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Density and Thermodynamics of Hydrogen Adsorbed on the Surface of Single-Walled Carbon Nanotubes

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Received December 15, 2004; in final form, May 31, 2005

Abstract—A method is proposed for calculating the adsorption of hydrogen in single-walled carbon nanotubes. This method involves solving the Schrödinger equation for a particle (hydrogen molecule) moving in a potential generated by the surrounding hydrogen molecules and atoms forming the wall of the carbon nanotube. The interaction potential for hydrogen molecules is taken in the form of the Silvera–Goldman empirical potential, which adequately describes the experimental data on the interaction between H₂ molecules (including the van der Waals interaction). The interaction of hydrogen molecules with carbon atoms is included in the calculation through the Lennard-Jones potential. The free energy at a nonzero temperature is calculated with allowance made for the phonon contribution, which, in turn, makes it possible to take into account the correlations in the mutual arrangement of the neighboring molecules. The dependences of the total energy, the free energy, and the Gibbs thermodynamic potential on the applied pressure P and temperature T are calculated for adsorbed hydrogen molecules. These dependences are obtained for the first time with due regard for the quantum effects. The pressure and temperature dependences of the hydrogen density $m(P, T)$ are also constructed for the first time.

PACS numbers: 65.80.+n, 82.60.Qr, 68.43.–h

DOI: 10.1134/S1063783406020351

1. INTRODUCTION

The experimental discovery of carbon nanotubes in 1991 [1] opened up new fields in engineering and fundamental physics. Owing to their nanometer sizes and periodicity in one dimension inherent in these structures, carbon nanotubes possess a unique combination of mechanical, chemical, and electrical properties [2]. One of the most interesting properties exhibited by carbon nanotubes (from the standpoint of practical application) is their ability to adsorb atoms and molecules of different types. Since carbon nanotubes have a very large specific surface (of the order of several hundred m²/g), they can adsorb considerable amounts of noble gases, hydrogen, metals, water, etc. It should be noted that, according to recent data, the limiting hydrogen content in carbon nanotubes intended for the commercial use of hydrogen in transport reaches 6–7 wt % [3].

Unfortunately, the experimental data available in the literature on the hydrogen adsorption in carbon nanotubes are very contradictory. For example, in the pioneering work by Dillon *et al.* [4], it was noted that the hydrogen content in single-walled carbon nanotubes can be as high as 5–10 wt % at room temperature and a pressure of 4×10^4 Pa. Ye *et al.* [5] and Liu *et al.* [6] reported that the content of adsorbed hydrogen reaches 8.25 wt % at a temperature of 80 K under a pressure of 10 MPa and decreases to 4.2 wt % at room temperature under the same pressure. As was shown by Chen *et al.* [7], the hydrogen content in

single-walled carbon nanotubes doped with alkali metals varies from 10 to 20 wt %. According to Nützenadel *et al.* [8] and Rajalakshmi *et al.* [9], the content of electrochemically adsorbed hydrogen in single-walled carbon nanotubes falls in the range from 0.4 to 4.0 wt %. Zhu *et al.* [3] produced single-walled carbon nanotubes in which the content of adsorbed hydrogen was approximately equal to 3.5 wt %.

This large scatter in the experimental data can be explained by the differences in the materials and techniques used in experiments on hydrogen adsorption in nanotubes. Furthermore, no unified theory of hydrogen adsorption in carbon nanotubes has been offered to date. Although this problem has been studied by many researches (see, for example, [10–12]), the mechanism of hydrogen adsorption in nanotubes is not completely understood.

Hydrogen adsorption has been theoretically studied within different approaches. It is common practice to use the Monte Carlo method (the diffusion and canonical variants) and molecular dynamics technique. The diffusion Monte Carlo method [13] makes it possible to calculate the thermodynamic quantities, correlation functions, and the equilibrium density of particles with the inclusion of the quantum effects through the calculated wave functions. However, the temperature effects, as a rule, are disregarded in these calculations because of the extremely complicated algorithm employed in

the diffusion Monte Carlo method. The canonical Monte Carlo method [14] takes into account the temperature effects but with the use of the equations of motion and interparticle potentials based on classical mechanics. In this case, the quantum-mechanical effects are ignored. Moreover, any Monte Carlo algorithm includes a large number of configurations ($\approx 10^6$), which can significantly complicate calculations.

