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Evaluation of Hydrogen Particle Volume on Surfaces of Selected Nanocarbons

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***Abstract*—**This paper describes an approach to the adsorption phenomena modeling aimed at specifying the adsorption mechanisms on localized or nonlocalized adsorbent sites, when applied to the nanocarbons. The concept comes from the fundamental thermodynamic description of adsorption equilibrium and is based on numerical calculations of the hydrogen adsorbed particles volume on the surface of selected nanocarbons: single-walled nanotube and nanocone. This approach enables to obtain information on adsorption mechanism and then as a consequence to take appropriate mathematical adsorption model, thus allowing for a more reliable identification of the material porous structure. Theoretical basis of the approach is discussed and newly derived results of the numerical calculations are presented for the selected nanocarbons.

***Keywords*—**Adsorption, mathematical modeling, nanocarbons, numerical analysis.

I. Introduction

ADSORPTION phenomena are widely studied because of both fundamental mechanism understanding and industrial applications viewpoint. The latter are mainly related to the gas separation or gas storage by means of physical adsorption on various types of porous materials. For those purposes carbon microporous materials, such as activated carbons, single– and multi–walled carbon nanotubes or synthetic carbons are commonly studied [1]–[3]. This is due to relatively high surface area, regular pore sizes and attractive surface potentials that enable adsorption of gases on carbon surface up to densities high enough to industrial applications, like gaseous fuel storage for automotive [4]. Recently, since the synthesis of novel carbon nanoparticles – single–walled carbon nanotubes [5] and later carbon nanocones [6] were reported for the first time, the use of these materials in gas adsorption has attracted a great interest. It results from both: theoretical researches and potential applications in gas storage of these materials [7], dedicated mainly to the clean burning and low cost gaseous fuels (e.g. methane, hydrogen) in automotive applications.

Nevertheless, further development of novel carbon nanomaterials of practical significance requires simultaneously the development of an efficient tool for this material structure identification. The material structure properties are commonly characterized based on adsorption isotherms of small, nearly spherical molecules of probing adsorbates e.g. nitrogen. However, in order to obtain useful information on material porous structure (e.g. surface area, pore structure, pore volume and energy with their distributions) a mathematical description of adsorption mechanism is required. The basic assumption of any mathematical model is an adsorption phenomena occurrence on localized or nonlocalized adsorbent sites.

Brunauer-Emmett-Teller (BET) theory [8], widely used in porous structure characterization, and its generalization, the universal theory of adsorption (uniBET) [9]–[11], elaborated in our team assume the localized adsorption, i.e. the adsorption process is viewed as a condensation of adsorbate molecules on localized adsorbent sites, where local minima of adhesion energy are reached (e.g. in cavities, niches etc. for nonpolar adsorbents). On the other hand, potential adsorption theories, i.e. Dubinin-Radushkievitch (DR) and Dubinin-Astachov (DA) models [11], [12], also used in characterization of microporous materials especially those of the carbonaceous origin, and recently strongly recommended Density Functional Theory (DFT) [13], [14], assume nonlocalized adsorption. Instead of discrete interactions between particles, they consider spatially distributed solid-fluid interactions, thus adsorbate is viewed as a quasi 2D fluid.

There may be found a number of theoretical studies concerning various mathematical adsorption models and their fitting to experimental data or improving fitting quality of these models, e.g. by introducing surface heterogeneity [15], [16]. However, no source provides direct analysis of adsorption phenomena assuming both the localized and nonlocalized mechanisms. In our opinion, identifying a proper mechanism allows to take the best mathematical adsorption model, enabling a more reliable evaluation of the material porous structure. Hence, identification of adsorption mechanisms, and their distinguishing criteria, seems to be significant in adsorption phenomena modeling.

In this paper, we present the novel method and its further development aimed to the adsorption process mechanism evaluation. Original results of numerical calculations, applied to the single–walled carbon nanotubes (SWCNT's) and carbon nanocones (CNC'c), are presented and discussed.

