means that the inter-IC interaction is weak and the predicted ordering temperature  $T_c$  is somewhat lower than the energy scale set by the well depth  $\varepsilon$  of the pair potential [1]. The transition is one to a very anisotropic liquid (in the case when the molecules are assumed to move freely along the channels) or crystal, depending on the system [5].

Two new aspects of the absorption problem alter this situation both qualitatively and quantitatively. One is that a study of three-body interactions found [6] that an effect of the NTs' dynamic polarization is to significantly screen the interaction between molecules, with drastic consequences [7]. If one includes only intra-IC interactions, the 1D H<sub>2</sub> ground state in this environment is a very low density gas

instead of the high density, strongly self-bound liquid mentioned above. However, inclusion of the inter-IC interactions does yield a weakly bound condensed state [7]. The other new ingredient in this problem is the possibility that adsorbed gases cause the bundle of NTs to swell [8,9]. In this paper, we consider the problem of such a dilation of the lattice of NTs. We report four predictions associated with this dilation: a greatly increased binding of the hydrogen, a significantly higher critical temperature for the condensed state, a measurably larger lattice constant of the NT array, and a higher breathing mode frequency for the tubes. Several other consequences merit future study. Especially interesting is the effect of this dilation on the electrical transport properties of the NTs, which have been found to be significantly altered by adsorption [10,11]. While we focus on the case of H<sub>2</sub>, we have found and summarize below qualitatively similar conclusions for the adsorption of He, Ne, Ar, and CH<sub>4</sub>. The unifying concept is that lattice dilation permits small molecules to increase their IC binding energy significantly without a substantial increase in the intertube interaction energy.

The logic of our calculation is the following. Consider an infinite array of NT's, each of which has radius  $R$  and a large length  $L$ , and whose parallel axes intersect an orthogonal plane to form a triangular lattice of spacing  $d_0 = 17$  Å at  $T = 0$ ; we are ultimately interested in the thermodynamic limit of infinite  $L$ . We assume that between the tubes, within the IC's, there exists a 1D density  $\rho$  of H<sub>2</sub> molecules, so that on average there are  $N = \rho L$  molecules per channel [12]. We then minimize the total energy of the system by allowing the lattice to dilate to a separation  $d$ . Such a resulting situation turns out to be stable only if  $\rho$  exceeds a threshold density,  $\rho_c$ . This threshold density and attendant dilated lattice represent the ground state of the system. The finding that any density lower than  $\rho_c$  is impossible is analogous to the familiar absence of a stable, uniform low density regime for conventional systems in free space at  $T = 0$ , i.e., the ground state of all 3D systems is a condensed liquid or solid. As in the latter case, at finite  $T$  a low density gas phase does exist within the NT bundle, as does a regime of coexistence between this dilute gas and the dense liquid.

The calculations themselves are straightforward, thanks to several simplifying assumptions which should not greatly affect the major conclusions; these include the neglect of any  $z$  dependence in the potential experienced by the  $H_2$  molecules. The total energy of the system, per unit length, per IC, indicated by  $\varepsilon$ , is written in terms of the single molecule's energy per particle ( $\varepsilon_1$ ), of the  $H_2$ - $H_2$  interaction energy per particle ( $\varepsilon_{\text{int}}$ ), and of the elastic energy per unit length representing the interaction between pairs of adjacent NTs as

$$\varepsilon \equiv E/L = \rho[\varepsilon_1(d) + \varepsilon_{\text{int}}(\rho, d)] + \frac{3}{4}k(d - d_0)^2. \quad (1)$$

