Density and Thermodynamics of Hydrogen Adsorbed Inside Narrow Carbon Nanotubes

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Abstract—A model is proposed for calculating the thermodynamic functions and the equilibrium density of a one-dimensional chain of molecules (atoms) adsorbed inside a narrow nanotube. The model considers both the interaction between introduced atoms (molecules) and their interaction with the nanotube walls. The quantum-mechanical effects resulting in discrete energy levels of a particle and in its smeared position between neighbors are taken into account. In calculating the free energy at a nonzero temperature, the phonon contribution and the particle transitions to excited levels are considered. The model is applied to calculate the thermodynamic parameters of adsorbed hydrogen molecules inside extremely narrow single-wall carbon nanotubes of the (3,3) and (6,0) type. It is shown that external pressure gives rise to a sequence of first-order phase transitions, which change the density of adsorbed hydrogen molecules. © 2004 MAIK "Nauka/Interperiodica".

1. INTRODUCTION

The experimental detection of carbon nanotubes in 1991 [1] has offered new opportunities for both technology and fundamental physics. The nanometer scale and one-dimensionality inherent to such structures have led to discoveries of interesting mechanical, chemical, and electrical properties in them [2]. One of the remarkable properties of carbon nanotubes (CNTs) is their ability to adsorb various atoms or molecules. The huge specific area of the CNT surface (as large as several hundred square meters per gram) allows adsorption of large amounts of inert gases, hydrogen, metals, water, etc. For example, it was experimentally shown in [3] that CNTs can absorb more than 3.5 wt % of hydrogen, which makes them promising hydrogen accumulators. It was also shown in [3] that this application of CNT can be economically advantageous in the motor industry even in the case of a hydrogen content of $\cong 6.5\%$.

One-dimensional chain systems in which particles cannot jump over one another (single-file systems) have been studied in a large number of papers [4–6]. Recently, such systems with an extremely small channel diameter (4–5 Å) have been successfully produced by annealing zeolite $AlPO_4$–5 whose channels contained hydrocarbons [7, 8]. A quantum theory of molecular separation was developed in [9, 10]. This theory predicts that isotopes (especially those of hydrogen) can be efficiently separated inside extremely narrow channels at low temperatures, because isotopes differ in the quantized energy levels of their transverse motion.

In other theoretical papers, dedicated to the diffusion of particles during their longitudinal motion in these systems, it was shown that diffusion is characterized by extraordinary properties under these conditions. For example, the mean square of particle displacements $\langle z^2 \rangle$ is proportional to the square root of the observation time $t^{1/2}$ rather than to the time t, as is usually the case. This extraordinary property was convincingly proved experimentally in [11]. Theoretical analysis of chain systems is significantly complicated by the fact that the positions of adsorbed particles strictly correlate with the positions of all other particles in the system. For this reason, analytical results are scarce or are obtained using various approximations. The conventional approximate techniques applied in such studies are the Monte Carlo methods [diffusion Monte Carlo (DMC) or canonical methods], the one-dimensional lattice gas model, and the molecular-dynamics (MD) method. The DMC method [12] allows one to perform quantum-mechanical calculations of the thermodynamic parameters, correlation functions, and the equilibrium particle density in terms of the wave function of the system. However, since calculations are complicated, the temperature effects are usually ignored in the DMC method. The canonical Monte Carlo method [13] makes it possible to include the temperature effects. However, this method is based on the classical-mechanical dynamics equations and interparticle interaction potentials; hence, the quantum-mechanical effects are ignored. Furthermore, any Monte Carlo computation involves a large number (~10^6) of different configurations, which complicates such calculations. The lattice

gas model [6] is also based on classical interaction potentials and disregards the quantum-mechanical effects. Moreover, in this model, particles are positioned discretely at N equidistant sites separated by potential barriers of height E_b. In this case, the frequency of hopping to a neighboring site is calculated as $P = P_0 \exp(-E_b/k_B T)$, where the pre-exponential factor P_0 is dictated by the activation mechanism. Unfortunately, this model is statistical and ignores actual motion of adsorbate molecules inside the nanotube. Moreover, the parameter P_0 cannot be calculated within the model and is fitted. The molecular dynamics methods [14, 15] (both the non-empirical one and that based on empirical interaction potentials of atoms or molecules) allow calculations of the dynamics of atoms in terms of the forces acting on the atoms. A fundamental constraint of any MD calculation is the fact that atoms are assumed to obey the classical Newtonian equations of motion rather than the quantum-mechanical laws. This method disregards the zero-point oscillations of atoms, energy quantization, and tunneling effect. Therefore, any MD calculation cannot adequately predict even qualitative results for particle motion at a low temperature when the particle kinetic energy is lower than the potential barrier height, $E_{kin} < E_b$. We also note that certain recent studies partially include the quantum effects in the MD calculation scheme for simple systems [16, 17].