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II. Adsorbate Particle Volume Evaluation - Theoretical Basis

A. Thermodynamics and Kinematics

Following a line of the approach previously used in [17], [18], adsorption phenomena can be considered as a two-stage process: transition of molecules from their volatile phase to the liquid like reference state (in the first stage), and then – "mixing" of these molecules with adsorbent surface layer in the next stage. Thus, adsorption system at a temperature T can be described by the thermodynamic potential:

$$F = U^* - TS \tag{1}$$

where F is the Helmholtz free energy, U^* and S are an internal energy and entropy of the system, respectively.

When adsorbate is viewed as a an individual particle, continuously moving in a volume V near to the adsorbent wall, the same probability of finding its mass center at any point of this volume can be assumed. The internal energy U^* of the system may be expressed as the sum of the potential and kinetic energy terms. Thus, the formulae for internal energy and entropy are given by:

$$U^* = -\frac{1}{V}\int_0^V U(v,T)dv + c_v T\ ,\ S = k_B \ln V + S_0 \tag{2}$$

where k_B is Boltzmann constant, S_0 is the constant of no importance, the kinetic energy term includes molar specific heat c_v component, and the potential energy term includes an interaction potential $U(v, T)$ of the adsorbate molecule with individual carbon atoms forming a discrete adsorbent surface.

When considering an individual particle we may assume the pressure p=0. At the equilibrium temperature and volume the free energy F reaches its minimum, thus the derivative with respect to the volume occupied by the center of molecule mass fulfills the following equation:

$$\begin{aligned} &\left.\frac{\partial F}{\partial V}\right|_T = 0 \\ &\frac{\partial}{\partial V}\left(-\frac{1}{V}\int_0^V U(v,T)dv\right) - k_B T\frac{\partial \ln V}{\partial V} = 0 \end{aligned} \tag{3}$$

This leads to the equation for the boundary potential $U(V,T)$:

$$U(V,T) = U_{adh}(V,T) - k_B T \tag{4}$$

which may be solved by numerical integration of the intermolecular potential (since 0 to volume V), thus enabling to find the volume V occupied by the particle mass center and corresponding adhesion energy $U_{adh}(V,T)$, expressed as an average of the interaction potential $U(V,T)$ of individual adsorbate particle with discrete adsorbent surface.

On the other hand, (4) may be derived based on kinematic rules of adsorbate molecule movement in the space of volume V. This space is limited by a boundary equipotential surface at which the particle mass center movement accounts for two degrees of freedom (molecule translation movements are limited to the equipotential surface). Hence, kinetic energy equilibrated by this surface potential $U(V,T)$ (together with the adhesion energy $U_{adh}(V,\ T)$) is represented by the term k_BT.

The formula (4) may be used to find directly the temperature T at which the individual particle mass center is able to occupy the space of volume V:

$$T = \frac{1}{k_B}(U(V,T) - U_{adh}(V,T)) \tag{5}$$

In our view, the localized adsorption occurs on adsorbent sites where local minimum of adhesion energy is produced and its depth is enough to imply the space of volume V relatively small and separated from the spaces occupied by other particles. Thus, it is useful to define dimensionless intermolecular effective contact ratio:

$$\zeta = \frac{U_{adh}(V,T)}{E_{adh}} \tag{6}$$

where E_{adh} is molar adhesion energy of an ideal adsorbent-adsorbate contact, evaluated with the Berthelot rule (implementing Flory-Huggins theory [19]) as a combination of adsorbate and adsorbent cohesion energies. For adsorption measurements performed at the liquid adsorbate boiling temperature, cohesion energy may be defined as the molar energy E_{vap} of adsorbate vaporization, whereas adsorbent cohesion energy expression involves adsorbent solubility parameter δ_c and adsorbate molar volume V_m:

$$E_{adh} = 2\delta_c\sqrt{E_{vap}V_m} \tag{7}$$

where parameter δ_c can be evaluated with the method of van Krevelen [20] and molar energy E_{vap} of adsorbate vaporization is reported elsewhere (i.e. H_{vap}-RT, where H_{vap} is molar enthalpy of vaporization) [21]. In our calculations the molar volume V_m is evaluated by replacing the real space V with the equivalent sphere of the same volume:

$$V_m = \frac{4}{3}\frac{\pi}{\eta}\left[\left(\frac{3}{4}\frac{V}{\pi}\right)^{\frac{1}{3}} + \frac{\sigma}{2}\right]^3 \tag{8}$$

where η is the fluid packing ratio (we assumed the cubic lattice, hence $\eta = 0.51$), σ is the hard sphere core diameter.

