STUDY OF THE TEMPERATURE DEPENDENCE OF THE λ-TRANSITION OF He^4 INSIDE A CARBON NANOTUBE[1]

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We report the results of iterative calculations of the temperature dependence of the λ-transition and distribution for the superfluid density of He^4 absorbed in a narrow single-wall carbon nanotube in the vicinity of the λ-transition. The calculations were made for different values of the carbon nanotube diameter and values of the inoculating interaction V_0 (the depth of a potential well). We demonstrate a decreasing of the temperature of the λ-transition and the superfluid density in He^4 absorbed in a nanotube and find the appropriate "temperature shift".

The fullerene prototype is C_{60}, a molecule formed out of 60 carbon atoms distributed on a sphere of a diameter of 7Å. Shortly after the fullerenes were discovered, the existence of related elongated structures of cylindrical form of one or several concentric graphite layers was reported. These structures are called carbon nanotubes. The diameter of a typical single-layer nanotube ranges between one and several nm, i.e. somewhat exceeds the diameter of the fullerene molecule C_{60}. A single-wall carbon nanotube (SWCNT) is constituted of a single graphite layer and graphite-like atomic arrangement of one monolayer thickness wrapped into a perfect cylinder.

Typical diameter values of SWCNTs were found experimentally, they are in a range of 1—2 nm. A multi-wall carbon nanotube (MWCNT) is composed of several coaxial SWCTs with increasing diameters. The diameter of MWCNTs may range to 100 nm. Shortly after the discovery of carbon nanotubes, the attention of researchers was attracted by a problem related to the possibility of filling nanotubes with various substances. The basic scientific interest in this problem is caused by the possibility of obtaining an experimentally justified answer to the question: at what minimum tube size do the capillary phenomena hold their peculiarities inherent to macroscopic objects? One of the ends of a nanotube can be opened by the action of a strong oxidizer [1]. In that case, we are able to fill the nanotubes with various substances. Liquid substances penetrate inside of an open-ended nanotube due to the effect of capillary action. On the other hand, if the nanotubes are filled with light atoms (He) or molecules (H_2) and the temperature is low enough, we deal with quasi-one-dimensional quantum fluids. Such an experimental realization has been carried out by Yano et al. [2] in a honeycomb of FSM-16. This is a mesoporous substrate with tubes approximately 18 Å in diameter. Using a torsional oscillator, this group proved the existence of superfluidity of He^4 atoms adsorbed in the pores below a critical temperature of 0.7 K. Superfluid helium absorbed to MWCNT and especially to SWCNT provides an excellent realization of a number of nearly one- or two-dimensional ($1D$, $2D$) phenomena.

The main purpose of this work is a study of properties of the helium four (^{4}He) absorbed in a narrow single-wall carbon nanotube (diameter $7 \leq d \leq 15$ Å). We study the dependence of the temperature of λ-transition of helium on the nanotube's diameter d and the value of an inoculating interaction V_0. As well known [3], the order parameter is usable for the description of helium near the λ-point as an effective wave function of the superfluid part of helium $\Psi(x,y,z) = \eta(x,y,z)e^{i\varphi}$. The superfluid density ρ_s and the superfluid velocity $\vec{V}_s$ are determined in the following way:

$$\rho_s = m|\Psi|^2 = m\eta^2, \qquad (1)$$

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$$\vec{V}_s = \frac{\hbar}{m}\vec{\nabla}\varphi, \tag{2}$$

where m is the mass of a helium atom ($m = 6.68 \times 10^{-24}$g) and the symbol $\hbar$ means Planck's constant.