The molecular dynamics technique [15, 16] (the *ab initio* method and variants based on the empirical interparticle potentials) makes it possible to calculate the forces acting on atoms and, hence, to investigate the atomic dynamics. Within this approach, atoms are treated in terms of classical mechanics (i.e., they obey the Newtonian equations of motion) rather than in terms of quantum mechanics. Moreover, zero-point vibrations of atoms, quantization of energy levels, and tunneling effects are ignored within the molecular dynamics approach. As a consequence, molecular dynamics calculations cannot correctly predict even qualitative results for motions of particles at low temperatures when the kinetic energy of the particles is less than the potential barrier height: $E_{\text{kin}} < E_b$. However, it should be noted that there are works in which quantum effects are partially included in the molecular dynamics algorithm for calculating simple systems [17].

In our recent paper [18], we proposed a new method for calculating the equation of state of hydrogen molecules adsorbed in single-walled carbon nanotubes. This method takes into account the quantum-mechanical effects that are responsible for the discrete energy levels and for the disordering of an adsorbed particle between the nearest neighbors. The proposed technique was used to calculate the thermodynamic functions and the equilibrium density of a one-dimensional chain consisting of hydrogen molecules adsorbed inside extremely narrow single-wall carbon nanotubes of the (3, 3) and (6, 0) types (according to the notation proposed by White *et al.* [19]). Those calculations included the interaction of the introduced molecules with each other and their interaction with the nanotube walls. When calculating the thermodynamic functions at a nonzero temperature, proper allowance was made for the phonon contribution and the transitions of the studied particle to excited levels. In the present paper, we advance this method as applied to the calculation of the hydrogen adsorption in single-walled carbon nanotubes with diameters $D = 13.56$ and 27.13 Å, in which the motion of hydrogen molecules cannot be considered strictly one-dimensional motion.

The purpose of this work is to investigate theoretically the thermodynamic properties of hydrogen molecules in carbon nanotubes with due regard for the quantum effects at different temperatures. It is assumed that the interaction of hydrogen molecules with each other and their interaction with the nanotube walls are adequately described by the pair interaction potentials.

2. CONSTRUCTION OF THE MODEL

Numerous experimental data indicate that hydrogen molecules in the absence of catalysts are adsorbed on the surface of carbon nanostructures only due to weak van der Waals interactions without the formation of strong covalent bonds (see, for example, [10]). In this respect, we consider only the physical adsorption. Hence, the interaction potential was taken in the form of the Silvera–Goldman potential, which adequately describes the experimental data on the interaction of H_2 molecules, including the weak van der Waals interaction [13, 20]. The interaction of hydrogen molecules with carbon atoms was included in the calculation through the Lennard-Jones potential [14].

The behavior of hydrogen molecules was investigated inside the (10, 10) and (20, 20) single-walled carbon nanotubes whose diameters were equal to ≈ 13.56 and 27.12 Å, respectively. Unlike the motion considered in [18], the motion of hydrogen molecules in the (10, 10) and (20, 20) single-walled carbon nanotubes cannot be treated as strictly one-dimensional: the molecules can be displaced from the nanotube axis and located at a certain distance (determined by the van der Waals radii) from the nanotube walls.

The model is based on the solution of the Schrödinger equation for the wave function $\Psi_i(r)$ describing the motion of the particle as a whole (for example, a hydrogen molecule) in the potential represented as the sum of the potential $V_{\text{C-H}}(r)$, which is generated by the interaction of the hydrogen molecule with carbon atoms of the nanotube wall, and the potential $V_{\text{H-H}}(r)$, which is induced by the interaction between the hydrogen molecule under consideration and the neighboring hydrogen molecules; that is,

$$\left(-\frac{\Delta}{2m} + V(r)\right)\Psi_i(r) = \varepsilon_i\Psi_i(r), \quad (1)$$

$$V(r) = V_{\text{C-H}}(r) + V_{\text{H-H}}(r).$$

Here, ε_i is the energy of the hydrogen molecule in the i th state and m is the mass of the hydrogen molecule.