B. Material Structure Model Description

In order to model the interaction potential of individual adsorbate particle with adsorbent surface, we selected armchair, one-side capped SWCNT and open CNC:

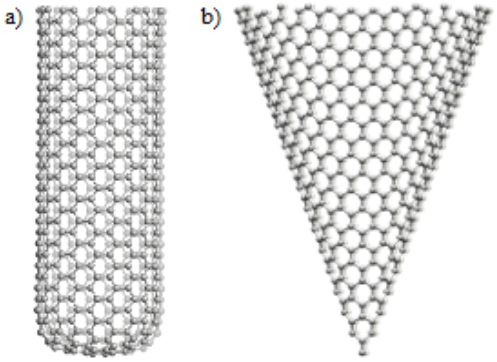

Fig. 1 a) Armchair, one-side capped SWCNT model, parameters: height 4,0 nm, diameter 1,1 nm, b) open CNC model, parameters: height 3,9 nm, diameter 2,5 nm, discilination angle 240° (parameters are measured as a distance between the centers of the carbon atoms)

A discrete description of the nanocarbons surface that distinguishes explicitly carbon atoms was achieved by the assumption of surface representation with a single graphene sheet. We further assumed that graphene surface is rigid, smooth and there are no surface functional groups. Therefore, only the physical adsorption is considered, while corrugation effects and bulges are eliminated and surface chemical heterogeneity is neglected.

Interaction of individual adsorbate particle with surface carbon atom is described with 12-6 Lennard-Jones (12-6 LJ) pair potential:

$$U(V) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{9}$$

where r is the separation distance between adsorbate molecule and graphene carbon atom, ε and σ are potential parameters: well depth of adsorbate-carbon atom site interaction and effective adsorbate-carbon intermolecular diameter, respectively. 12-6 LJ parameters were simply obtained applying Lorentz-Berthelot mixing rules, as suggested by Steele [22]:

$$\sigma = \frac{\sigma_{ss} + \sigma_{ff}}{2}, \quad \varepsilon = \sqrt{\varepsilon_{ss}\varepsilon_{ff}} \tag{10}$$

where subscript *ss* denotes the parameter value for surface carbon-carbon interaction and subscript *ff* denotes fluid-fluid interaction of pure adsorbate.

The 12-6 LJ potential parameters were chosen to provide the best calculation results. Adsorbate molecular diameter σ_{ff} was calculated with the following formula [23], [24]:

$$\sigma_{ff} = 2\left(\sqrt[3]{\frac{3}{4}\frac{V_c\eta_c}{\pi}}\right) \tag{11}$$

where V_c is adsorbate critical volume and η_c is critical packing ratio (in our earlier papers we have found that $\eta_c = 0{,}13$ [23], [24]). The molecular diameters for SWCNT and CNC, carbon-carbon interactions are reported elsewhere [25]. Potential well depth values were fitted to the numerical calculations in order to fulfill numerical constraints, nevertheless newly obtained parameters are close to the standard literature values [22]. Potential parameters used in numerical calculations are summarized in Table I.

III. Adsorbate Particle Volume Evaluation – Numerical Calculations

Numerical calculations of adsorbed particle volume were performed for hydrogen – open, armchair, one-side capped SWCNT and hydrogen – open CNC pairs with 12-6 LJ interaction parameters presented in Table I.

