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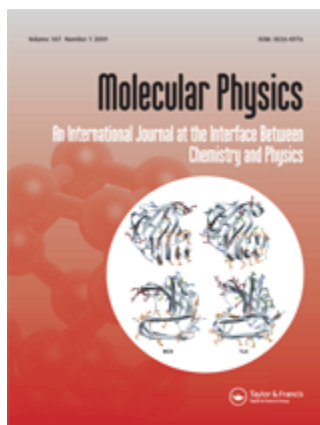
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Density profiles of atoms in nano-tubes from an analytic method. Hydrogen in a cylindrical pore

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17 Density profiles of atoms in nano-tubes from an analytic
18 method. Hydrogen in a cylindrical pore.
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Knowledge of the structure of simple fluids in nano-tubes constitutes an important information in many scientific and technical branches. Computer simulations and density functional theory (DFT) offer accurate but laborious results. We have proposed a simple analytical method to determine the background correlation function on the basis of the residual chemical potentials of a pair of interacting bodies and of the corresponding combined body. These potentials are obtained in terms of geometric quantities. In this paper we dealt with the combination rule for the geometric quantity Q ; the harmonic mean rule was proposed and verified at low densities by calculating the third cross virial coefficient, and by comparing calculated density profiles of the inhomogeneous systems of hard sphere-wall at higher densities. A slight improvement over the previous results were found. Next, we applied our analytic method to realistic systems of a simple molecule in the graphite cylindrical pore. Hydrogen (and carbon monoxide), interacting with carbon of the graphite *via* the modified LJ potential are considered and the density profile was determined taking into account only the soft-sphere interaction within Weeks-Chandler-Andersen approximation. The considered approach was found to yield a fair description of the realistic simple fluid-cylindrical pore system.

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Key words: Inhomogeneous system, Cylindrical pore, Hydrogen, Carbon oxide, Graphite nanotube, Background correlation function, Geometric method for rdf

Introduction

Presently available products of nanotechnologies show very promising potential in rather different branches of human activities, such as e.g. in medicine, biochemistry, applied chemistry (sorption, separation, catalysis), electro-technique[1], and simple gas storage[2,3]. At present the nanoproducts are the result of preparative work performed in several world laboratories; among these products graphite nanotubes seem to be the most important.

In theory, the basic information stem from the simulations of different simple inhomogeneous systems[4-6]; these simulations mimic the behavior of molecules (their simple models) near a planar wall (adsorption), in pores or tubes. These data have been also used to verify purely theoretical results. Theoretical approaches represent extensions of physical methods used for the description of the homogeneous systems - e.g. solutions of the integro-differential equations, i.e. BBGY[7] or Ornstein-Zernicke integral equation[8]; most often the density functional theory (DFT)[9,10] has been considered. These approaches are often very successful, however, some input data are necessary at the beginning and the calculations are up to now performed for simple models of molecules - spheres and dumbbells.

Recently, we have proposed a simple analytical method, which allows to determine the background correlation function on the basis of the residual chemical potentials of a pair of interacting hard spheres (and other hard bodies) and that of the so called combined body (resulting from overlapping of the pair of molecules). The residual chemical potentials, derived from the expressions for the residual Helmholtz energy (or the equation of state) of considered systems are a function of the bulk density (packing fraction) and geometric quantities (volume, surface area, mean radius), characterizing the geometry of the individual hard models inclusive the combined body.

In the case of inhomogeneous systems, the self-consistent expressions for the chemical potential and/or equation of state is adequate to use, because of conditions similar to the colloidal limit. Such expressions were used in the previous applications of the mentioned "geometric" method to get the density profiles of the hard molecules in the different inhomogeneous systems *via* the background correlation function (cavity function), Y , defined as $Y(x) = \exp[u(x)/kT]g(x)$ (where u and g stand for the pair potential and radial distribution function and x is the reduced distance). In the hard sphere system, $Y = g^{hs}$ for $x \geq 1$; for $x < 1$ Y is related to the direct correlation

function, c .

In the case of molecular models with soft-sphere repulsions, the (reference) radial distribution function results from multiplying the definition expression of Y by $\exp[-u(x)/kT]$, similarly as was used in the case of homogeneous systems by Barker and Henderson[8] and Weeks, Chandler and Andersen(WCA)[11].

The residual chemical potentials might be evaluated on the basis of geometric characteristics - a volume, V , surface area, S , mean radius, R (more precisely the mean curvature integral, divided by 4π) and by quantity Q , defined by inequalities $S/4\pi \leq Q \leq R^2$. In treatments of the hard body virial coefficients, Q has been approximated by the arithmetic or geometric mean (GM) from $S/4\pi$ and R^2 . In this paper we employ the harmonic mean. This rule proved to fit our recent quantum mechanical calculations of intermolecular interactions[12] of N_2 and CO (it is known e.g. from the kinetic theory of gases[8] as a rule to get the mean molecular mass \bar{m}).

The paper is organized as follows: In the first part, the new rule for Q is considered. We employed the third cross virial coefficient and the corresponding simulation data to verify the validity of the rule at low densities; density profiles of several inhomogeneous systems were evaluated and compared with simulation data in order to verify the rule (in comparison with GM) at higher densities.

Next, we evaluate density profile of hydrogen in the cylindrical pore - graphite nanotube. In this study we assume that the distribution function is governed by the repulsive part of the interaction potential.

Theory

Basic considerations

The expression which forms a basis of the determination OF THE DENSITY PROFILES [I.E. DEPENDENCE OF THE LOCAL DENSITY $\rho(x^*) = \rho_{bulk} \cdot g(\rho_{bulk}, x^*)$ (WITH g STANDING FOR THE DISTRIBUTION FUNCTION) ON THE REDUCED DISTANCE $x^* = r_{ij}/\sigma$] OF THE HARD SPHERE (HS) SYSTEMS IS OBTAINED *via* A RELATION BETWEEN THE BACKGROUND CORRELATION FUNCTION (OR CAVITY FUNCTION), $Y = \exp[u/kT] \cdot g(\rho_{bulk}, x^*)$, AND RESIDUAL CHEMICAL POTENTIALS OF THE PAIR OF HSs AND THE CORRESPONDING COMBINED BODY (CB), $\Delta\mu_i$, resp. $\Delta\mu^{CB}$. FUNCTION Y IS CONTINUOUS

FOR ALL $x^* \geq 0$; for $x^* \geq 1$ $g(x^*) = Y(x^*)$. (FOR $x^* < 1$ THE SIMPLEST CB IS A DUMBBELL WITH SITE-SITE DISTANCE x^*). THE EXPRESSION FOR THE BACKGROUND FUNCTION, Y , IN TERMS OF THE RESIDUAL CHEMICAL POTENTIALS OF HARD BODIES FOLLOWS FROM THE DEFINITION OF THE CHEMICAL POTENTIAL IN TERMS OF THE CONFIGURATIONAL INTEGRALS; FOR $Y_{ij}(x^*)$ IT HOLDS [13,14]

$$kT \ln Y_{ij}(x^*) = \Delta\mu_i + \Delta\mu_j - \Delta\mu^{CB}(x^*) \quad (1)$$

where $\Delta\mu_i$ stands for the residual chemical potential of a molecule of type i , index CB denotes the combined body, k - Boltzmann constant and T - temperature. The relation for $\Delta\mu_i$ can be derived from the expression for the residual Helmholtz energy of the hard body mixtures, ΔA_s . In the case of inhomogeneous systems it is desirable to use a self-consistent equation (c.f. Refs.[15-17]), such as

$$\Delta A_s/NkT = -\ln(1-\eta) + \frac{3\alpha\eta}{(1-\eta)} + \frac{\beta\eta^2(3/2 - 2\eta/5)}{(1-\eta)^2} \quad (2)$$