2. MODEL

This paper is devoted to a theoretical study of the equilibrium properties of a one-dimensional chain of atoms (molecules) interacting with one another via a pair potential $V(r)$ and with the tube walls via a potential $V_{tube}(r)$. The study is based on a model that allows calculation of the thermodynamic properties of such a system at various temperatures and includes the quantum effects. The interaction potentials are determined using *ab initio* calculations. The behavior of hydrogen molecules inside ultrathin single-wall carbon nanotubes of the (3,3) and (6,0) type [18] with a diameter of 4.07 and 4.70 Å, respectively, is studied. To verify the assumption of strictly one-dimensional motion of adsorbate molecules along the axis of each of these nanotubes, molecular-dynamic calculations are carried out for the hydrogen molecule dynamics inside the nanotubes at various temperatures. It is established that the maximum value of the angle α between the moving molecule and the nanotube axis is small ($\alpha \cong 5°$ for the (3,3) tube at $T = 200$ K); hence, the motion of adsorbed particles can be considered one-dimensional.

The model is based on the solution of the one-dimensional Schrödinger equation for a particle (hydrogen molecule) moving along the nanotube axis in the potential that is the sum of the potentials $V(r - R_r)$ and $V(r - R_l)$ produced by the right-hand and left-hand neighbors (identical molecules) of the particle, respec-

tively, and of the potential produced by the nanotube atoms:

$$\left(-\frac{\nabla^2}{2m} + V(r)\right)\Psi_i(r) = \varepsilon^i \Psi_i(r), \quad (1)$$

$$V(r) = V(r - R_l) + V(r - R_r) + V_{tube}(r), \quad (2)$$

where ε^i is the particle energy in state i. Both neighbors of the particle are assumed to be fixed. This case corresponds to the mean-field approximation, in which the positions of the neighbor particles inducing the potential are replaced with their averages. The position of the particle itself is described by the probability density $|\Psi_i(r)|^2$. In the case of $T \neq 0$, where the particle can transfer to the excited energy levels ε^i, the average energy of the particle is calculated using the Gibbs distribution

$$\langle U \rangle = \frac{1}{Z}\sum_i \varepsilon^i \exp\left(-\frac{\varepsilon^i}{k_B T}\right), \quad Z = \sum_i \exp\left(-\frac{\varepsilon^i}{k_B T}\right), \quad (3)$$

where Z is the partition function.

The interaction potential $V_{tube}(r)$ between the molecule and the nanotube walls is defined as the change ΔE_{tot} in the total energy of the system consisting of the nanotube and the hydrogen molecules at its axis (with a sufficiently large distance between hydrogen molecules to remove their interaction) as the molecule position along the tube axis is varied. The maximum values (in kelvins) of the potential $V_{tube}(r)$ for the (6,0) and (3,3) nanotubes are $V_{max} \cong 2300$ and 211 K, respectively. Such a significant difference is explained as follows. In the (6,0) nanotube, atoms on its sides are opposite to each other and their influences on the hydrogen molecule are in phase. In the (3,3) nanotube, atoms on opposite sides alternate and their influences on the hydrogen molecule are in antiphase, which decreases the potential $V_{tube}(r)$ amplitude by an order of magnitude. The period of the potential $V_{tube}(r)$ for the (6,0) tube is longer than that of the (3,3) tube by a factor of $\sqrt{3}$. Similarly, the interaction potential $V(r - R)$ between the hydrogen molecules is defined as the change in the total energy of the system (consisting of the nanotube and the hydrogen molecules at its axis) as the distance between the molecules is varied.