Interestingly, interaction potential and adhesion energy of individual hydrogen particle in SWCNT (Fig. 2) are noticeably lower than in case of hydrogen particle in open CNC (Fig. 3) – lower energy minimum well depth is produced. Moreover, the obtained, relatively high values of adsorbate particle molar volumes for SWCNT calculations suggest low adsorbate average density, whereas in the case of CNC hydrogen properties are closer to a liquid like state. Concentration degrees, related directly to the adsorbate-adsorbent intermolecular contact, are also confirmed by the intermolecular effective contact ratio values in its temperature profile presented in Fig. 4 for armchair SWCNT and in Fig. 5 for CNC.

Moreover maximum value for SWCNT is noticeably lower, ζ=0.6 (and was obtained beyond boiling temperature region) than in case CNC calculations where ζ=0.9 (maxim ratio region is obtained near boiling temperature).

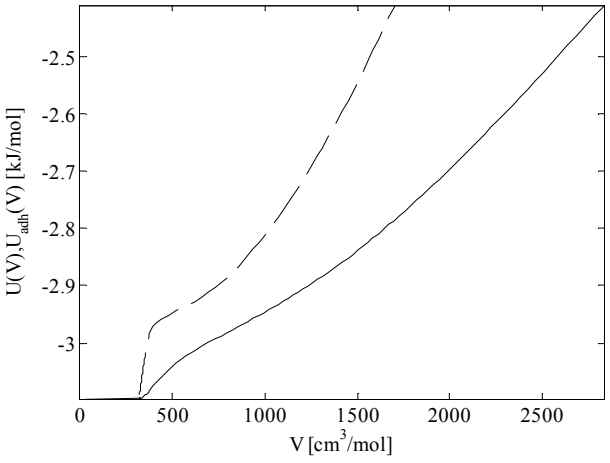

Fig. 2 Results of numerical calculations: interaction potential $U(V)$ (dashed line) and adhesion energy $U_{adh}(V)$ (solid line) of individual hydrogen particle in armchair, one-side capped SWCNT

TABLE I
12-6 Lennard-Jones Interaction Parameters Used in Particle Volume Numerical Calculations

Adosrbate/ adsorbent	Parameter	Value [nm]	Parameter	Value [K]
Hydrogen	σ_{ff}	0,3011	ε_{ff}/k_B	29,2
SWCNT	σ_{ss}	0,3514	ε_{ss}/k_B	35,9
CNC	σ_{ss}	0,3350	ε_{ss}/k_B	23,7

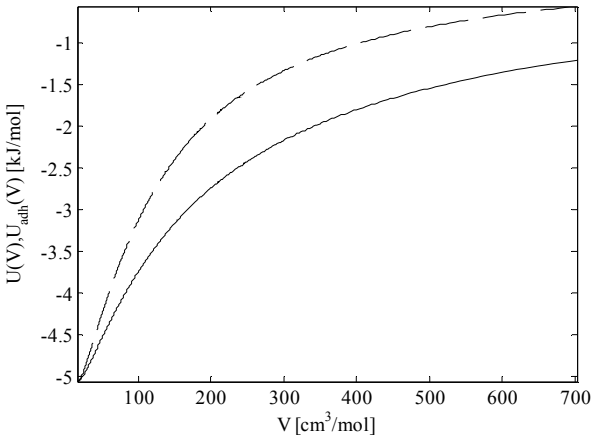

Fig. 3 Results of numerical calculations: interaction potential $U(V)$ (dashed line) and adhesion energy $U_{adh}(V)$ (solid line) for individual hydrogen particle in open CNC

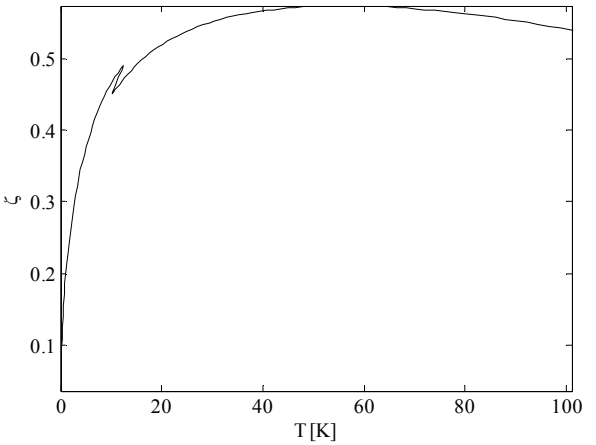

Fig. 4 Results of numerical calculations: intermolecular effective contact ratio ζ versus temperature T for individual hydrogen particle in armchair, one-side capped SWCNT