Here η denotes the packing fraction $\eta = \rho_{bulk} \cdot V^{HB}$ and α and β two non-sphericity parameters

$$\alpha = r_s s_s / 3v_s, \quad \beta = q_s s_s^2 / 9v_s^2$$

(with $r_s = \rho \sum x_k R_k$, $s_s = \rho \sum x_k S_k$, $v_s = \rho \sum x_k V_k$, $q_s = \rho \sum x_k Q_k$; S, V, R, Q are geometric characteristics of hard bodies, I.E. SURFACE AREA, VOLUME, MEAN RADIUS = THE MEAN CURVATURE INTEGRAL, DIVIDED BY 4π , AND A QUANTITY OF THE DIMENSION [l^2], DISCUSSED LATER ON). The corresponding hard sphere equation of state possesses a form

$$Z = \frac{1}{(1-\eta)} + \frac{3\alpha\eta}{(1-\eta)^2} + \frac{\beta\eta^2(3 - 6\eta/5 + 2\eta^2/5)}{(1-\eta)^3} \quad (3)$$

(For pure hard spheres the calculated compressibility factor $Z = 13$, in agreement with the generally accepted value).

The corresponding expression for the residual chemical potential reads as

$$\Delta\mu_i/kT = -\ln(1-\eta) + \frac{\eta}{(1-\eta)} [3\alpha(R^* + S^*) + V^*] +$$

$$+\frac{\eta^2}{(1-\eta)^2}[\beta(Q^*+2S^*)(3/2-\eta/3)+3\alpha V^*]+\frac{\eta^3}{(1-\eta)^3}[12/5-2\eta/5]\beta V^* \quad (4)$$

For pure HS system $R^* = 2R/\sigma$, $S^* = S/\pi\sigma^2$, $V^* = V/(\pi\sigma^3/6)$ and $Q^* = 4Q/\sigma^2$; for mixtures $2R_i^* = R_i/(x_i\sigma_i + x_j\sigma_j)$ etc. If we define

$$\Delta X = X_i^* + X_j^* - X^{CB*} \quad (5)$$

where $X = R, S, V, Q$ we can write for pure HS fluid (for which $\alpha = 1, \beta = 1$)

$$kT \ln Y_{ij} = -\ln(1-\eta) + \frac{\eta}{(1-\eta)}[3(\Delta R^* + \Delta S^*) + \Delta V^*] +$$

$$\frac{\eta^2}{(1-\eta)^2}[(\Delta Q^* + 2\Delta S^*)(3/2-\eta/3) + 3\Delta V^*] + \frac{\eta^3}{(1-\eta)^3}[12/5-2\eta/5]\Delta V^* \quad (6)$$

EXPRESSING Y IN TERMS OF DIFFERENCES OF GEOMETRIC QUANTITIES INSTEAD OF INDIVIDUAL CONTRIBUTIONS TO $\Delta\mu_i$ SIMPLIFIES NOTABLY THE FURTHER CONSIDERATIONS. THUS, FOR PURE HARD SPHERE SYSTEMS AND $\theta = \arcsin(x^*/2) \leq \pi/3$ WE OBTAINED

$$\Delta R^* = 1 - \sin \theta + \theta \cos \theta \quad \Delta S^* = 1 - 2\theta \cos \theta$$

$$\Delta V^* = 1 - 2 \sin \theta - 4 \cos^2 \theta \sin \theta + 3\theta \cos \theta \quad \Delta Q_{NL}^* = \Delta S^* - (1/2)(x^{*2}/4)$$

Geometric quantities

In this paper we study the behavior of hard or soft sphere near a hard wall or in a pore. In the former case the pair of interacting bodies is composed of a hard sphere and hard disc (eventually a thin hard cylinder); in the case of a pore we have HS and a spherical cup; see Fig. 1. FOR PURE HS FLUIDS, the geometric characteristics of HS possess simple values: $R_i^* = S_i^* = V_i^* = Q_i^* = 1$. Similar characteristics of the disc (a cylinder of the reduced height $l^* = 0$) are $R_w^* = (\pi/2) \cos \theta$, $S_w^* = 2 \cos^2 \theta$, and $V_w^* = 0$. The reduced value of Q_w^* for the wall, taken as an infinitely thin disc is (see further discussion) $Q_w^* = 4\pi^2 \cos^2 \theta / (8 + \pi^2)$.

The combined body is composed of a part of the sphere (with radius $r = \sigma/2$, saddle part, given by the probe sphere with radius r_p , WHICH FOR PURE HS IS EQUAL TO r . COMBINED BODY is closed by the disc (of radius

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8 $r_w = \sigma \cos \theta$). IF we denote GENERALLY the ratio $2r_i/\sigma = p$, $2r_p/\sigma = q$
9 and employ the method of Connolly[18], we can express R^{CB*} , S^{CB*} , V^{CB*}
10 as follows
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$$12 \quad R^{CB*} = R_i^* - \frac{1}{2}(p - q) + \frac{1}{2}(p + q) \sin \theta - \frac{1}{4}(p + q) \left(\frac{\pi}{2} + \theta - 2\phi \right) \cos \theta + \\ 13 \quad \quad \quad + \frac{1}{2}(p + q) \left(\frac{\pi}{2} + l^* \right) \cos \theta - q \sin \phi \quad (7)$$

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$$19 \quad S^{CB*} = S_i^* - \frac{1}{2}(p^2 + q^2) + \frac{1}{2}(p^2 - q^2) \sin \theta + \frac{1}{2}q(p + q) \left(\frac{\pi}{2} + \theta - 2\phi \right) \cos \theta \\ 20 \quad \quad \quad + [(p + q) \cos \theta / 2]^2 (1 + 4l^*) + q^2 \sin \phi \quad (8)$$

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23 and

$$24 \quad V^{CB*} = V_i^* - \frac{1}{2}(p^3 - q^3) + \frac{1}{2}(p^3 + q^3) (\sin \theta + \cos^2 \theta \sin \theta / 2) + \\ 25 \quad \quad \quad + \frac{3}{4}q(p + q) \cos^2 \theta [p(1 + \sin \theta) + q] - \frac{3}{4}q^2(p + q) \left(\frac{\pi}{2} + \theta - 2\phi \right) \cos \theta - \\ 26 \quad \quad \quad - q^3 \sin \phi - \frac{1}{2}q(p + q)^2 \cos^2 \theta \sin \phi + 6(p + q)^2 \cos^2 \theta / 4 * l \quad (9)$$

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36 The above expressions are valid for inhomogeneous systems of hard bodies
37 (hard sphere, hard dumbbell perpendicular to the wall, etc.) near a hard wall,
38 with R_i^* , S_i^* , V_i^* standing for the geometric quantities of the fluid molecules.
39 For θ , which is defined for THE HARD WALL on the basis of the distance
40 HS center - wall, $z^* = z/\sigma$ $\theta = \arcsin(z^*)$; if $\theta < \pi/3$ $\phi = 0$, for larger θ it
41 holds true $\cos \phi = (p + q) \cos \theta / q$.