The effective wave function is macroscopic, so we can use it only for measuring little larger distances than an atomic size $a \approx 3 \times 10^{-8}$ cm. On the other side, the superfluid density changes on the interatomic distance if the boundaries (of a carbon nanotube in our case) exist. The boundary influence causes an unhomogeneity of the absolute value of the order parameter $|\Psi| = \eta = \sqrt{\rho_s/m}$. The external field action provokes the same effect. As a result, the field changes a temperature of λ-transition $T_\lambda \equiv T_\lambda(\rho)$ also. Consequently, the phase transition to the superfluid state occurs nonconcurrently in whole volume if the potential $V(\vec{r})$ of an external field is not constant. At first, the regions with much lower density go into the superfluid state. Those "superfluid" regions are separated from "normal" regions by diffuse phase boundaries. The wideness and shape of that boundaries (a distribution character of superfluid density $\rho_s(\vec{r})$ in the boundary phase) depend on a field gradient, correlation effects, and a form of the density of the thermodynamic potential.

Taking into account the existence of the boundaries (of the nanotube) and an external field (which is created by C_{60} atoms), we study an appropriate "temperature shift" $\triangle T_\lambda = T_\lambda - T_\lambda(d, V_0)$, where $T_\lambda = 2.17$ K, near the λ-point, provided that $\frac{T_\lambda - T}{T_\lambda} \ll 1$. As stated in the literature [3], we can use the thermodynamic potential

$$\widetilde{\Omega}_{II}(\mu, T; \Psi, \rho) = \int \left[F_{II0}(\rho, T, |\Psi|^2) + \frac{\hbar^2}{2m}|\nabla\Psi|^2 - \right.$$

$$\left. - \rho(\mu + V(\vec{r}) + \frac{\delta}{2}(\nabla\rho)^2) \right] \vec{V} \tag{3}$$

by solving the space-inhomogeneous tasks when the density ρ changes essentially. Here μ is a chemical potential of helium, T is a temperature, $F_{II0}(\rho, T, |\Psi|^2)$ is the density of free energy, the term $\rho V(\vec{r})$ describes a potential energy of helium in an external field and the term $\frac{\delta}{2}(\nabla\rho)^2$ allows the correlations of density. Now we do not define the potential $V(\vec{r})$, as it will be done later. The thermodynamic potential $\widetilde{\Omega}_{II}(\mu, T; \Psi, \rho)$ is minimized in $\Psi^*(\vec{r})$ and $\rho(\vec{r})$ simultaneously and the system of the following differential equations is obtained:

$$\frac{\hbar^2}{2m}\triangle\Psi = \left(\frac{\partial F_{II0}}{\partial|\Psi|^2}\right)_{\rho,T}\Psi,$$

$$\delta\triangle\rho = \left(\frac{\partial F_{II0}}{\partial\rho}\right)_{|\Psi|^2,T} - \mu + V(\vec{r}). \tag{4}$$

By solving these equations, we will determine the equilibrium values of $\Psi^*(\vec{r})$ and $\rho(\vec{r})$. It is convenient to use the density of free energy $F_{II0}(\rho, T, |\Psi|^2)$ instead of the density of thermodynamic potential $\Omega_{II0}(\mu_0, T, |\Psi|^2)$ in $\mu_0, T, |\Psi|^2$ variables, where μ_0 is the chemical potential without external field:

$$\mu_0 = \left(\frac{\partial F_{II0}}{\partial\rho}\right)_{|\Psi|^2,T} = \mu - V(\vec{r}). \tag{5}$$

Equations (4) can be separated as follows:

$$\frac{\hbar^2}{2m}\triangle\Psi = \left(\frac{\partial\Omega_{II0}}{\partial|\Psi|^2}\right)_{\mu_0,T}\Psi, \tag{6}$$

$$\rho = -\left(\frac{\partial\Omega_{II0}}{\partial\mu_0}\right)_{|\Psi|^2,T}. \tag{7}$$