The coefficient  $k = 1740 \text{ K } \text{\AA}^{-3}$  is derived from the semiempirical NT interaction constant of Mizel *et al.* [13]. This value is consistent with the experimental value of the interlayer force constant and interaction energy of graphite. The function  $\varepsilon_{\text{int}}(\rho, d)$  is our variational upper bound to the ground state energy per particle of fully interacting  $H_2$ , computed with the screened interaction. This quantity is the sum of the "exact" ground state energy of 1D  $H_2$  (computed by Boronat and Gordillo [14], using the diffusion Monte Carlo method and an assumed isotropic interhydrogen interaction) and the small interchannel interaction, computed in the Hartree approximation. Finally,  $\varepsilon_1(d)$  is the ground state energy per  $H_2$  molecule subjected to the potential energy within an IC of a bundle of tubes which are spaced a distance  $d$  apart. We deduce this potential energy from the model of Stan and co-workers [15] and solve the Schrödinger equation using the diffusion method in order to obtain  $\varepsilon_1(d)$ .

Figure 1 shows the potential energy and wave function for the cases  $d = d_0 = 17 \text{ \AA}$  and a slightly larger value,  $d = 17.18 \text{ \AA}$ . A key difference between these two cases is that the ground state of the dilated lattice has a much lower value of  $\varepsilon_1(d)$ . The reasons for this decrease are the lower potential energy and zero-point energy (ZPE) associated with the increased distance of the  $H_2$  molecules from their neighboring NT's. This decrease in  $\varepsilon_1$  (equivalently, the quantum pressure, which in  $H_2$  is near 100 atm at threshold) is what drives the NT's apart [16]. Figure 2 shows the chemical potential ( $\mu = \frac{\partial E}{\partial N} = \frac{\partial \varepsilon}{\partial \rho}$ ) of the hydrogen as a function of  $\rho$ , taking into account the lattice dilation. Also shown is the analogous result in the case of an undiluted lattice: The curve exhibits an extremely shallow minimum near  $\rho = 0.1 \text{ \AA}^{-1}$ , which is not discernible in the figure; the binding energy in that case is  $\sim 0.1 \text{ K}$  [7]. In the present case of dilation, the chemical potential is seen to decrease rapidly with increasing  $\rho$  because the expanding lattice becomes progressively more attractive, as seen in Fig. 1; the eigenvalue of this potential has a minimum at lattice constant  $17.55 \text{ \AA}$ , corresponding to a very large density. However, the mutual  $H_2$  repulsion at such high density is huge. The ground state energy of the system is obtained by minimizing the grand potential,

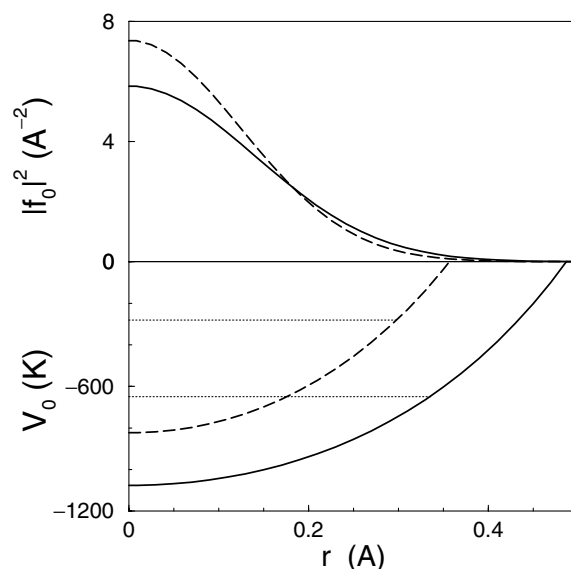


FIG. 1. Azimuthally averaged potential energy and ground state eigenvalue (bottom panel) and probability density (top panel) of  $H_2$  as a function of perpendicular distance from the center of the interstitial channel. Dashed curves correspond to the undiluted NT lattice and full curves correspond to the lattice dilated by 1% (the predicted ground state of the system).