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43 In the case of hard sphere in a spherical pore, the geometric quantities of the
44 wall and CBs depend on the reduced pore radius $R_r^* = R_r/\sigma$. For detailed
45 calculation, angle γ was introduced; it determines the size of the contact
46 area, see Fig 1. For the single wall pore ($l=0$), the following equations for
47 the respective geometric functionals were used:
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$$49 \quad R^{CB*} = R_i^* - \frac{1}{2}(p - q \cos \gamma) + \frac{1}{2}(p + q) \sin \theta - \frac{1}{4}(p + q) \left(\frac{\pi}{2} + \theta + \gamma - 2\phi \right) \cos \theta \\ 50 \quad \quad \quad - q \sin \phi + \frac{\pi}{2} R_r^* \sin \gamma \quad (10)$$

$$S^{CB*} = S_i^* - \frac{1}{2}(p^2 + q^2 \cos \gamma) + \frac{1}{2}(p^2 - q^2) \sin \theta + \frac{1}{2}q(p+q)\left(\frac{\pi}{2} + \theta + \gamma - 2\phi\right) \cos \theta + q^2 \sin \phi + 2R_r^2(1 - \cos \gamma) \quad (11)$$

$$V^{CB*} = V_i^* - \frac{1}{2}(p^3 - q^3) + \frac{1}{2}(p^3 + q^3)(\sin \theta + \cos^2 \theta \sin \theta/2) + \frac{3}{4}q(p+q) \cos^2 \theta [p(1 + \sin \theta) + q] - \frac{3}{4}q^2(p+q)\left(\frac{\pi}{2} + \theta - 2\phi\right) \cos \theta - q^3 \sin \phi - \frac{1}{2}q(p+q)^2 \cos^2 \theta \sin \phi + 2R_r^3(2 + \cos \gamma)(1 - \cos \gamma)^2 \quad (12)$$

These two sets of the reduced geometric quantities find their use in evaluation of the residual chemical potentials either in the case of a hard body (HB) near a hard wall or HB in a spherical pore. In the case of cylindrical pore the probe sphere creates on the inner surface of the cylinder a 3D ellipses. We approximated its geometric quantities as a mean of values for planar and spherical pore walls.

BY LEAVING THIS PART WE WOULD LIKE TO MENTION THAT, BESIDES z^* , ALSO THE DISTANCE $r^* = r\sigma$ MEASURED FROM THE PORE CENTER OR TUBE AXIS HAS BEEN USED IN THE RELEVANT STUDIES

Approximation for functional Q

The geometric quantity Q , which is of the dimension $[l^2]$, is defined by the inequality

$$S/(4\pi) \leq Q \leq R^2 \quad (13)$$

Naumann and Leland[19] (NL) approximated Q by the arithmetic mean of the utmost quantities, i.e. $Q^* = (R^{*2} + S^*)/2 \simeq S^* + (1/2)(x^{*2}/4)$. We originally considered[20] the geometric mean(GM), i.e. $Q^* = R^* \sqrt{S^*}$. Later on, the modified GM of the form

$$Q^* = R^{*2}(\sqrt{S^*/R^*})^{1/2} \quad (14)$$

has been used in several papers[21]. Here we introduce a harmonic mean (HM), which we found recently to describe fairly well quantum mechanical results found for interactions of simple molecules[12]

$$2/Q^* = 1/R^{*2} + 1/S^* \quad (15)$$

Simulation data on the third cross virial coefficients of a pair of hard spheres plus a hard dumbbell(HD) yield the indirect information on the dependence of Q^* on the site-site distance in a dumbbell. Such data are available from the study of Labik et al[14]. In Fig.2. we plotted C_{112} as a function of the reduced HD site-site distance, x , for the harmonic mean (dashed line) and corrected geometric mean (full line) approximations. From the comparison better performance of the presently proposed method is obvious. Thus, harmonic mean approximation is used in the following part.

Interaction potentials of simple fluid-wall system

In this study we assume that hydrogen, carbon monoxide and carbon molecules of the wall interact originally *via* Lennard-Jones 12-6 potential. However, for the graphite wall a smeared potential has been considered. For single planar wall the potential possesses a form[22]

$$u^{10-4}(z) = 2\pi\varepsilon_{gs}/\sigma_{ss}^2 \left[\frac{2\sigma_{gs}^{12}}{5z^{10}} - \frac{\sigma_{gs}^6}{z^4} \right] \quad (16)$$

where subscript gs and ss denote gas-solid and solid-solid interaction parameters. Similar form with an additional term was used to describe interaction of fluid molecules with several layers of the solid wall.

For interaction of a LJ molecule with CARBON ATOMS OF a graphite cylindrical pore, a different potential form was proposed[23,24]

$$u^{10-4}(r, R_r) = 3\pi\varepsilon_{gs}\Phi\sigma_{gs}^2 \left[\frac{21}{32} \left(\frac{\sigma_{gs}}{R_r} \right)^{10} M_{11}(x) - \left(\frac{\sigma_{gs}}{R_r} \right)^4 M_5(x) \right] \quad (17)$$

where Φ denotes surface number density and M_n an integral

$$M_n(x) = \int_0^\pi \frac{d\phi}{(1+x^2-2x\cos\phi)^{n/2}} \quad (18)$$

The M_n integrals are determined numerically for the single reduced distances, x . The course of this potential is relatively sensitive to value of

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8 R_r^* . In Fig. 3. the reduced potential u/ε is plotted against x for H_2 - single
9 walled pore of the reduced radius $R_r^* = R_r/\sigma_{H_2}=3.5$.

10 The part of the potential curve on the left from the minimum, enlarged by
11 $|u_{min}|$), is taken in the Weeks-Chandler-Andersen variant[11] of the pertur-
12 bation theory as expression characterizing repulsive forces and $\exp[-(u +$
13 $u_{min})/kT]Y(r)$ is assumed to determine the structure of the soft-sphere sys-
14 tem. This approach is applied here, for inhomogeneous systems, too.
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17 Results and Discussion

18 Hard sphere inhomogeneous systems

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21 Determination of the density profile of hydrogen and its mixture starts with
22 evaluation of the background correlation function, Y . Thus, we studied firstly
23 the behavior of hard sphere - hard wall (PLANAR, SPHERICAL, CYLIN-
24 DRICAL) systems at conditions similar to those at which hydrogen (and its
25 mixture with CO) in the pore are considered.
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28 To this end we determined the density profile (given as a product of the
29 background correlation function, Y , and bulk density ρ_b) of HS in a spheri-
30 cal pore of the reduced radius $R_r^* = 2.1$ and $\rho_b = 0.5$. The calculated density
31 $\rho^*(x^*)$ is compared with data of González et al[25] in Fig. 4. One can
32 find very good agreement with the simulation data in the whole interval
33 $r^* \in (0.4, 1.4)$. (A slight improvement in comparison with results obtained
34 from an approach with the corrected geometric mean was found). Next, we
35 determined the HS-density profile in the hard sphere-cylindrical pore of $R_r^* =$
36 4 and the bulk density $\rho_b^* = 0.6$. Fig. 5. reveals again a good agreement with
37 pseudo-experimental data[26]. In the next figure, Fig. 6. we compare the-
38 oretical and experimental[25] results for HS in a cylindrical pore of $R_r^*=1.9$
39 and $\rho_b^*=0.55$; fair agreement is found. Finally, we considered the hard sphere
40 mixture[27] (with HS-diameters $\sigma_2/\sigma_1=2$, mole fraction of component 2 x_2
41 $= 0.2$ and bulk density $\rho_b^* = 0.3209$) near a hard wall ($r_p = \sum x_i r_i^2 / \sum x_i r_i$).
42 From Fig. 7. a fair agreement is apparent. Theoretical results plotted in
43 all four figures were calculated by means of the same procedure which was
44 formulated for a cylindrical pore, where Y is determined from differences in
45 all the geometric quantities obtained as an arithmetic mean of values for the
46 spherical pore (of the radius equal to that of a cylinder) and that of the
47 planar wall.
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53 Hydrogen and its mixture with CO in the graphite tube