The total energy E_{tot} of the system is determined from *ab initio* calculations using the VASP software package [19, 20], based on an expansion in terms of plane waves and on the Vanderbilt pseudopotentials [21], within the density functional formalism. The use of the plane-wave basis is appropriate for studying periodic one-dimensional systems such as CNTs. The use of the Vanderbilt pseudopotentials allows one to significantly decrease the number of plane waves necessary for the calculation. In the calculations we carried out, the maximum kinetic energy E_{cut} defined by the carbon pseudopotential was 286 eV.
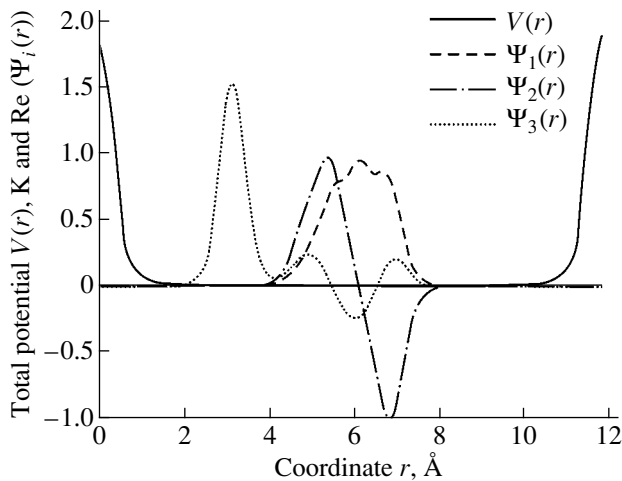
Fig. 1. Potential $V(r)$ (in kelvins) and the wave functions $\Psi_i(r)$ for the lowest states $i = \{1, 2, 3\}$ of an H_2 molecule in the (3,3) CNT.

Fig. 2. Same as in Fig. 1 but for the (6,0) CNT.

The Schrödinger equation for the adsorbate molecule was solved by expanding the wave function with respect to plane waves:

$$\Psi_i(r) = \sum_{\mathbf{G}} C_k^i \exp(i\mathbf{G}r). \qquad (4)$$

In the calculations, we used the reciprocal lattice vectors $\mathbf{G}$ with the maximum magnitude $G \leq G_{max} = 50$ (measured in units of $2\pi/a$, where $a = 2d$; d is the distance between the adsorbed particles).

Figures 1 and 2 show the total potentials acting on the hydrogen molecule inside the (3,3) and (6,0) nanotubes, respectively; the distance between the particles is equal to 6 Å. The potentials consist of two parts. One of them is defined by the interaction potential between the particle and its left-hand and right-hand neighbors (described by the steeply rising portions of the curve of the total potential near the ends). The other part is defined by the interaction potential between the particle and the nanotube atoms and is responsible for oscillations of the potential with a relatively small amplitude. Figures 1 and 2 also show the corresponding wave functions $\Psi_{1,2,3}(r)$ of the three lowest levels of the hydrogen molecule. We can see the difference in the molecule localization, which is due to the difference in the amplitude of the potential exerted on the particle by the nanotube atoms. Inside the (3,3) tube, this potential is weak and the particle is weakly localized and does not correlate with the positions of the minima of the potential. Inside the (6,0) nanotube, oscillations of the potential are ten times larger and the particle is mostly localized at the minima of the potential. These differences cause the average distances between hydrogen molecules inside the (6,0) tube to be more sensitive to external pressure than inside the (3,3) tube. External pressure causes molecules to jump from one local minimum to another.
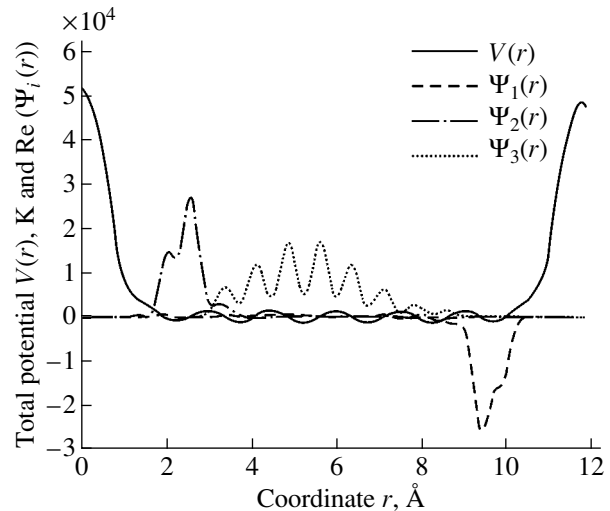
We studied the dependence of the equilibrium distance between particles on external parameters, namely, the pressure p and temperature T. The equilibrium of the system at $\{p, T\} \neq 0$ corresponds to a minimum of the Gibbs thermodynamic potential $\Phi = \langle U \rangle - TS + PV = G + PV$ (where G is the free energy, S is the entropy, P is the external pressure, V is the volume of the system). Therefore, in addition to the internal energy $\langle U \rangle$, we should take into account the contributions from the entropy S and the volume energy PV. In the free energy G (per adsorbate molecule), we included two contributions. One of them is the free energy G_1 related to the average energy $\langle \varepsilon \rangle$ of the particles (determined at fixed positions of both neighbor adsorbate molecules) and to the entropy S_1 of their distribution over the energy levels; the other contribution, G_{ph}, is associated with deviations of the neighbors from their equilibrium positions. These deviations cause a change in the energy levels of the central molecule and, hence, a change in the total energy of the system. This change, in turn, gives rise to a restoring force acting on the neighbor molecules and produces the contribution G_{ph} to the free energy associated with phonon vibrations (with frequencies ω_i) of the chain of adsorbed molecules. Thus, we have