$\omega = \varepsilon - \mu\rho$ . This is equivalent to a Maxwell construction in the chemical potential-density plane, as seen in the figure. It corresponds equivalently to setting the 1D pressure of the  $H_2$  equal to the stress of the tubes, associated with the change of their total interaction energy with respect to density. The resulting values of the ground state density, lattice constant, and chemical potential,  $\rho_c$ ,  $d_c$ , and  $\mu_c$ , are reported in Table I. Note that the chemical potential at this threshold is about 200 K lower than the

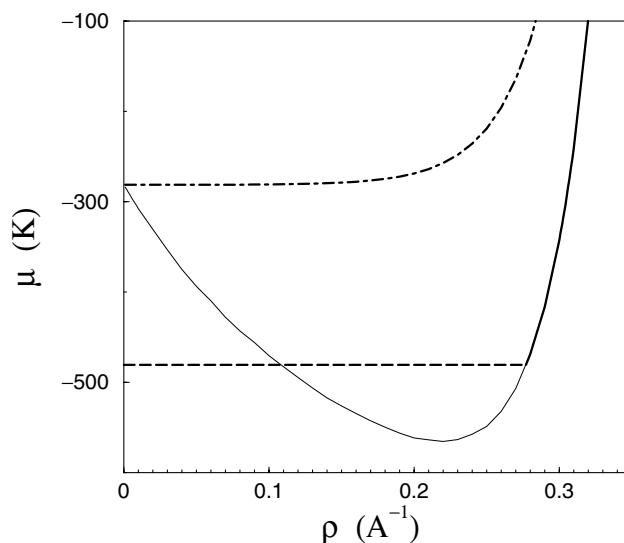


FIG. 2. Chemical potential as a function of the 1D density  $\rho$  of  $H_2$  (full curve). The horizontal line exhibits the equilibrium (two-phase) behavior obtained from Maxwell construction which determines the uptake threshold density  $\rho_c$ . Dash-dotted curve is the hypothetical result in the absence of dilation.

TABLE I. Density, NT lattice constant, and chemical potential at threshold for gas uptake. Also shown is the value of the chemical potential in the absence of dilation  $\mu_{\text{ndil}}$ .

	$^4\text{He}$	Ne	$\text{H}_2$	$\text{D}_2$	Ar	$\text{CH}_4$
$\rho_c$ ( $\text{\AA}^{-1}$ )	0.215	0.327	0.277	0.275	0.273	0.270
$d_c$ ( $\text{\AA}$ )	17.024	17.069	17.166	17.154	17.330	17.373
$\mu_c$ (K)	-380.7	-927.5	-480.7	-621.4	-1270	-1290
$\mu_{\text{ndil}}$ (K)	-378.0	-895.6	-281.5	-446.9	227.6	787.1

value  $-281.5$  K found in the absence of dilation. This is a measure of the greater incentive to absorb within this environment than within an undiluted NT bundle. Such a dramatic result should be testable by thermodynamic measurements, either adsorption isotherms or direct measurements of the heat of adsorption. We note that the computed value of  $\mu_c$  is higher than the corresponding threshold, near  $\sim -600$  K, for absorption within the tubes (which is relevant only if the tubes are open) or in the grooves formed on the external surface of the bundle. The difference is a consequence of the much lower zero-point energy in these sites than in the IC's. Figure 3 shows the various contributions to the total energy per particle as a function of  $\rho$ .

Figure 4 presents our predictions for the dependence of  $d$  on  $\mu$  for various gases. The isotope dependence arises because the smaller mass of  $\text{H}_2$  implies a larger ZPE. Hence, in the  $\text{D}_2$  case the lattice is dilated less and the threshold values of  $\rho$  and the chemical potential are both lower than in the  $\text{H}_2$  case [17]. Note that the swelling is predicted to be an  $\sim 1\%$  change in the value of  $d$  at the threshold for gas uptake. This is measurable by x-ray diffraction from the NT lattice [18]. Table I reports results of the effects of dilation on various gases.