It was assumed that the hydrogen molecules should form a regular lattice. This lattice can be distorted as a result of thermal displacements of the molecules. (Note that these displacements will be included in the subsequent calculations through the phonon contribution). Since the lattice formed by the hydrogen molecules should be commensurate with the lattice of the carbon atoms covering the surface of the nanotube, the lattice of the hydrogen molecules on the surface of the nanotube should also be hexagonal.

The probability distribution of the particle position at each temperature was calculated from the quantity $|\Psi_i(r)|^2$ averaged over the Gibbs distribution. The potential acting on the hydrogen molecule from the neighboring molecules was calculated under the assumption that the positions of all the neighbors are fixed and correspond to the maximum probabilities of

their geometric distribution (the mean-field approximation).

It should be noted that the symmetry of the system is similar to the cylindrical symmetry and that the hydrogen atoms (as well as the carbon atoms) form a graphite-like lattice. For this reason, the unit cell used to simulate the motion of the hydrogen molecule was chosen in the form of a triangular prism that bounds the motion of the molecule within the region whose projection onto the surface of the single-walled carbon nanotube is depicted in Fig. 1. The top of the triangular prism is located at a distance of 1.5 Å from the surface of the single-walled carbon nanotube, whereas the bottom of the prism is positioned in the immediate vicinity of the tube axis ($R = 0.1$ Å). When the hydrogen molecules come closer together to a distance shorter than the van der Waals radius, the repulsive forces are enhanced drastically. Hence, the boundary conditions were chosen so that the probability of the hydrogen molecule escaping from the prism was equal to zero. Then, the Schrödinger equation with the potential describing the interaction of the hydrogen molecule both with its neighbors and with the nanotube atoms was numerically solved by partitioning the cell in the cylindrical coordinates.

When analyzing the properties of the system at $T \neq 0$, we took into account that the particle can transfer to the excited energy levels ε_i and calculated the average energy of the particle from the Gibbs distribution:

$$\langle U \rangle = \frac{1}{Z} \sum_i \varepsilon_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right), \quad (2)$$

$$Z = \sum_i \exp\left(-\frac{\varepsilon_i}{k_B T}\right),$$

where Z is the partition function and k_B is the Boltzmann constant.

In this study, most attention was concentrated on investigating the dependences of the density of adsorbed particles and the equilibrium interparticle distance on external parameters, such as the pressure P and the temperature T . Since the equilibrium of the sys-

tem at external parameters $\{P, T\} \neq 0$ is governed by the minimum condition for 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, and V is the volume of the system), this potential should be calculated with allowance made not only for the internal energy $\langle U \rangle$ but also for the contributions of the entropy S and the volume energy PV . The free energy G (per adsorbate molecule) involves two contributions: (i) the free energy G_1 related to the average energy of particles $\langle \varepsilon \rangle$ (determined at fixed positions of the neighboring molecules of the adsorbate) and to the entropy S_1 of their distribution over the energy levels and (ii) the phonon contribution G_{phon} determined by the deviations of these neighboring molecules from equilibrium positions. These deviations of the neighboring molecules from the equilibrium positions lead to a change in the energy levels of the molecule under consideration and, correspondingly, to a change in the total energy of the system. The change in the energy upon displacements of the neighboring molecules gives rise to restoring forces acting on the neighbors and leads to the contribution G_{phon} to the free energy due to the phonon vibrations of the adsorbed molecules at frequencies ω_{ij} ; that is,

$$G = G_1 + G_{\text{phon}}, \quad G_1 = \langle U \rangle - TS_1, \quad (3)$$

$$S_1 = -k_B \sum_i P_i \ln(P_i), \quad P_i = \frac{1}{Z} \exp\left(-\frac{\varepsilon_i}{k_B T}\right), \quad (4)$$

$$\begin{aligned} G_{\text{phon}} &= \langle U \rangle_{\text{phon}} - TS_{\text{phon}} \\ &= \sum_i \left[\frac{\eta \omega_i}{2} + k_B T \ln\left(1 - \exp\left(-\frac{\eta \omega_i}{k_B T}\right)\right) \right]. \end{aligned} \quad (5)$$