To determine the density profile of hydrogen in a tube we applied the perturbation theory, in which it was assumed that the fluid structure depended mainly on the repulsive forces; for soft sphere repulsions the distribution function might be, within WCA approximation[11], evaluated as the product of $\exp[-\beta(u + |\varepsilon|)]Y$.

Hydrogen in the single wall graphite nanotube was studied theoretically by Gu, Gao and Yu[24] who applied density functional theory (DFT) and compared their results with simulation data; the authors determined also density profiles for hydrogen and carbon monoxide (as compounds with simple, roughly spherical molecules); an equimolar mixture at 300 K was considered in armchair tubes (18,18), (30,30) and (35,35) at several bulk densities. The used characteristic potential parameters were $\sigma_{H_2} = 0.296$ nm, $\varepsilon_{H_2}/k = 36.7$ K, $\sigma_{CO} = 0.3763$ nm, $\varepsilon_{CO}/k = 100.2$ K and $\sigma_C = 0.335$ nm, $\varepsilon_C/k = 28.2$ K. The Lorentz-Berthelot combining rules were used to determine values of parameters of H₂-C-atom (of the tube wall). Gu, Gao and Yu in their paper presented the course of the interaction potentials of H₂ and CO in the mentioned tubes. We fitted their data for $r^* \leq r_{min}^*$, add $|\varepsilon|$ and determined u_{ref} . Similarly as Gu, Gao and Yu, we assumed $\sigma_{ref1} = \sigma_{C-H_2}$ (and $\sigma_{ref2} = \sigma_{C-CO}$).

In our calculations, we considered the bulk density $\rho_b = 0.5$, and the reduced radius of the tube (with respect to σ_{H_2}) $R_r^* = 2$ and 3.5. The courses of the representative pair potentials corresponding to the repulsive forces (left from the minimum) were obtained by fitting the results of Gu et al, see Fig. 8. With mentioned simplifications (concerning determination of the representative HSs) we obtained density profiles plotted in Fig. 9. One can see a fair agreement with simulation data[24] obtained for pure hydrogen (in the graphite pore) at similar conditions. Finally, we attempted to determine density profiles of a binary mixture of hydrogen and carbon oxide in a tube of radius $R_r^* = 3.5$. In our calculations we assumed, similarly as Gu et al, the representative diameters to be equal to the σ_{C-H_2} and σ_{C-CO} . The ratio of $\sigma_2/\sigma_1 = 1.271$, bulk density $\rho_b^* = 0.5$ and mole fraction $x_2 = 0.5$ were considered. We first determined Y_{C-H_2} and Y_{C-CO} in the equimolar mixture of hard spheres, assuming single walled tube; the obtained background functions, Y_i , were then multiplied by $\exp[-\beta(u_{rep})]$. The resulting profiles are plotted in Fig. 10. For sake of comparison we include results presented by Gu et al for the same mixture and armchair (30,30) graphite nanotube. It is obvious that the agreement is fair in the region around $z^* = 1$, but only

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8 qualitative for $z^* \approx 2$.
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10 11 Conclusion

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14 In this work we dealt firstly with the approximation for the geometric quantity Q which is included in the non-sphericity parameter β_s and consequently in the expression for the residual chemical potential. The comparison of the third cross virial coefficient C_{112} (of two HS and one HD), calculated with help of the harmonic mean, in comparison with that for the geometric mean, has shown slightly better prediction of C_{112} ; this finding gives evidence in favor of the new version of the Q -determination in the low-density systems. The general improvement is verified by applying the rule to variety of inhomogeneous systems, considered in figures 4-6.

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25 In the last paragraph we attempted to determine the density profile of realistic molecule in a tube. To this end, hydrogen was considered as a Lennard-Jones spherical molecule, whereas interactions of carbon atoms of graphite wall were approximated by carbon atoms uniformly distributed within the wall surface. For planar wall the (10-4) potential is often used. Contrary to these systems, the interaction of LJ-particle with the cylindrical wall is more demanding. Different ways of determining molecular interactions with planar and pore surfaces COMPOSED FROM SEVERAL LAYERS cause a problem when applying our method (in which we describe behavior of an atom in a cylindrical pore as a combination of results for planar wall and a spherical pore). Because of this fact we haven't solved the interaction potential in details and employed data in Ref.[24] to get the dependence of the repulsive part of the potential on the atom-wall distance.

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42 In conclusion it can be said that our analytical method and consecutive computer program, formulated on the basis of expressions (6)-(12) is quite general: with only minimum changes one can determine Y for planar wall, spherical or cylindrical pore. The procedure can also be easily modified for the case of HS outside the pore. In comparison with the physical (density functional) theory the discussed method is rather simpler and yields results immediately. With the expansion of nanotechnologies a quick information on the structure of the system might be quite important.

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53 **Acknowledgement** This work has been financially supported by the Grant Agency of the Academy of Sciences of the Czech Republic (Grant

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References

- [1] P.C. Collins, M.S. Arnold and P. Avouris, *Science* **292**, 706 (2001).
- [2] B. Buczek and L. Czepirski, *Energy and Environment* **1-2**, 1042 (2003).
- [3] H. Becher, H. Haluska, M. Hirscher et al, *Compt. Rend. Phys.* **4**, 1055 (2003).
- [4] B.K. Peterson, K.E. Gubbins, G.S. Heffelfinger, U. Marini, B. Marconi, and F. Vanswol, *J. Chem. Phys.* **88** 6487 (1988).
- [5] J.J Magda, M. Tirrell and H.T. Davis, *J. Chem. Phys.* **83**, 1888 (1985).
- [6] J. Vermesse and D. Levesque, *J. Chem. Phys.* **101**, 9063 (1994).
- [7] Y.Q. Zhou and G. Stell, *Molec. Phys.* **66**, 767 (1989).
- [8] D.A. McQuarrie, *Statistical Mechanics*. Harper and Row, New York 2003.
- [9] Y. Rosenfeld, *Phys. Rev. Lett.* **63**, 980 (1989).
- [10] Y. Rosenfeld, *Phys. Rev. E* **50**, R3318 (1998).
- [11] J.D. Weeks, D. Chandler and H.C. Andersen, *J. Chem. Phys.* **54**, 5237 (1971).
- [12] J. Fišer, T. Boublík and R. Polák, *Molec. Phys.* **101**, 3409 (2003).
- [13] E. Meeron and A.J.F. Siegert, *J. Chem. Phys.* **48**, 3139 (1968).
- [14] S. Labík, A. Malijeviský and I. Nezbeda, *Molec. Phys.* **60**, 1107 (1987).
- [15] D.H.L. Yau, K.Y. Chen and D. Henderson, *Molec. Phys.* **91**, 1137 (1997).
- [16] T. Boublík, *Molec. Phys.* **100**, 3443 (2002).
- [17] T. Boublík, *Collect. Czech. Chem. Commun.* **75**, 289 (2010).
- [18] M. Connolly, *J. Am. Chem. Soc.* **107**, 1118 (1985).
- [19] K.H. Naumann and T.W. Leland, *Fluid Phase Equil.* **18**, 1 (1984).
- [20] T. Boublík, *Molec. Phys.* **83**, 1285 (1994).
- [21] M. Šindelka M. and T. Boublík, *Molec. Phys.* **96**, 243 (1999).
- [22] L.L. Lee, *Molecular Thermodynamics of Nonideal Fluids*. Butterworths, Boston 1988.
- [23] G. Stan and M.W. Cole, *Surf. Sci.* **395**, 280 (1998).
- [24] C. Gu, G.-H. Gao and Y.-X. Yu, *Int. J. Hydrogen Energy* **29**, 465 (2004).
- [25] A. González, J.A. White, F.L. Román and S. Velasco, *J. Chem. Phys.* **125**, 064703 (2006).