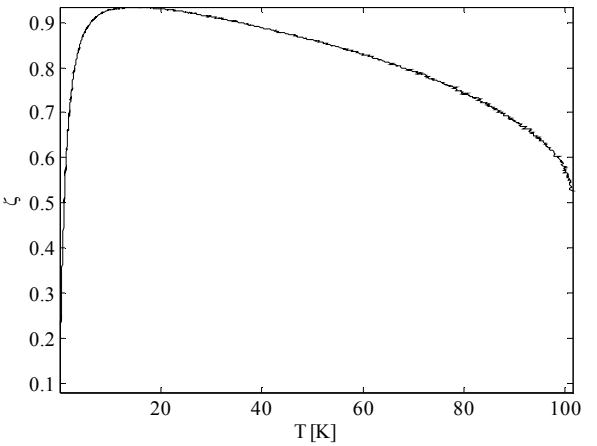

Fig. 5 Results of numerical calculations: intermolecular effective contact ratio ζ versus temperature T for individual hydrogen particle in open CNC

Finally, evaluated adsorbate molar volumes are shown in Fig. 6 for SWCNT and Fig. 7 for CNC. Resultant molar volume of individual hydrogen particles in contact with SWCNT surface lies above the critical volume, which means that hydrogen is in a dilute liquid like state. Considering both the latter and the fact that local minimum of adsorption energy is produced, suggests localized adsorption mechanism. Nevertheless, it is also noticeable that the space available for the adsorption of hydrogen molecule inside the nanotube is almost equal to the molecule size (compare nanotube diameter and effective diameter of 12-6 LJ parameters). This strongly affects calculation results and should be considered as the model application constraint. Thus probably the obtained results come from exohedral adsorption (instead of endohedral) on the edges of open side of nanotube. As a consequence, the assessment of adsorption mechanism in case of small SWCNT's is ambiguous.

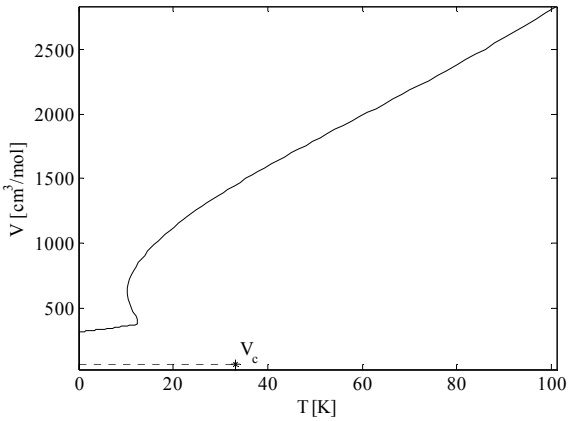

Fig. 6 Results of numerical calculations: adsorbate particle volume V versus temperature T for individual hydrogen particle in armchair, one-side capped SWCNT

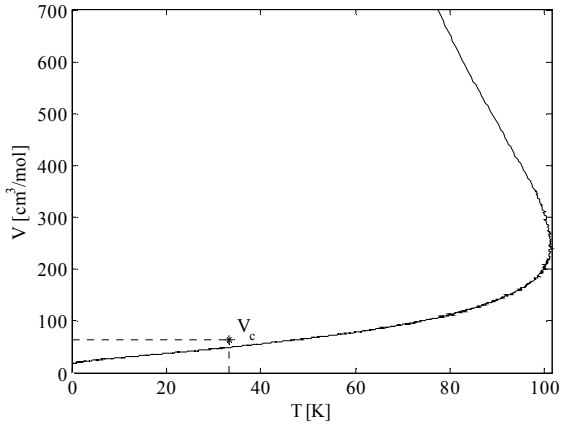

Fig. 7 Results of numerical calculations: adsorbate particle volume V versus temperature T for individual hydrogen particle in open CNC

The results of volume calculations for individual hydrogen particle in contact with CNC surface clearly suggests localized adsorption mechanism inside the cone. In this case the local

minimum of adhesion energy enables hydrogen molecules to occupy volume lower than the critical volume. As a result hydrogen molecules are compressed to a liquid like state.