The phonon frequencies were calculated from the dispersion relation for phonons in the hexagonal structure formed by particles with mass M , which are separated by a distance d and interact with the nearest neighbors through elastic constants $f(r, T)$; that is,

$$\begin{aligned} \omega_i(q_x, q_y, d, T) &= \frac{f(d, T)}{M} (3 \pm \sqrt{2[\cos(\{q_x - q_y\}d) + \cos(q_x d) + \cos(q_y d)] + 3}), \\ f(d, T) &= \frac{\partial^2 \langle U_{\text{pot}}(r, T) \rangle}{\partial r^2}. \end{aligned} \quad (6)$$

Here, the wave vectors q_x and q_y change within the first Brillouin zone of the hexagonal cell.

Then, we can calculate the free energy G at each value of $f(d, T)$. By using the formula $P = -\left. \frac{\partial G}{\partial V} \right|_T$, it is possible to determine the pressure P for each distance d .

The functions $G(P, T)$ and $\Phi(P, T)$ can be determined through inversion.

3. RESULTS AND DISCUSSION

The internal and free energies of particles and the Gibbs thermodynamic potential $\Phi = \Phi(P, T)$ were cal-

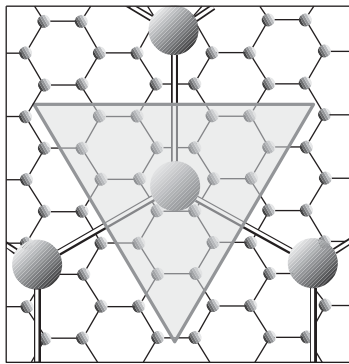


Fig. 1. Projection (gray triangle) of the unit cell (used for simulating the motion of the H₂ molecule) onto the surface of the single-walled carbon nanotube. The positions of the H₂ molecule under investigation (central sphere) and the neighboring H₂ molecules (three surrounding spheres) are shown.

culated at different temperatures and average intermolecular distances d . Then, the hydrogen density $m(P, T)$ (content, wt %) in the nanotubes under investigation at each pressure P was calculated from the minimum condition for the Gibbs thermodynamic potential $\Phi = \Phi(P, T)$. The data obtained are presented in Figs. 2 and 3. It can be seen from these figures that, at different temperatures, an increase in the external pressure leads to a sequence of phase transitions, which are accompanied by a stepwise change in the density of adsorbed hydrogen molecules. This is explained by the manifestation of the quantum properties of adsorbed hydrogen molecules, which are characterized by a set of quantized energy levels populated at nonzero temperatures. Figure 4 shows the dependence of the average energy of the hydrogen molecule inside the (10, 10) single-walled carbon nanotube on the temperature and pressure (P, T). The dependence of the free energy of the hydrogen

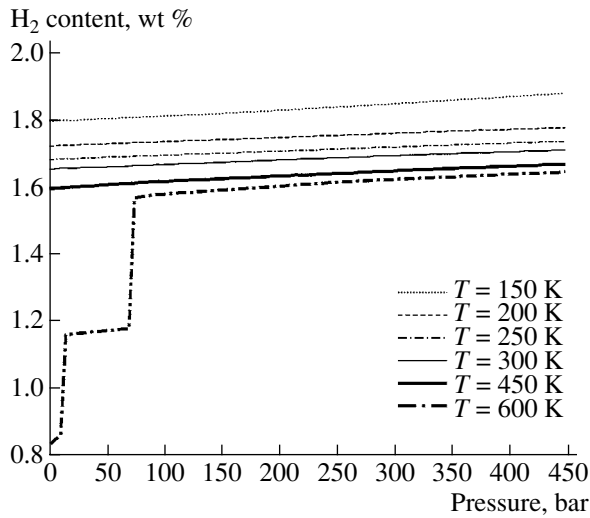


Fig. 2. Content of H₂ molecules inside the (10, 10) single-walled carbon nanotube.