These equations can be rewritten in terms of the ψ-function as

$$\psi = \frac{\Psi}{\Psi_{00}}, \qquad \Psi_{00} = \eta_{00} = \sqrt{\frac{1.43\rho_\lambda}{m}} = \sqrt{\frac{\rho_{00}}{m}}, \tag{8}$$

where $\rho_\lambda = 0.146$ g/cm^{-3} is the helium density at the λ-point, and, for the non-dimensional coordinate $\vec{r}_{**}$, we have

$$\vec{r_{**}} = \frac{\vec{r}}{\xi_{00}}, \qquad \xi_{00} = \frac{\hbar^2}{2mdT_\lambda\triangle C_p}, \tag{9}$$

where $\triangle C_p = C_{pII} - C_{pI}$ is the jump of heat capacity at the λ-point and d is the diameter of a carbon nanotube. Equation (6) with overdetermined variables reads

$$\triangle_{**}\psi = \frac{3}{3+\alpha}\left(-t|t|^{1/3} + (1-\alpha)|t|^{2/3}|\psi|^2 + \right.$$

$$\left. + \alpha|\psi|^4\right)\psi, \tag{10}$$

where symbols "t" and "α", respectively, mean

$$t = t_0 - (dT_\lambda/d\mu)V(\vec{r}), \qquad \alpha = d^{\frac{3}{2}}\eta_{00}, \tag{11}$$

and $t_0 = T_{\lambda0}(\mu_0) - T + (dT_\mu/d\mu)(\mu - \mu_{\lambda0})$ is the initial distance to a certain point $(T_{\lambda0}, \mu_{\lambda0})$ on the λ-curve of the helium phase diagram without external field, and $(dt_\mu/d\mu)$ is the slope of a λ-curve at the indicated point.

Usually it is convenient to count the coordinate from the plane $t = t_0 - (dT_\lambda/d\mu)V(\vec{r}) = 0$, which corresponds to the boundary HeI—HeII in an external field. Here and