Interestingly, for both adsorption systems we observe a temperature range in which one temperature value produces two volume values. We believe this is the consequence of hydrogen metastable states due to coexistence of two phases: liquid like and bulk (orthobaric volume description).

In order to get more insight into the adsorption mechanisms, the numerical calculations were completed with the analysis of the shape of equipotential surfaces. It may be seen in Fig. 8 – SWCNT and Fig. 10 – CNC, that surface contour sections in both cases are closed. This important feature implies localized adsorption in both cases. Nevertheless, as it was pointed out before, the obtained volume is higher in case of SWCNT. Moreover, roughness of the contour along the SWCNT z(x) axis is the result of the discrete surface description.

Example cross sections of the equipotential surfaces for SWCNT and CNC are presented in Figs. 9 and 11.

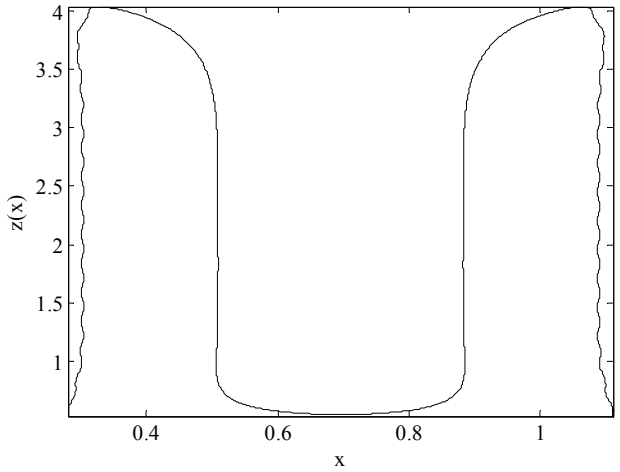

Fig. 8 Contour of the section of equipotential surface along the (z(x) axis) armchair one-side capped SWCNT

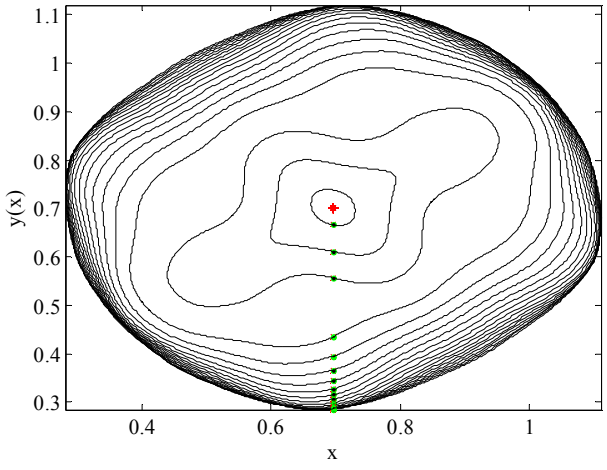

Fig. 9 Contours of the cross section of equipotential surface across armchair, one-side capped SWCNT

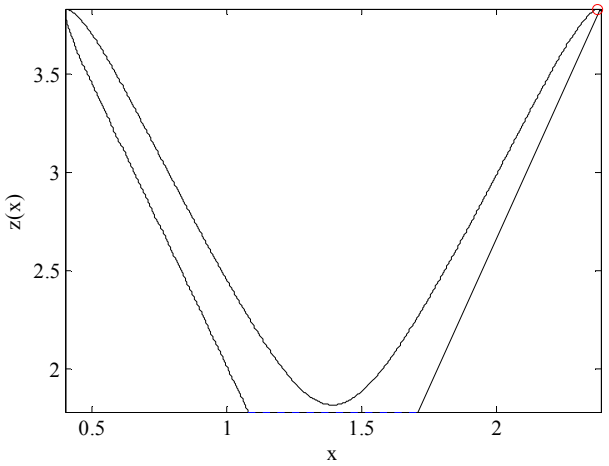

Fig. 10 Contour of the section of equipotential surface along the (z(x) axis) open CNC