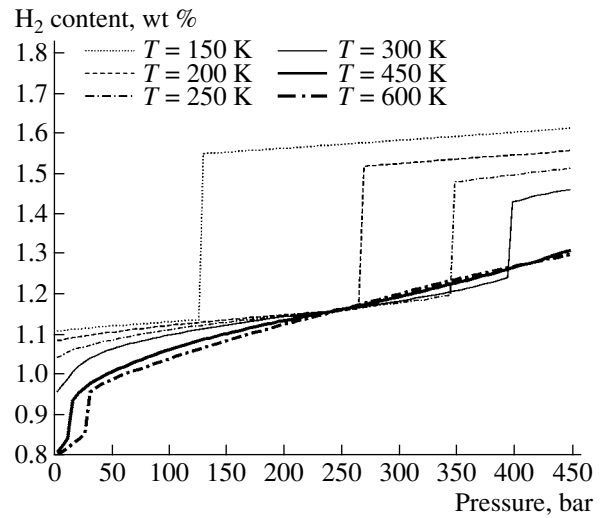


Fig. 3. Content of H₂ molecules inside the (20, 20) single-walled carbon nanotube.

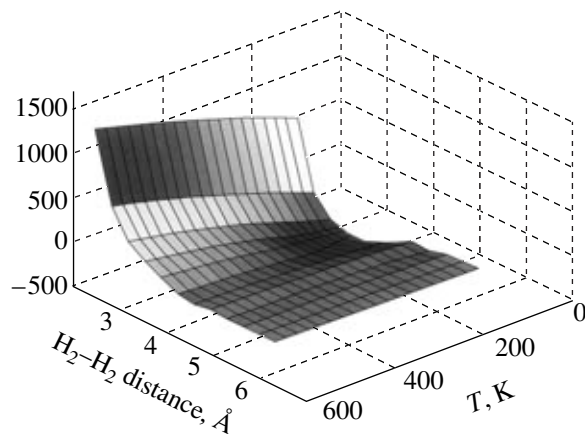


Fig. 4. Average energy of the H₂ molecule inside the (10, 10) single-walled carbon nanotube.

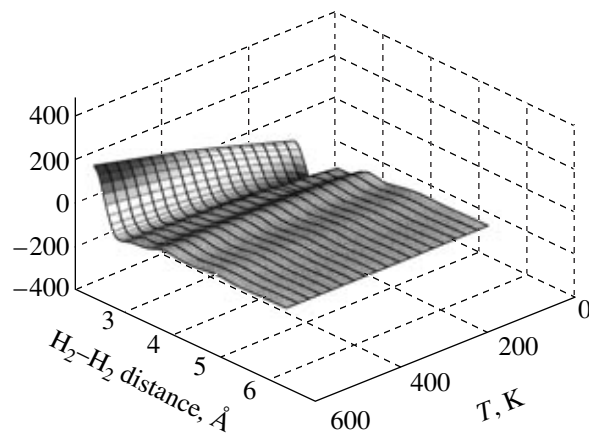


Fig. 5. Free energy of the H₂ molecule inside the (10, 10) single-walled carbon nanotube.

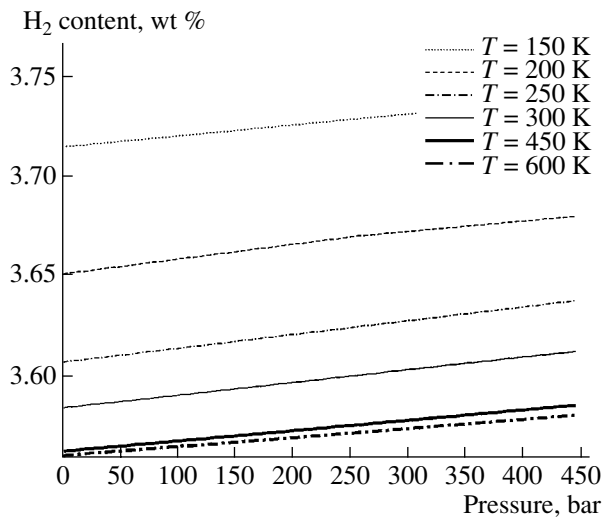


Fig. 6. Content of H₂ molecules with a mass of 200 au inside the (10, 10) single-walled carbon nanotube.