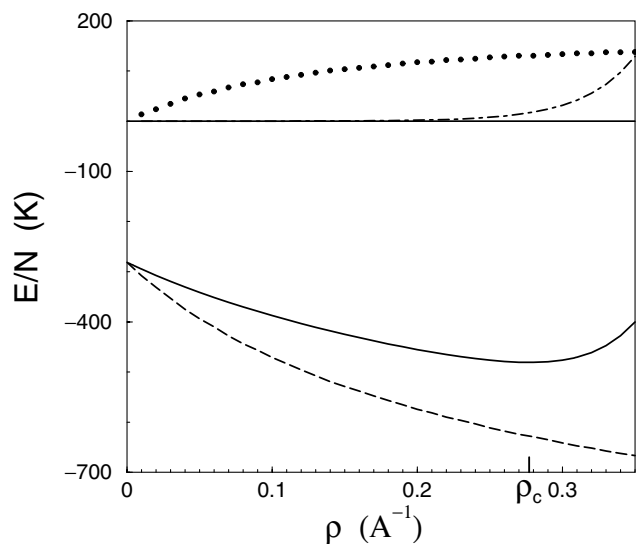


FIG. 3. Energies as a function of the 1D density  $\rho$  of  $\text{H}_2$ . Filled circle is the NT-NT elastic interaction energy, dash-dotted curve is the  $\text{H}_2$ - $\text{H}_2$  interaction energy per molecule and dashed curve represents the  $\text{H}_2$  molecule's eigenvalue in the dilated lattice. Full curve is the sum of the above contributions. Notice that its minimum occurs at  $\rho_c$ .

Two of these, He and Ne, fit nearly perfectly in the undiluted lattice; hence the dilation  $d$  is less than  $0.5\%$  and the increase in binding is small ( $\sim 3\%$  for Ne). For  $\text{H}_2$ , Ar, and  $\text{CH}_4$ , the energetic consequence of the dilation is significant. One factor to bear in mind is the sensitivity of these results to the potential parameters. As examples, in the case of both  $\text{H}_2$  and  $\text{CH}_4$ , a  $2.5\%$  decrease in the gas-carbon length parameter ( $\sigma_{GC}$ ) results in about a  $25\%$  increase in the magnitude of  $\mu_c$ . In contrast, the dependence on the gas-carbon energy parameter ( $\epsilon_{GC}$ ) is much weaker: a  $2.5\%$  increase in it yields a  $6\%$  increase in the magnitude of  $\mu_c$ . An additional source of uncertainty is that we have ignored band structure effects due to the potential's corrugation, but these should yield energy corrections no more than the band width, a  $5\%$  effect [1].

The nanotubes should exhibit other consequences of the  $\text{H}_2$  confinement. One, possibly surprising, finding is a significant shift in the breathing mode frequency of the tubes. To evaluate this, we consider the degree of freedom corresponding to the variation in radius of the tubes,  $R$ . "Breathing" corresponds to a uniform radial expansion and contraction of a tube. We evaluate the shift by adding an extra term  $\delta\epsilon(R) = \frac{1}{2}\gamma(R - R_0)^2$  to the previous expression for the total energy per unit length, Eq. (1). Here  $R_0$  is the equilibrium radius in the absence of the  $\text{H}_2$  and

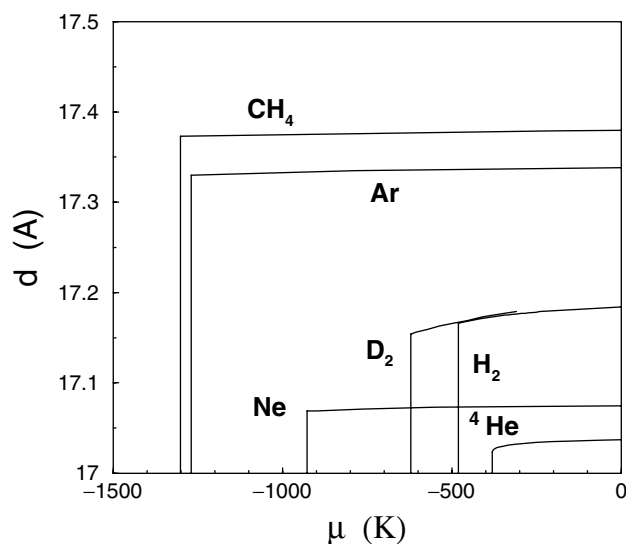


FIG. 4. Lattice constant of the NT array as a function of chemical potential for several gases. The discontinuities occur at the respective  $T = 0$  thresholds for gas uptake.