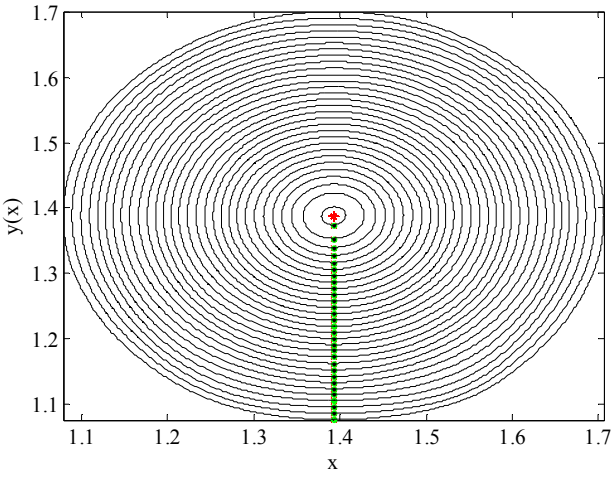

Fig. 11 Contours of the cross section of equipotential surface across (xy axes) open CNC

All calculations and plots were performed with our own software working on MATLAB® platform.

IV. Conclusions

Application of the numerical tools presented in this paper is a significant development of the works lead in Authors' team, focused on adsorption phenomena mathematical modeling and aimed at identifying the material porous structure.

The proposed thermodynamic description and calculation tools enable to get an insight into adsorption mechanisms on armchair, one-side capped SWCNT and open CNC. This allows to employ more appropriate adsorption model (e.g. uniBET or DFT), thus to obtain more reliable information on the material porous structure.

Numerical calculations discussed in the paper allow to evaluate adsorbate particle molar volume, intermolecular effective contact ratio ζ, and show the shape of the equipotential surface. The analysis of this shape enables to get

a direct insight into hydrogen adsorption on nanocrabon surfaces mechanism. This possibility is the important advantage of the discussed numerical tool.