molecule inside the same nanotube on the temperature and pressure is plotted in Fig. 5. As can be seen from Fig. 5, the free energy of the hydrogen molecule is a nonlinear function of the temperature and the distance between hydrogen molecules. As a consequence, a variation in the pressure or in the temperature results in a phase transition attended by a change in the density of adsorbed hydrogen. The possibility of similar transformations occurring the system is indirectly confirmed by the experimental data obtained in [3].

In order to prove that adsorbed hydrogen molecules exhibit quantum properties, we calculated the pressure and temperature dependences of the energy $E_{\text{tot}}(P, T)$ and the density $m(P, T)$ for the case in which the hydrogen molecules with an increased (by a factor of 100) mass are adsorbed inside the (10, 10) single-walled carbon nanotube. The corresponding dependence is depicted in Fig. 6.

The effect of the mass on the adsorption was estimated according to the Arrhenius formula describing the frequency of desorption of particles from the surface [21]:

$$v_{\text{adsorb}} = v_{\text{vib}} \exp\left(-\frac{E_c}{kT}\right), \quad (7)$$

where v_{adsorb} is the frequency of desorption from the surface, v_{vib} is the frequency of surface normal vibrations of the particle, and E_c is the cohesive energy of particles on the surface. By assuming that $m(P, T) \sim v_{\text{adsorb}}^{-1}$, we found that the capacity of adsorption of particles with mass $m = 100m_{\text{H}_2}$ should increase by a factor of 10 (due to the square dependence of the frequency v_{vib} on the mass m). A comparison of Figs. 2 and 6 shows that the corresponding increase in the molecular mass does not lead to a tenfold increase in the den-

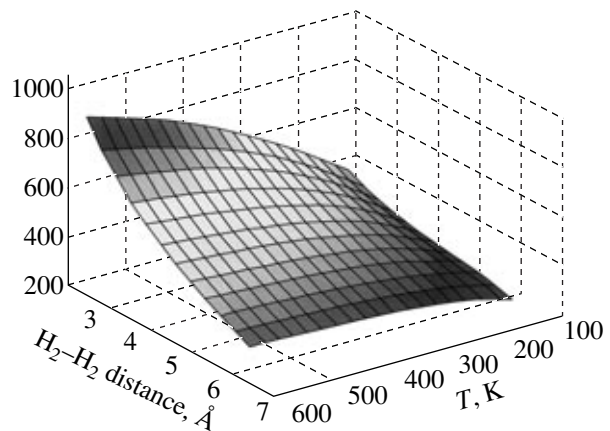


Fig. 7. Average energy of the H₂ molecule outside the (10, 10) single-walled carbon nanotube.

sity $m(P, T)$. This indicates that the quantum properties of light adsorbed molecules must be taken into account.

Apart from the calculations of the physical adsorption of hydrogen inside the (10, 10) and (20, 20) single-walled carbon nanotubes, we carried out the calculations of the adsorption of hydrogen molecules on the outer surface of the nanotubes under investigation (Figs. 7–9). It can be seen from Figs. 8 and 9 that, upon the phase transition, the pressure increases linearly with an increase in the temperature for both nanotubes. In this case, the adsorption capacity inside the nanotubes is higher than that outside them. A comparison of the data presented in Figs. 2, 3, 8, and 9 shows that the adsorption capacity (both inside and outside the single-walled carbon nanotubes) decreases with an increase in