$$G = G_1 + G_{ph}, \quad G_1 = \langle U \rangle - TS_1, \qquad (5)$$

$$S_1 = -k_B \sum_i P_i \ln P_i, \quad P_i = \frac{1}{Z} \exp\left(-\frac{\varepsilon^i}{k_B T}\right), \qquad (6)$$

$$G_{ph} = \langle U \rangle_{ph} - TS_{ph} \qquad (7)$$

$$= \sum_i \left[\frac{\hbar \omega_i}{2} + k_B T \ln\left(1 - \exp\left(-\frac{\hbar \omega_i}{k_B T}\right)\right) \right]. \qquad (8)$$

Since the adsorbed molecules in the model interact via pair potentials, half the particle potential energy $[(1/2)\langle U_{\text{pot}}\rangle = (1/2)\langle E - E_{\text{kin}}\rangle]$ should be subtracted from the total internal and free energies ($\langle U\rangle$, G_1) in order to avoid counting the pairs twice. The particle kinetic energy in state i is calculated as $E_{\text{kin}}^i = \langle \Psi_i^*(r)| -\dfrac{\nabla^2}{2m}|\Psi_i(r)\rangle$.

The phonon frequencies $\omega_i(r, T)$ are calculated from the dispersion relation for phonons in a one-dimensional chain of particles of mass m mutually spaced at a distance d and interacting via the forces characterized by elastic constants $f(r, T)$. The result is

$$\omega_i(r, T) = 2\left(\frac{f(r, T)}{m}\right)^{1/2}\left|\sin\left(\frac{1}{2}q_i d\right)\right|, \qquad (9)$$

$$f(r, T) = \frac{\partial^2 \langle U_{\text{pot}}\rangle(r, T)}{\partial r^2}. \qquad (10)$$

The elastic constants $f(d, T)$ are calculated for various temperatures, and the intermolecular distances d, by considering the displacement Δ of a particle positioned between two neighbors. The energy levels ε^i of the neighbors and, therefore, their average energies $\langle U(r \pm \Delta)\rangle$ and the total energy of the system vary in the second order with respect to Δ, giving rise to phonon vibrations. It should be noted that, although the model is based on the mean-field approximation, in which the positions of both neighbors of the particle are assumed to be fixed, the inclusion of the phonon contribution G_{ph} in the free energy partially eliminates the disadvantages of this approximation. In this case, perturbations in the positions of the neighboring particles with respect to their average positions are taken into account in the harmonic approximation.