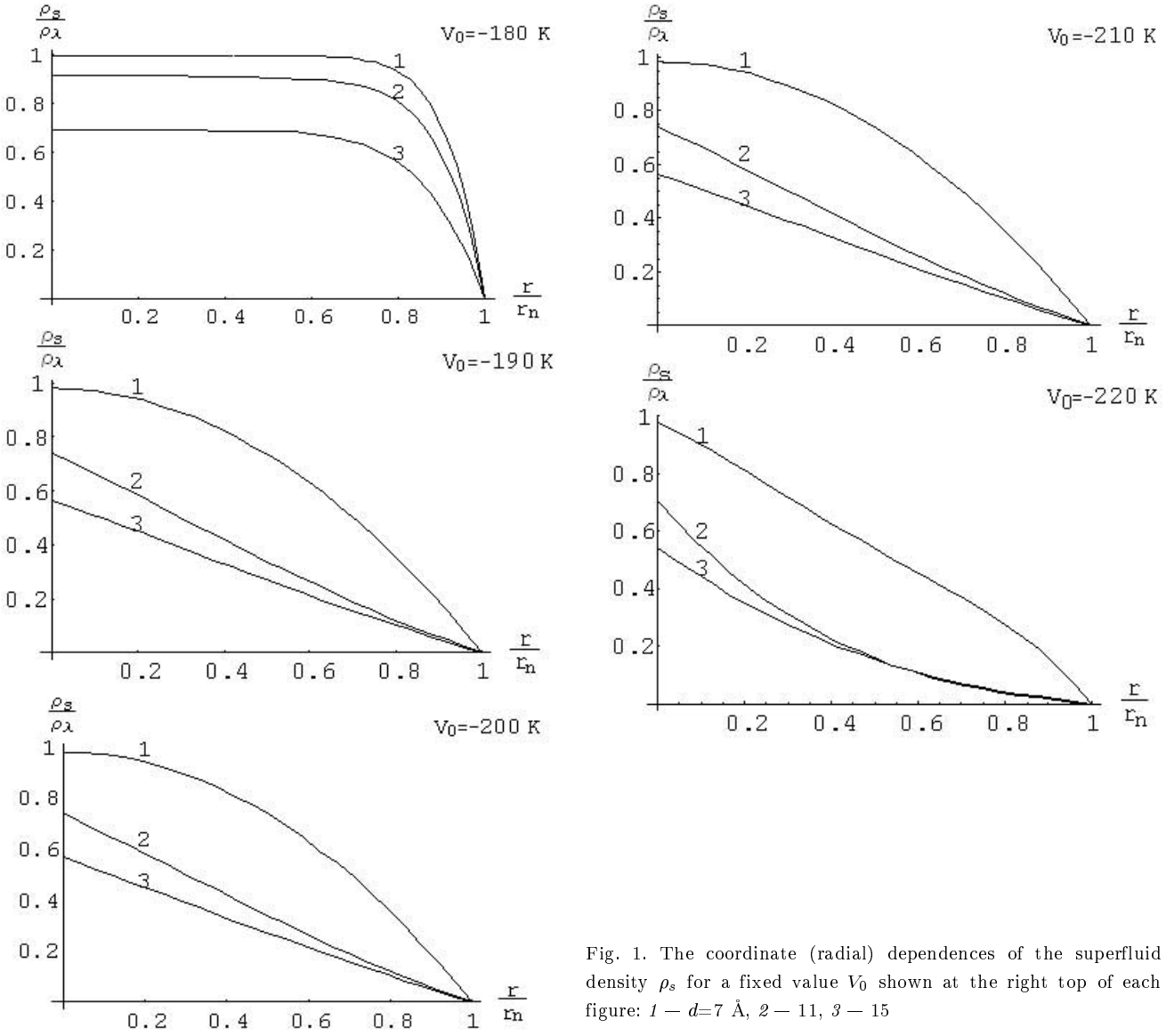

Fig. 1. The coordinate (radial) dependences of the superfluid density ρ_s for a fixed value V_0 shown at the right top of each figure: *1* — d=7 Å, *2* — 11, *3* — 15

below, it is convenient to introduce a new wave function $\widetilde{\psi}$ and a new variable y

$$\widetilde{\psi} = \frac{\Psi}{\Psi_{V_0}}, \qquad y = \frac{r_{**}}{l_{V_0}}, \tag{12}$$

where

$$\Psi_{V_0} = \left(\frac{\rho_{T_\lambda}}{m}\right)^{1/2},$$

$$\rho_{T_\lambda} = 1.54\rho_\lambda \left(\frac{\xi_{00}}{l_{V_0}}\right) = 0.352 \left(\frac{\xi_{00}}{l_{V_0}}\right) \text{ g/cm}^3,$$

$$l_{V_0} = \left(\frac{V_0}{T_\lambda}\left|\frac{dT_\lambda}{d\mu}\right|\right)^{2/3}, \tag{13}$$

ρ_λ is the value of helium density at the corresponding point of the λ-curve ($\rho_\lambda = 0.146$ g/cm^3) and $V(\overrightarrow{r}) = V_0 f(\overrightarrow{r})$, where V_0 is an approximate value of an inoculating interaction and $f(\overrightarrow{r})$ is an approximate interaction function. After the substitution, Eq. (10) has the form

$$\triangle_{yy}\widetilde{\psi} = -\frac{3}{3+\alpha} l_{V_0} f(y) \left(y|y|^{1/3} + (1-\alpha)y^{2/3}|\widetilde{\psi}|^2 + \right.$$

$$\left. + \alpha|\widetilde{\psi}|^4\right)\widetilde{\psi} \tag{14}$$

Thus, we have to solve the non-linear differential equation (14), where α and V_0 are free