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8 [26] D. Bratko, L. Blum and M.S. Wertheim, J. Chem. Phys.
9 **90**, 2752 (1989).
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11 [27] A. Malijevský, J. Chem. Phys. **125**, 194519 (2006).
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Captions

Figure 1. Geometry of hard-sphere - pore

Figure 2. Third cross virial coefficient; full line for the geometric mean, dash line for the harmonic mean, o - exp. C_{112}

Figure 3. Interaction potential of HS-pore.

Figure 4. Hard-sphere in a spherical pore of $R_r=2.1$, $\rho_b^*=0.5$.

Figure 5. Hard-sphere in a cylindrical pore of $R_r=4$, $\rho_b^*=0.6$.

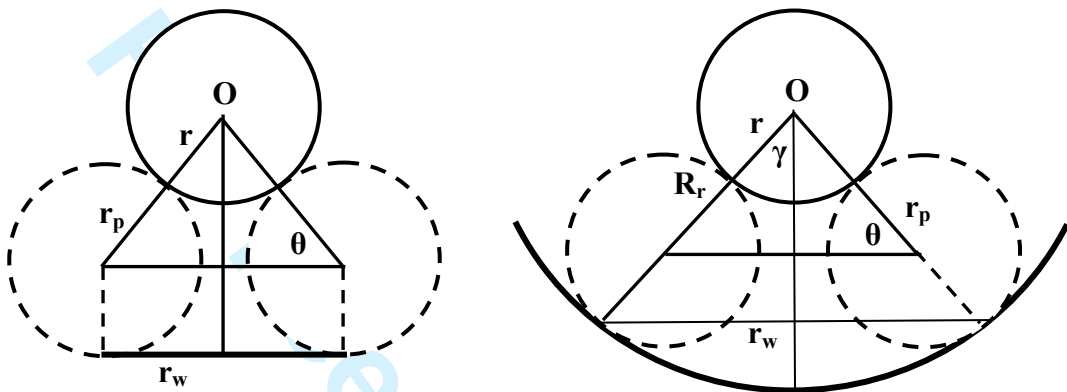
Figure 6. Hard-sphere in a cylindrical pore; $R_r=1.9$, $\rho_b^*=0.55$.

Figure 7. Hard-sphere mixture near a planar wall; $\sigma_2/\sigma_1=2$, $x_2=0.2$, $\rho_b^*=0.6$.

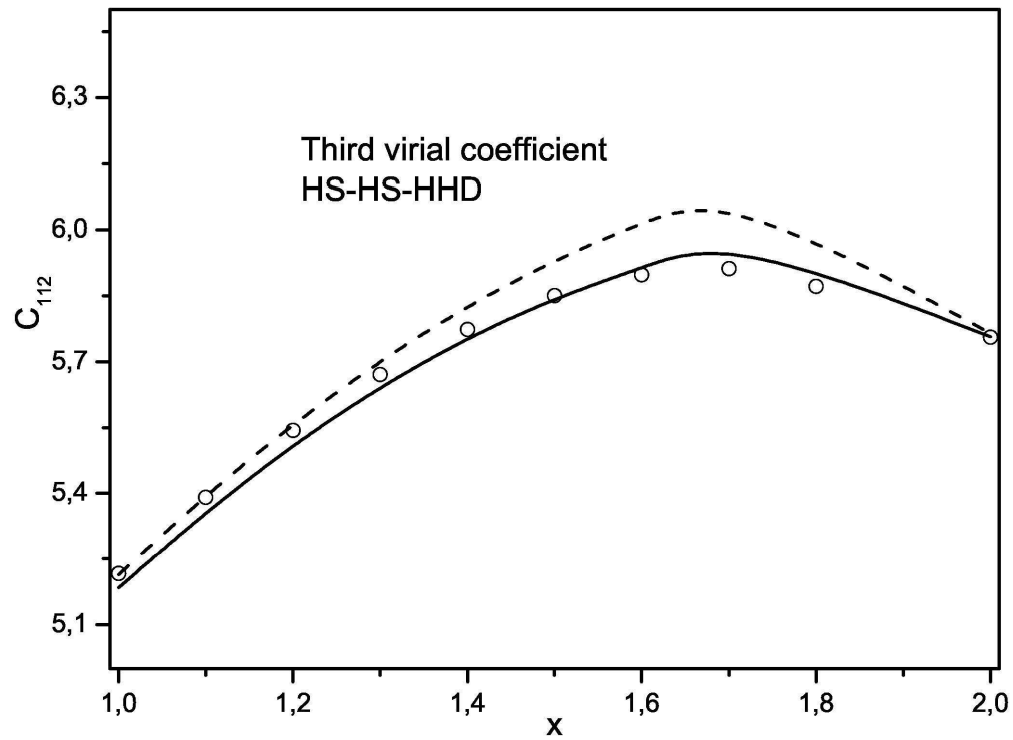
Figure 8. Reference H₂-C and CO-C potentials.

Figure 9. Density profile of H₂ in a graphite single wall nanotube

Figure 10. Density profiles of the equimolar mixture of H₂ and CO in a graphite nanotube.