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REFERENCES

[1] J. T. Duda, J. Milewska-Duda, M. Kwiatkowski, M. Ziółkowska, "A geometrical model of random porous structures to adsorption calculations", *Adsorption*, vol. 19, pp. 545-555, Feb. 2013.
[2] H.-M. Cheng, Q.-H. Yang, C. Liu, "Hydrogen storage in carbon nanotubes", *Carbon*, vol. 39, pp. 1447-1454, Aug. 2001.
[3] Y. Gogotsi, R. K. Dash, G. Yushin, T. Yildirim, G. Laudisio, J. E. Fischer, "Tailoring of nanoscale porosity in carbide-derived carbons for hydrogen storage", *J. Am. Chem. Soc.*, vol. 127, pp. 16006-16007, Oct. 2005.
[4] X. Zhang, W. Wang, J. Chen, Z. Shen, "Characterization of a sample of single-walled carbon nanotube array by nitrogen adsorption isotherm and Density Functional Theory", *Langmuir*, vol. 19, pp. 6088-6096, May 2003.
[5] S. Iijima, "Helical microtubules of graphitic carbon", *Nature*, vol. 354, pp. 56-58, Nov. 1991.
[6] S. N. Naess, A. Elgsaeter, G. Helgesen, K. D. Knudsen. "Carbon nanocones: wall structure and morphology", *Sci. Technol. Adv. Mater.*, vol. 10, pp. 065002-065008, Dec. 2009.
[7] O. O. Adisa, B. J. Cox, J. M. Hill, "Open carbon nanocones as candidates for gas storage", *J. Phys. Chem. C*, vol. 115, pp. 24528–24533, Nov. 2011.
[8] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, "Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity", *Pure Appl. Chem.*, vol. 57, pp. 603-619, Apr. 1985.
[9] J. Milewska-Duda, J.T. Duda, "New BET-like models for heterogeneous adsorption in microporous adsorbents", *Appl. Surf. Sci.*, vol. 196, pp. 115-125, Aug. 2002.
[10] J. T. Duda, J. Milewska-Duda, „Modeling of Surface Heterogeneity of Microporous Adsorbents with LBET Approach", *Langmuir*, vol. 21, pp. 7243-7256, Jun. 2005.
[11] M. M. Dubinin, "Modern state theory of gas and vapour adsorption by microporous adsorbents", *Pure Appl. Chem.*, vol. 10, pp. 309-322, Apr. 1965.
[12] M. M. Dubinin, "Fundamentals of the theory of adsorption in micropores of carbon adsorbents: characteristics of their adsorption properties and microporous structures", *Pure Appl. Chem.*, vol. 61, pp. 1841-1843, Nov. 1989.
[13] M. Ziółkowska, J. T. Duda, J. Milewska-Duda, "Adsorption mechanisms in a view of DFT and clustering-based models", in *Proc. of International Youth Science Festival: Litteris et artibus, Chemistry and Chemical Technology*, Lviv, 2013, pp. 184-187.
[14] C. M. Lastoskie, K. E. Gubbins, N. Quirke, „Pore size distribution analysis of microporous carbons: a Density Functional Theory approach", *J. Phys. Chem.*, vol. 97, pp. 4786-479, May 1993.
[15] A. Dąbrowski, "Adsorption from theory to practice", *Adv. Colloid Interface Sci.*, vol. 93, pp. 135-224, Oct. 2001.
[16] J. Jagiełło, J. P. Olivier, "2D-NLDFT adsorption models for carbon slit-shaped pores with surface energetical heterogeneity and geometrical corrugation", *Carbon*, vol. 55, pp. 70-80, Apr. 2013.
[17] M. Kwiatkowski, M. Ziółkowska, J. Milewska-Duda, J. T. Duda, "Applicability of the universal uniBET adsorption theory to silica gel structure description", in *Proc. Science and Technology Conference "Mineral Sorbents": Raw Materials, Energy, Environment, Modern Technologies*, Cracow, 2013, pp. 269-284.
[18] M. Ziółkowska, J. T. Duda, J. Milewska-Duda, M. Kwiatkowski, "Applicability of mathematical description of adsorption measurements and adsorption mechanism in prediction of gas deposits in microporous materials", in *Proc. International Forum – Contest: Topical Issues of Rational Use of Natural Resources*, Saint Petersburg, 2014, pp. 44-46.
[19] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.
[20] D. W. van Krevelen, *Coal: Typology, Physics, Chemistry, Constitution.* Elsevier, New York, 1993.
[21] Chemical Engineering and Materials Research Center (CHERIC), on-line, 26.07.2014: http://www.cheric.org.
[22] W. A. Steele," The physical interaction of gases with crystalline solids I. Gas-solid energies and properties of isolated adsorbed atoms", *Surf. Sci.vol.* 36, pp. 317-352, Apr. 1973.
[23] J. Milewska-Duda, Jan Duda, G. Jodłowski, M. Wójcik, „A new state equation for sorptives in near-critical and overcritical temperature regions", *Langmuir*, vol. 16, pp. 6601-6612, Jul. 2000.
[24] J. Milewska-Duda, Jan Duda, „High-accuracy PVT relationship for compressed fluids and their application to BET-like modelling of CO_2 and CH_4 adsorption", *Adsorpt. Sci. Technol.*, vol. 25, pp. 543-559, 2007.
[25] M. Kaukonen, A. Gulans, P. Havu, E. Kauppinen, "Lennard-Jones Parameters for Small Diameter Carbon Nanotubes and Water for Molecular Mechanics Simulations from van der Waals Density Functional Calculations", *J. Comput. Chem.*, vol. 33, pp. 652–658, Jan. 2012.