parameters, defined by the diameter nanotube d and the inoculating interaction V_0. This equation does not have an exact solution, so we will find it by approximating computations. Before solving the equation, we shortly consider boundary conditions. It is well known [4] that helium atoms adhere to a wall. So, the normal $\overrightarrow{j_n} = \rho_n \overrightarrow{\nu_n}$ and superfluid $\overrightarrow{j_s} = \rho_s \overrightarrow{\nu_s}$ flows of helium must be equal to zero on the wall. The equality $\overrightarrow{j_n} = 0$ on the wall follows from the usual condition for a viscous liquid $\overrightarrow{\nu_n} = 0$ on the wall, which is correct for normal velocity $\overrightarrow{\nu_n}$. According to the Landau theory [5], for superfluid velocity $\overrightarrow{\nu_s}$, we exploit the condition for an ideal liquid on the wall, i.e. $\overrightarrow{\nu_s} \neq 0$ on the wall though $\overrightarrow{j_{s\ \mathrm{wall}}} = 0$. So, to satisfy this condition, we must use the boundary condition $\rho_{s\ \mathrm{wall}} = 0$, whence the boundary condition $\widetilde{\psi}_{y=d/2} = 0$ follows.

The further study is based on the simplified helium carbon interaction. We take this to be the mean interaction averaged across the substrate plane: thus, it is a function of y alone. We consider the nanotubes as smooth cylinders by making a y-average of the corresponding sum of all the C—He interactions. Thus, the potential felt by a particle only depends on distance from the particle to the center of the cylinder. For the potential (interaction via a pairwise central potential), we have chosen that due to the Aziz potential [6], which was used in studies of both bulk three-dimensional helium [7] and two-dimensional helium [8]. The potential energy, $V(y_i)$, is the potential of the ith atom due to a smooth carbon nanotube. We used the form developed by Carlos and Cole [9]:

$$V(y_i) = \left(\frac{4\pi V_0 \sigma^4}{a_s d^4}\right)\left[\frac{2}{5}\left(\frac{\sigma}{d}\right)^6 \xi(10, \frac{y_i}{d}) - \xi(4, \frac{y_i}{d})\right], \quad (15)$$

with $\sigma = 2.74$ Å, $a_s = 2.74$ Å^2, and $\xi(n, y)$ is the generalized Riemann zeta function [10]. We note the $V(y_i)$ is a much stronger potential than the Aziz potential.

In this study of He^4 absorbed in a narrow single walled carbon nanotube, we have used the iteration procedure. Detailed descriptions have been given in [11, 12]. We made calculation of the next values: V_0 from -180 to -220 °C with a step of 10 K and d from 7 to 15 Åwith a step of 4 Å. We fix by turns one parameter and change other. The results of numerical calculations done according to (14), (15), (1) are presented in Fig. 1 and Fig. 2, where we show the coordinate (radial) dependence of the superfluid density ρ_s ($\rho_\lambda = 0.146$ g/cm^3 is the helium density at the λ-point, $r_n = d/2$ is radius of the carbon nanotube).