$\gamma = 2.5 \times 10^5 \text{ K } \text{\AA}^{-3}$  is the force constant derived from the breathing mode frequency of the unperturbed lattice [19]. Such a change in  $R$  yields a change in potential energy experienced by the  $\text{H}_2$  molecules, which we compute from the formulation of Stan *et al.* [15]. As expected by analogy with the dilation problem, there ensues a small decrease in the tube radius (of order  $0.01 \text{ \AA}$ ). Much more dramatic is the effect on the breathing frequency, which can be evaluated by computing the second derivative of the total energy with respect to  $R$ . Our calculations yield a 2.7% increase in the breathing frequency at the threshold ( $\rho = \rho_c$ ) for  $\text{H}_2$  uptake at  $T = 0$  [20]. This should be easily measured spectroscopically [19]. The magnitude of the shift is a manifestation of the sensitivity of the  $\text{H}_2$  potential to the positions of the nearby carbon atoms; it is comparable to the shift of this frequency due to tube-tube interactions.

We may also make some predictions concerning the finite temperature phase diagram of this unusual system. Below a critical temperature  $T_c$  there occurs a region of two-phase coexistence, between a low density quasi-1D “vapor” phase, in a nearly unswollen NT environment, and a high density phase in swollen ICs. At very low  $T$ , this latter phase is essentially the ground state fluid, with a negligible thermal excitation so its chemical potential satisfies  $\mu(\rho_c, T) \simeq \mu(\rho_c, 0)$ . The vapor density at coexistence may be determined by equating the chemical potentials, a procedure which is particularly simple at very low  $T$ . Since this vapor phase is dilute, its chemical potential is well approximated by the 1D ideal gas relation  $\mu = k_B T \ln \rho \lambda + \epsilon_1(d)$  where  $\lambda$  is the de Broglie wavelength of the molecules. By equating these we determine the curve:  $\rho_v \lambda = e^{\beta\{\mu[\rho_c(0)] - \epsilon_1(d_0)\}}$  describing coexistence of the low density phase and the high density phase. At temperatures above a critical value  $T_c$ ,  $\mu(\rho)$  will no longer exhibit a minimum and only one phase will be possible.

Lacking a better theory, we estimate  $T_c$  by mapping our system to an Ising system with weak long range forces with Hamiltonian  $H = -\frac{1}{2} \frac{J}{N} \sum_{i,j} \sigma_i \sigma_j$ , for which the mean field approximation is exact and provides a critical temperature:  $T_c = J/k_B$ . The mapping is easily found by identifying  $J/N$  with the effective NT-mediated  $\text{H}_2$ - $\text{H}_2$  interaction energy per particle:  $v_{\text{eff}} = 2[\epsilon - \epsilon_1(d_0)]$ . For  $^4\text{He}$ ,  $\text{Ne}$ ,  $\text{H}_2$ , and  $\text{D}_2$  we find, respectively,  $T_c = 5.4, 63.8, 398.4$ , and  $698 \text{ K}$ .

To summarize, we have proposed that lattice dilation plays an important role in gas uptake. Because the stimulus to this dilation is the resulting increase in adsorbate binding energy, the expansion is very sensitive to the gas-tube interactions. The intertube and intermolecular interactions also play an important role in determining the uptake threshold condition. We have used plausible, but uncertain, semiempirical models for these interactions. Experimental investigation (thermodynamic, diffraction, and Raman

scattering) will shed light on these assumptions. The existence and nature of this dilation phenomenon and accompanying transition are robust conclusions, evidently not dependent on the approximations used in the interactions.

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