The energy levels ε^i of a particle and, hence, the free energy per adsorbed particle depend on the phase r_{phase} of the periodic potential $V_{\text{tube}}(r - r_{\text{phase}})$ exerted on the particle by the nanotube atoms, $\varepsilon^i = \varepsilon^i(r_{\text{phase}})$. Therefore, we should perform Gibbs averaging of ε^i over various phases r_{phase}. Since the phases r_{phase} of the potential $V_{\text{tube}}(r - r_{\text{phase}})$ acting on neighboring particles are mutually correlated, this correlation should be correctly taken into account in the averaging. To this end, for each value of the average interparticle distance d, a cluster (chain of neighbors) of N particles is selected so that the phases of the potential $V_{\text{tube}}(r - r_{\text{phase}})$ acting on the first and last particles in the cluster are identical (the accuracy was 1/20 of the interatomic distance in the nanotube). Generally, this required setting approximately ten particles in the cluster. Then, positions i of interior particles in the cluster are varied to minimize
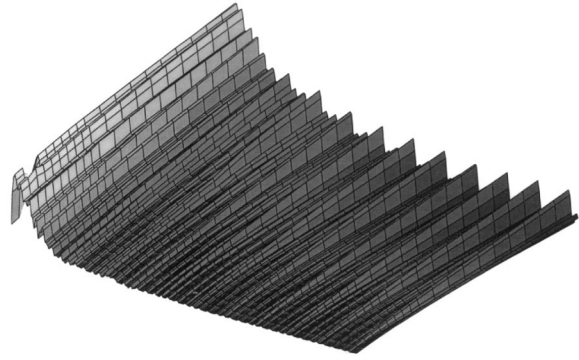

Fig. 3. Dependence of the average Gibbs free energy $\langle G(d, T)\rangle$ of a H_2 molecule on temperature T and interparticle distance d in the (3,3) CNT.
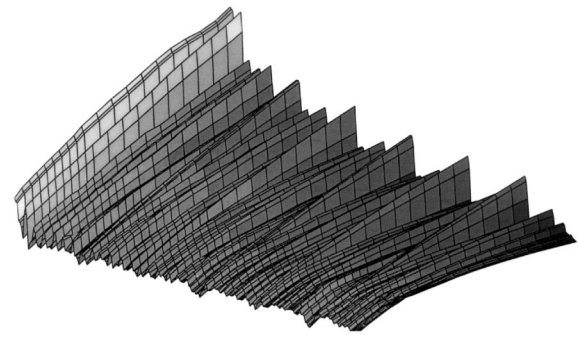

Fig. 4. Same as in Fig. 3 but for the (6,0) CNT.

the total free energy G_{cl} of the cluster and to calculate the average free energy of a particle:

$$\langle G(d, T)\rangle = 1/N\langle G_{\text{cl}}(T)\rangle, \qquad (11)$$

$$G_{\text{cl}}(T, r_{\text{phase}}) = \min_{r_{\text{phase}\,i}}\left\{\sum_{i=2}^{N-1} G_i(T, r_{\text{phase}\,i})\right\}, \qquad (12)$$

$$\langle G_{\text{cl}}(T)\rangle$$
$$= \frac{1}{\tilde{Z}}\sum_{r_{\text{phase}}} G_{\text{cl}}(T, r_{\text{phase}})\exp\left(-\frac{G_{\text{cl}}(T, r_{\text{phase}})}{k_B T}\right), \qquad (13)$$

$$\tilde{Z} = \sum_{r_{\text{phase}}}\exp\left(-\frac{G_{\text{cl}}(T, r_{\text{phase}})}{k_B T}\right). \qquad (14)$$

These energies $\langle G(d, T)\rangle$ for hydrogen molecules inside both nanotubes are shown in Figs. 3 and 4. We note that the contribution of phonons to the free energy vanishes at certain interparticle distances l for which the force constants $f(l, T)$ are negative, which gives rise to the free-energy oscillations in Figs. 3 and 4.