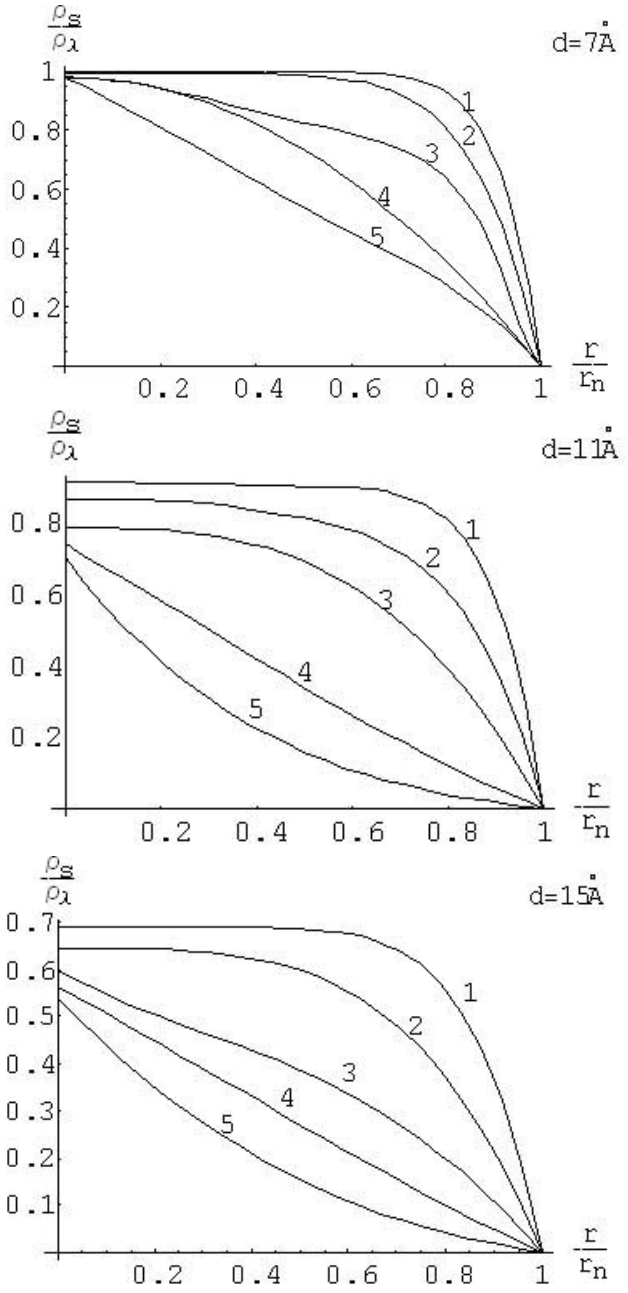

Fig. 2. The coordinate (radial) dependences of the superfluid density ρ_s for a fixed value d shown at the right top of each figure: *1* — $V_0 = -180$ °C, *2* — -190, *3* — -200, *4* — -210, *5* — -220

In Fig. 1, curve *1* corresponds to a value d =7 Å, curve *2* to d=11Å, and curve *3* to d=15 Å. These curves have been received with a fixed value V_0 shown at the right top of each figure. In Fig. 2, curve *1* corresponds to $V_0 = -180$ °C, curve *2* to $V_0 = -190$ °C, curve *3* to $V_0 = -200$ °C, curve *4* to $V_0 = -210$ °C, and curve *5*

d/ V_0	$V_0 = -180$ °C	$V_0 = -190$ °C	$V_0 = -200$ °C	$V_0 = -210$ °C	$V_0 = -220$ °C
d=7 Å	6.33×10^{-4}	7.09×10^{-4}	8.07×10^{-4}	9.35×10^{-4}	11.12×10^{-4}
d=11 Å	8.43×10^{-4}	9.44×10^{-4}	10.73×10^{-4}	12.43×10^{-4}	14.79×10^{-4}
d=15 Å	10.73×10^{-4}	12.03×10^{-4}	13.67×10^{-4}	15.84×10^{-4}	18.83×10^{-4}

to $V_0 = -220$ °C. These curves have been derived with a fixed value of d shown at the right top of each figure.

In helium intercalated to a carbon nanotube, various dimensional effects appear because of the equality $\rho_{s\ \mathrm{wall}} = 0$. Really, a middle value of ρ_s for helium in a carbon nanotube is less than ρ_s in a large capacity. In particular, increasing the average value of superfluid density reduces to decreasing the temperature of the λ-transition. On the base of our previous calculation, we can find an appropriate "temperature shift" $\triangle T_\lambda = T_\lambda - T_\lambda(d, V_0)$. For that, we use the relation

$$\triangle T_\lambda = T_\lambda - T_\lambda(d, V_0) =$$

$$= \frac{2.12 \cdot 10^{-11}[(3+\alpha)/3]^{3/4}}{l_{\nu_0}^{3/2}}. \qquad (16)$$

The results of calculations are shown in the table.

We found the distribution of superfluid density of He^4 inside a carbon nanotube around the point of the λ-transition for different values of the diameter d of a carbon nanotube, and values of an inoculating interaction V_0 (the depth of a potential well).