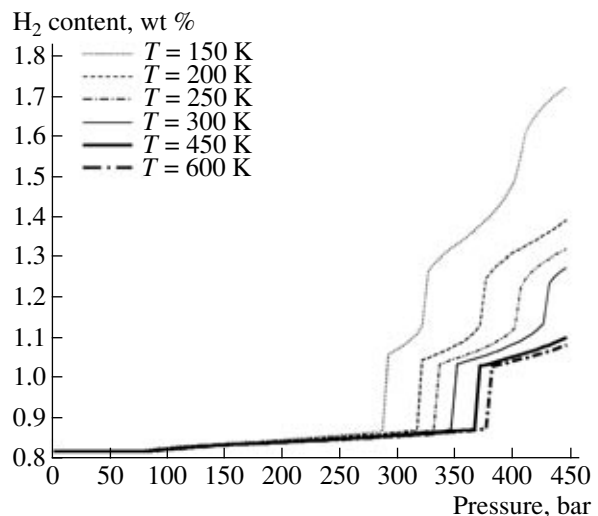


Fig. 8. Content of H₂ molecules outside the (10, 10) single-walled carbon nanotube.

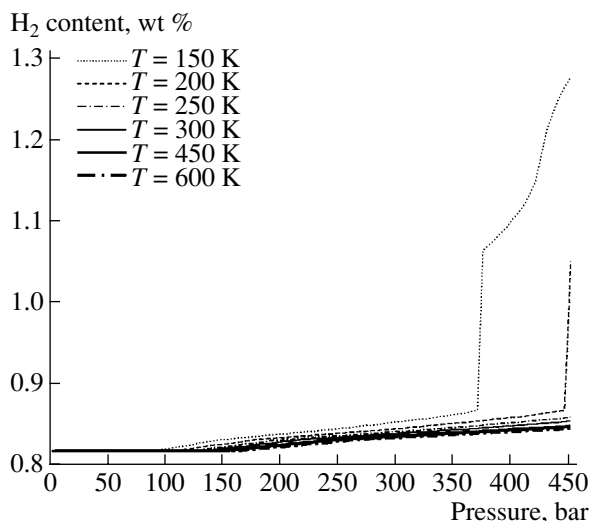


Fig. 9. Content of H₂ molecules outside the (20, 20) single-walled carbon nanotube.

the nanotube diameter. This behavior can be explained by the fact that the effective potential of the attractive van der Waals interaction of the hydrogen molecules increases inside the nanotubes and decreases outside them as the nanotube curvature increases.

4. CONCLUSIONS

Thus, we proposed a method for calculating the thermodynamic functions and the equilibrium density of hydrogen molecules adsorbed inside and outside single-walled carbon nanotubes of various diameters. This method makes it possible to take into account not only the interaction between hydrogen molecules (in the mean-field approximation) but also the interaction of the hydrogen molecules with the walls of the carbon nanotube. Within this approach, all the interactions, including the weak van der Waals intermolecular interaction, are described by the Silvera–Goldman potential.

The proposed model correctly accounts for the quantum-mechanical effects, which are responsible for the discrete energy levels of the particle under investigation, as well as for the transitions of the particle to excited levels. The free energy at a nonzero temperature was calculated with allowance made for the phonon contribution. The phonon contribution makes it possible to improve the mean-field approximation and to include the partial contribution from vibrations of the neighboring particles with respect to their equilibrium positions in the harmonic approximation. The method was used to calculate the adsorption of hydrogen molecules inside and outside the (10, 10) and (20, 20) single-walled carbon nanotubes. It was demonstrated that variations in the pressure and temperature lead to a sequence of first-order phase transitions, which are accompanied by a stepwise change in the density of adsorbed hydrogen upon adsorption outside and inside the carbon nanotubes. The adsorption capacity inside

the carbon nanotubes is higher than that outside the nanotubes and, in both cases, decreases with an increase in the nanotube diameter. The maximum adsorption capacity on both sides of the nanotubes ~14 Å in diameter can reach 3.5 wt % at a pressure of up to 500 bar and at a temperature of 150 K.

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Translated by O. Borovik-Romanova