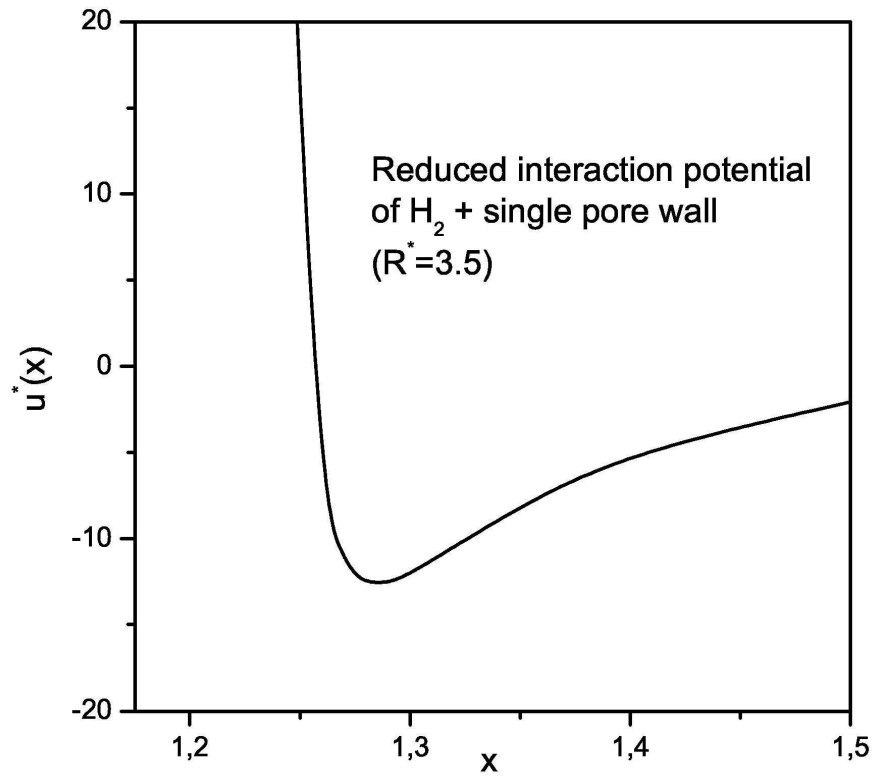


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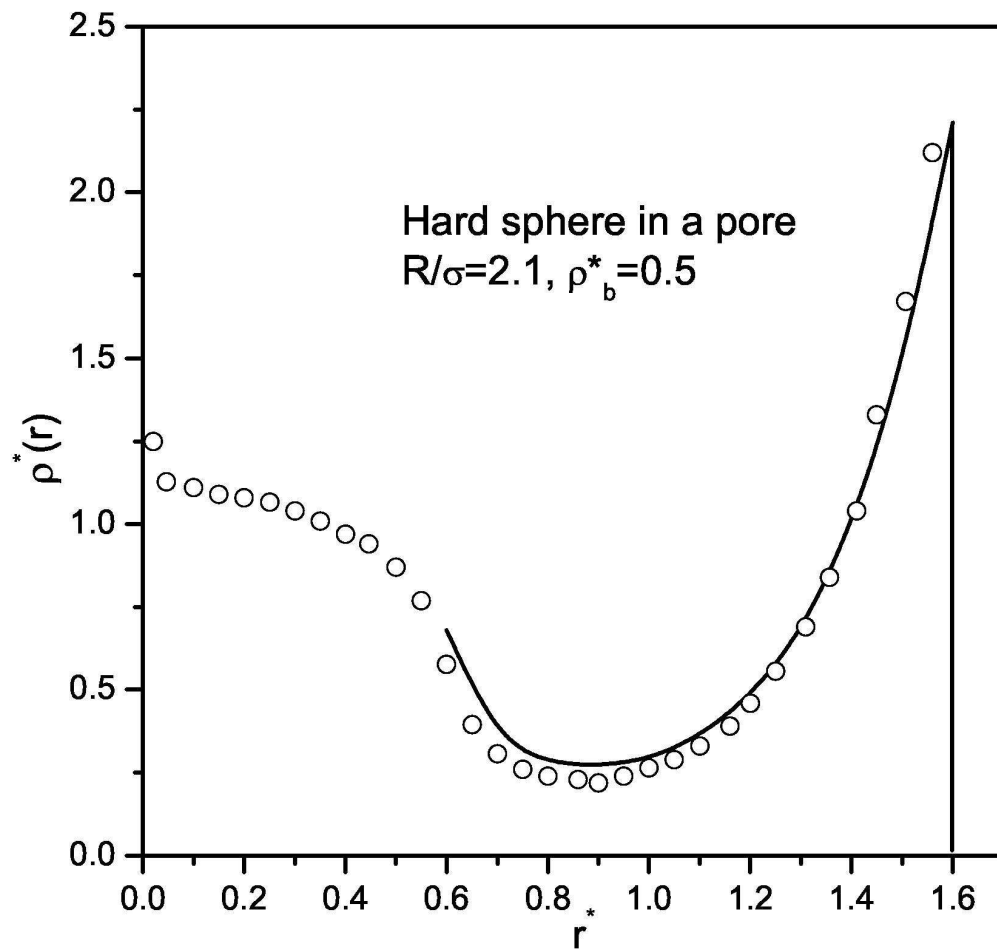
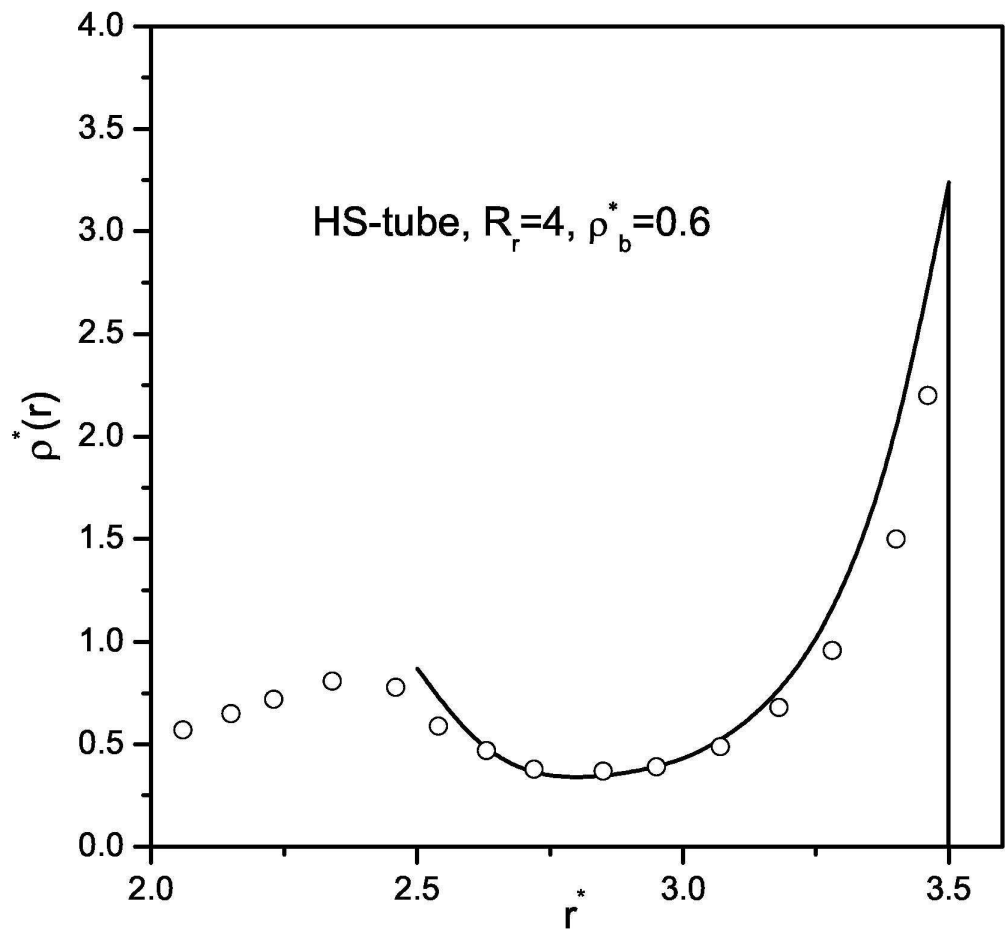