The obtained results allow us to conclude the following:

1. If the nanotube's diameter is invariable, the increment of the interaction between superfluid helium and carbon atoms will reduce to decreasing the superfluid density (but to increasing the "temperature shift"). In this case, the appearance of the superfluid component is decelerated.

2. If the interaction between helium and carbon atoms is invariable, a decrease of the nanotube's diameter will accelerate the appearance of the superfluid component, which is decreasing essentially stronger than that in the previous case.

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1. *Ajayan P.M., Iijima S.* // Nature. – 1991. – **361**. – P. 333.
2. *Yano H., Yoshizaki S., Sinagaki S. et al.* // J. Low Temp. Phys. – 1998. – **110**. – P. 573.
3. *Khalatnikov I.M.* Theory of Superfluidity. – Moscow: Fizmatgiz, 1971 (in Russian).
4. *Putterman S.J.* Superfluid Hydrodynamics. – New York: North. Holland, 1968.
5. *Landau L.D.* // Zh. Eksp. Teor. Fiz. – 1941. – **II**. – P. 592 (in Russian).
6. *Aziz R.A., Nain V.P.S., Earley J.S. et al.* // J. Chem. Phys. – 1979. – **70**. – P. 4330.
7. *Kalos M.H., Lee M.A., Whitlock P.A., Chester G.V.* // Phys. Rev. B. – 1981. – **24**. – P. 115.
8. *Kalos M.H., Whitlock P.A., Chester G.V.*// Ibid. – 1988. – **38**. – P. 2418.
9. *Carlos W.E., and Cole M.W.* // Surf. Sci. – 1980. – **91**. – P. 339.
10. *Haynsworth E.V., and Goldberg K.* //Handbook of Mathematical Functions/ Ed. by M. Abramovich and I.A. Stegun. – New York: Dover, 1970. – Ch. 23.
11. *Schmidt K.E., and Ceperley D.M.* //Monte Carlo Methods in Condensed Matter Physics: Topics in Modern Physics. – 1991. – **71**. – P. 205–245.
12. *Whitlock P.A., Caperley D.M., Chester G.V., and Kalos M.H.* // Phys. Rev. B. – 1979. – **19**. – P. 5598.

ДОСЛІДЖЕННЯ ТЕМПЕРАТУРНОЇ ЗАЛЕЖНОСТІ λ-ПЕРЕХОДУ В He^4 ВСЕРЕДИНІ ВУГЛЕЦЕВИХ НАНОТРУБОК

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Р е з ю м е

Наведено результати обчислень температурної залежності λ-переходу і розподілу надплинної густини He^4, який інтеркальовано у вузькі одностінні вуглецеві нанотрубки в околі λ-переходу. Обчислення було проведено для різних значень діаметра вуглецевих нанотрубок і для різних значень затравкової взаємодії V_0. В результаті отримано, що температура λ-переходу і значення надплинної густини зменшуються, якщо He^4 знаходиться всередині вуглецевих нанотрубок. Було знайдено також відповідний "температурний зсув".

ИССЛЕДОВАНИЕ ТЕМПЕРАТУРНОЙ ЗАВИСИМОСТИ λ-ПЕРЕХОДА В He^4 ВНУТРИ УГЛЕРОДНЫХ НАНОТРУБОК

Е. Ткаченко, С.Вильчинский

Р е з ю м е

Представлены результаты вычислений температурной зависимости λ-перехода и распределения сверхтекучей плотности He^4, который интеркалирован в узкие одностенные углеродные нанотрубки, вблизи λ-перехода. Вычисления были выполнены для разных значений диаметра углеродных нанотрубок и для разных значений затравочного взаимодействия V_0. В результате получено, что температура λ-перехода и значение сверхтекучей плотности уменьшаются, если He^4 находится внутри углеродных нанотрубок. Был найден также соответствующий "температурный сдвиг".