By calculating the internal and free energies of particles and the Gibbs thermodynamic potential $\Phi = \Phi(P, T)$ at various temperatures and average intermolecular
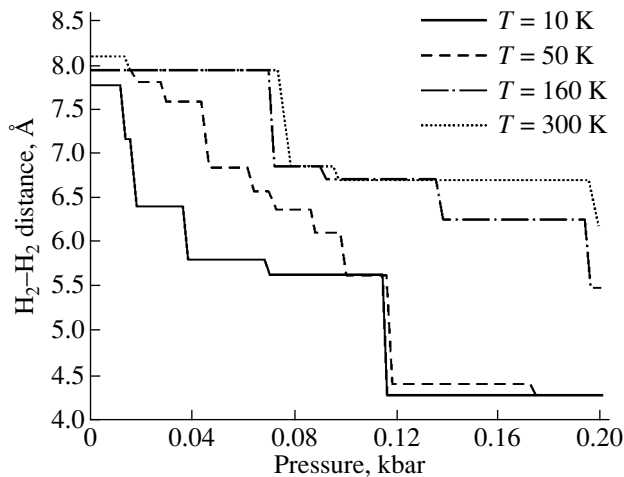
Fig. 5. Dependence of the equilibrium intermolecular H_2–H_2 distance $\langle d(P, T)\rangle$ in the (3,3) CNT on temperature T and external pressure P.
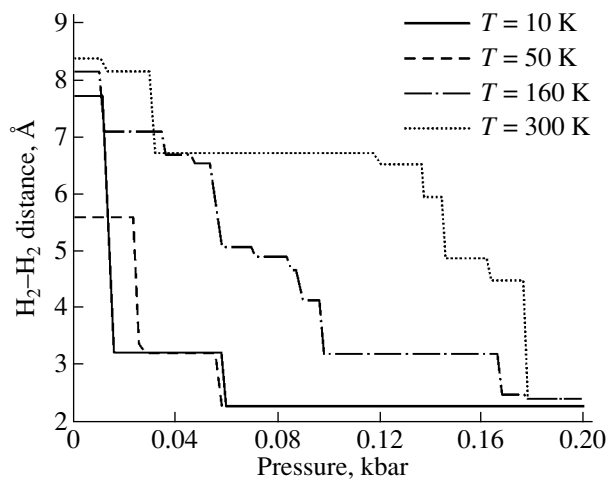

Fig. 6. Same as in Fig. 5 but for the (6,0) CNT.

distances d and by minimizing $\Phi(P, T)$ at each value of external pressure P, we found the equilibrium intermolecular distances $\langle d\rangle = \langle d(P, T)\rangle$ for both nanotubes (Figs. 5, 6). We can see that the density of adsorbed hydrogen molecules undergoes a series of phase transitions at all temperatures (not exceeding the upper limit $T_{max} = 300$ K of the temperature range covered in this study) as the external pressure increases (up to 0.2 kbar). The transitions are caused by the fact that, as the pressure increases, the hydrogen molecules begin to jump from deeper to less deep minima, since the change $\Delta(PV)$ in the contribution from the volume energy to Φ in this case becomes larger than the change in the free energy in the local minima. We can see from Figs. 3 and 4 that the number of local minima in the (6,0) nanotube is larger than that in the (3,3) tube. A particle jumps into these minima as the external pressure increases, which results in a larger compressibility

of hydrogen inside the (6,0) nanotube in comparison with that for the (3,3) nanotube.

These results qualitatively agree with the experimental data from [3] (although CNTs of a significantly larger diameter were used in [3]). For example, the density of adsorbed hydrogen in [3] was ≈0.3 wt % at T = 290 K and P = 0.1 kbar. In our model, the calculated density of adsorbed hydrogen at this pressure and temperature is 0.42 wt %. In [3], the density of adsorbed hydrogen increased essentially nonlinearly with pressure, as was the case in our model.

3. CONCLUSIONS

A method for calculating the thermodynamic functions and the equilibrium density of a one-dimensional chain of molecules adsorbed inside a nanotube has been proposed. The model takes into account the interactions of incorporated molecules with one another (within the mean-field approximation) and with the nanotube walls. Data obtained in *ab initio* calculations using the pseudopotential method in the framework of the density functional formalism were used to calculate all the interactions. The model is quantum-mechanical and, hence, correctly includes the quantization of the energy levels of a particle and transitions of the particle to excited levels. The contribution from phonons is taken into account in calculating the free energy at nonzero temperature. This contribution improves the mean-field approximation and partly takes into account the contribution from vibrations of particles with respect to their average positions in the harmonic approximation. The method can be readily generalized to the case of adsorption in more complex systems (on two- and quasi-two-dimensional surfaces). The method has been applied to calculate hydrogen molecule adsorption in (3,3)- and (6,0)-type CNTs. It was shown that under pressure a sequence of first-order phase transitions occurs in which the density of adsorbed hydrogen changes in a jump.

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