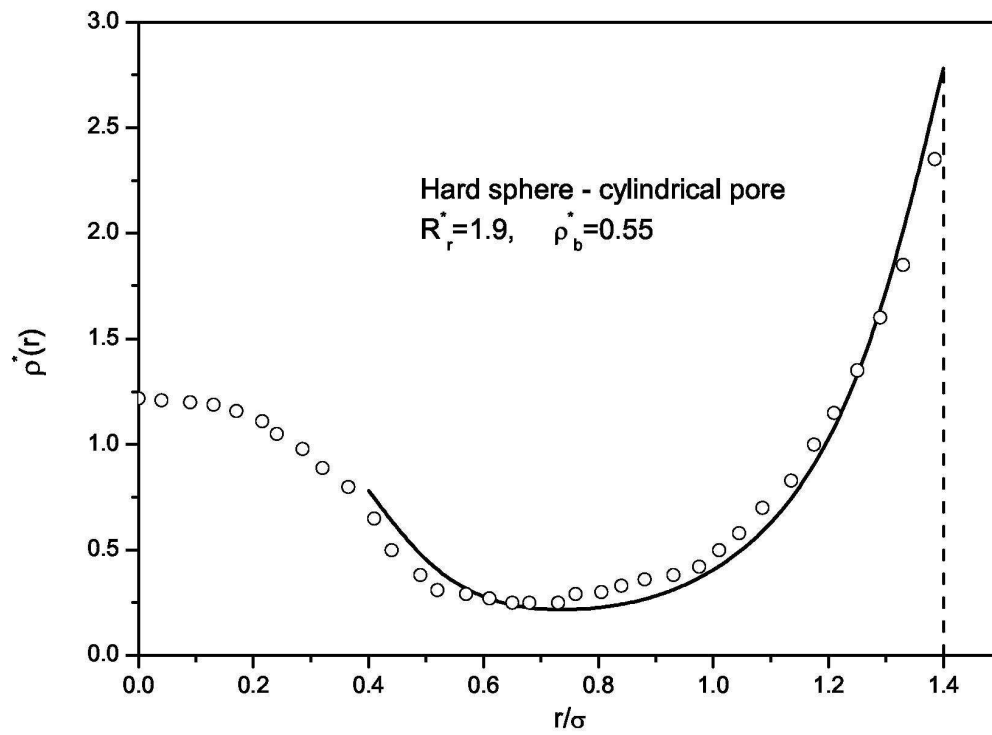
Figure 4
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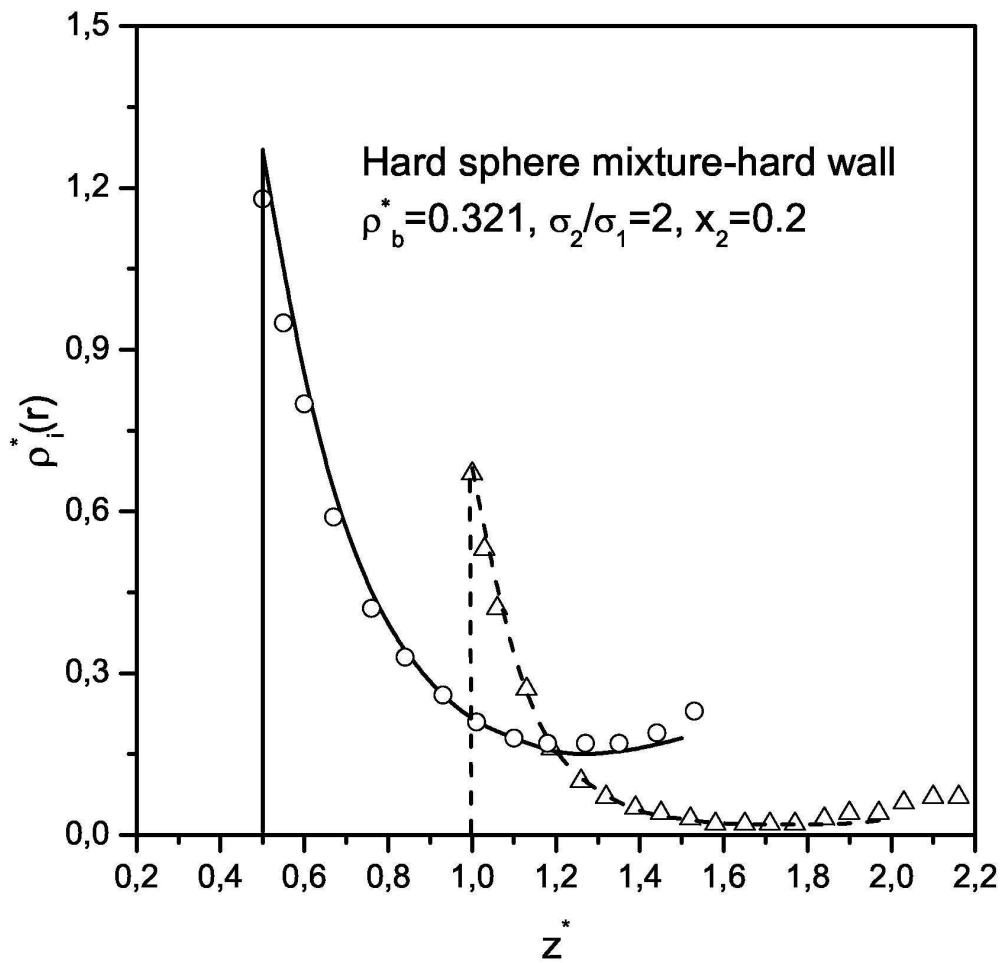
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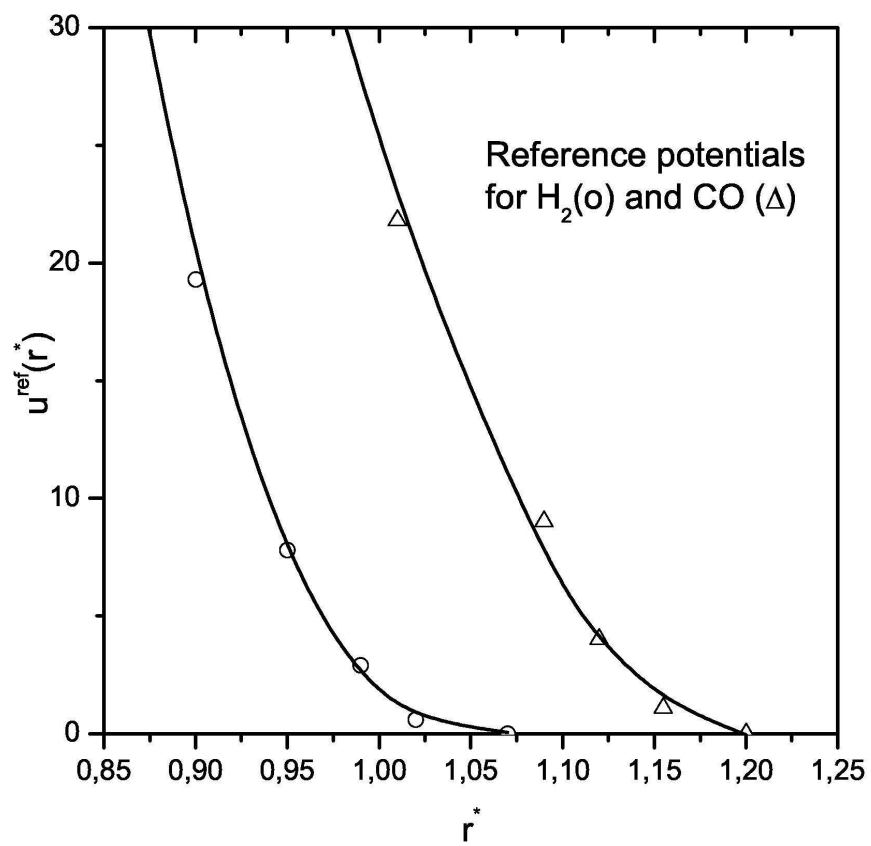
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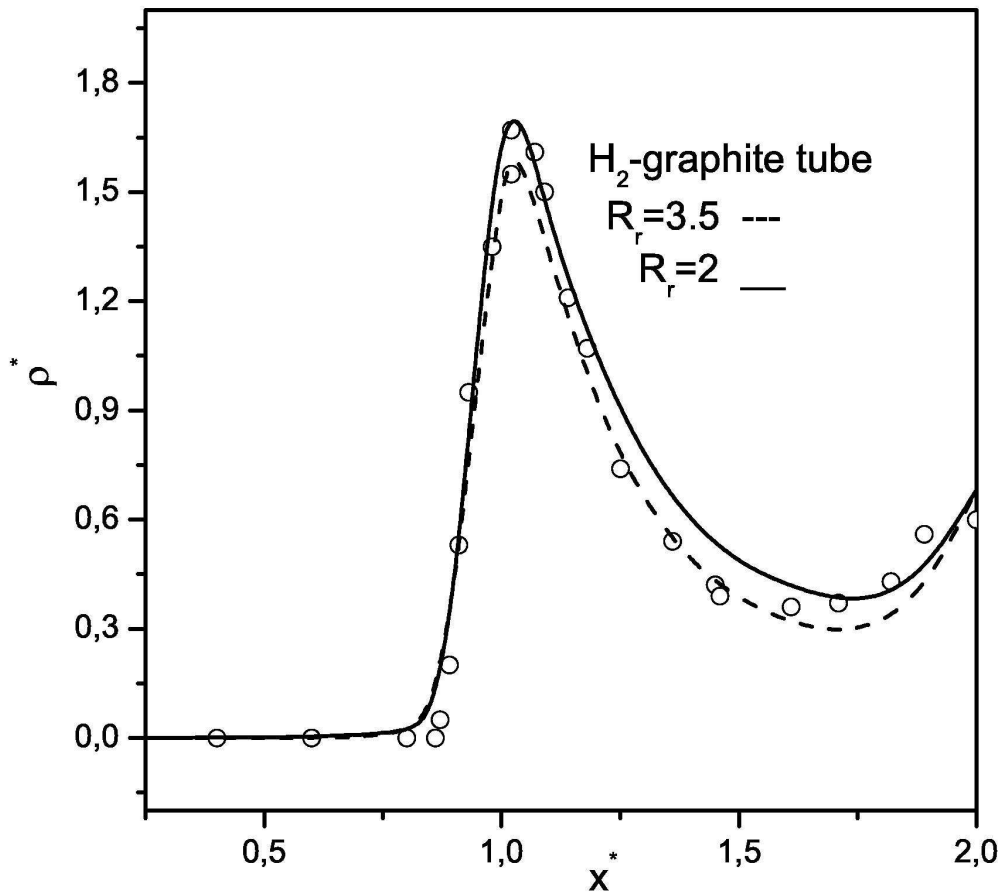
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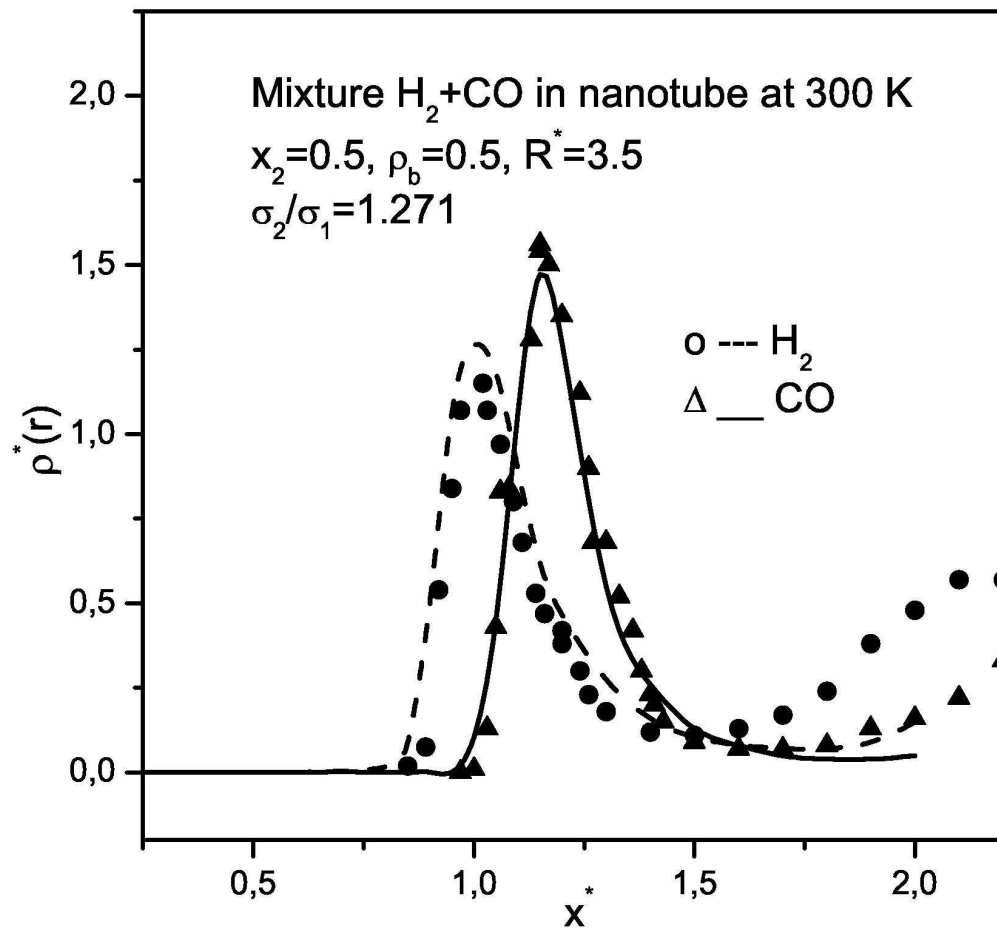
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4 I apologize for a delay with corrections oh my paper TMPH-2010-0244. The reason- I took
5 few days off and have found your message only on Monday.
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8 Besides substituting some parts of my text – In upper case - I added several math.

9 Expressions:

10 Page 5, row 3 $\eta = \rho_{\text{bulk}} V^{\text{HB}}$

11 p.5, r. 13 $A/NkT \sim A_s/NkT$

12 p.6, r.6, $l=0\dots$ For

13 p.7. last row enlarged

14 p.8, r. 10 red – dash, blue – full line

15 p. 10, r.19 incl. definition of r_p

16 p.10, r 32 $r_p = 1$). From...
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19 Because of changes from colour figures to black lines it is necessary to change Fig 9 and 10.
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22 Best wishes

23 Tomas
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