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Numerical analysis of Horvath–Kawazoe equation

P. Kowalczyk [a], A.P. Terzyk [b,*], P.A. Gauden [b], L. Solarz [c]

[a] *Department of Respiratory Protection, Military Institute of Chemistry and Radiometry, gen. Chruściel Avenue 105, 00-910 Warsaw, Poland*
[b] *Physicochemistry of Carbon Materials Group, Department of Chemistry, N. Copernicus University, Gagarin St. 7, 87-100 Toruń, Poland*
[c] *Institute of Physics, Military Technical Academy, Kaliski St. 2, 00-908 Warsaw, Poland*

Abstract

A new Determining Horvath–Kawazoe (DHK) program for the evaluation of pore-size distribution curve based on the HK method (J. Chem. Eng. Jpn. 16 (1983) 470) is described. The standard bisection procedure (Gerald, C.F., 1977. Applied Numerical Analysis, 2nd ed. Addison-Wesley, CA) is used as a kernel in the proposed algorithm. The calculation of the effective pore-size distribution and the comparative analysis with the previous data published by Horvath and co-workers (J. Chem. Eng. Jpn. 16 (1983) 470; Fraissard, J., Conner, C.W., 1997. Physical Adsorption: Experiment, Theory and Applications. Kluwer Academic, London) and recalculated by Do (Do, D.D., 1998. Adsorption Analysis: Equilibria and Kinetics. Imperial College Press, London) were done. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Many porous materials are characterized by structural and energetic heterogeneity (Wojsz, 1989). The sources of the structural heterogeneity are pores differing in shape as well as in dimension. The recommendation by IUPAC classification of the pore sizes (Sing et al., 1985) is often used to divide pores into micropores (diameter < 2 nm), mesopores (diameter between 2 and 50 nm), and macropores (diameter > 50 nm). Dubinin and co-workers have shown that the sorption properties of porous solids strictly depend on the number of micropores (Dubinin, 1975). It is widely accepted that in activated carbons these pores are slit-shaped and the main stage of the mechanism of adsorption is the so-called volume filling of micropores.

Several methods have been put forth for the evaluation of pore-size distribution on the basis of gas adsorption data (Rudziński and Everett, 1992). Most of the methods assume that a solid is composed of independent regions characterized by different adsorption energies (the patch model of surface topography, Rudziński and Everett, 1992). On the other hand, the random model of surface topography, proposed by Ross and Oliver, is also used for the description of structural and energetic heterogeneity (Ross and Oliver, 1964).

One of the most popular methods of the determination of pore-size distribution curve in the micopore range is that proposed by Horvath and Kawazoe. It is based on the thermodynamics of adsorption and for strictly microporous solids it leads to almost identical results as obtained from the new and most sophisticated method of the determination of microporosity, namely Density Functional Theory (DFT) (Lastoskie et al., 1997). Thus, the HK method still remains a very

* Corresponding author. Fax: + 48-56-654-2477.
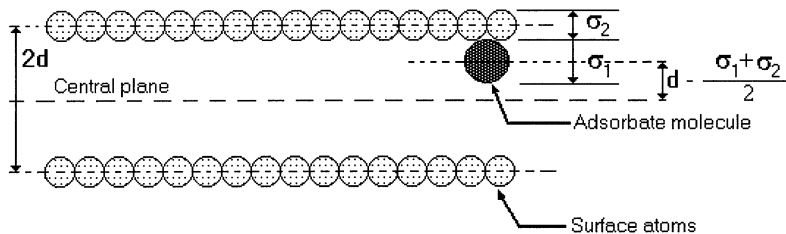*E-mail address:* aterzyk@chem.uni.torun.pl (A.P. Terzyk).

Fig. 1. Schematic diagram of a slit composed of two parallel lattice planes (Do, 1998).
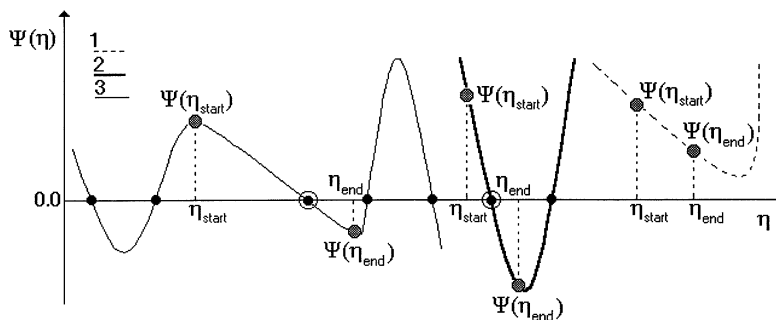

Fig. 2. Schematic representation of three types of function analyzed by DHK program.

attractive procedure and it was adopted for the description of adsorption of different gases for example Ar (Rychlicki et al., 1993), C_6H_6 (Świątkowski et al., 1996) and many others (Terzyk and Gauden, 2001).

In the current paper, a new DHK program for the evaluation of pore-size distribution on the basis of HK method is presented. The validity of the program is confirmed by the analysis of the data published by Horvath and Suzuki (Fraissard and Conner, 1997) as well as those presented by Horvath and Kawazoe, (1983) and recalculated by Do, (1998). Besides, some additional numerical considerations are done.

2. Horvath–Kawazoe method

In this section we present a short summary of Horvath and Kawazoe approach (Horvath and Kawazoe, 1983). The potential energy between two carbon layers filled with adsorbates is defined by:

$$\phi = \frac{N_1 A_1 + N_2 A_2}{(2\sigma)^4} \left[\left(\frac{\sigma}{d+z}\right)^{10} + \left(\frac{\sigma}{d-z}\right)^{10} - \left(\frac{\sigma}{d+z}\right)^{4} - \left(\frac{\sigma}{d-z}\right)^{4} \right] \quad (1)$$

where N_1 is the number of molecules per unit area of the adsorbate and A_1, A_2, and σ are defined as follows:

$$A_1 = \frac{3mc^2\alpha_1\chi_1}{2} \quad (2)$$

$$A_2 = \frac{6mc^2\alpha_1\alpha_2}{\dfrac{\alpha_1}{\chi_1} + \dfrac{\alpha_2}{\chi_2}} \quad (3)$$

$$\sigma = \left(\frac{2}{5}\right)^{1/6} \frac{\sigma_1 + \sigma_2}{2} \quad (4)$$

where σ_1, α_1, and χ_1 are the diameter, polarizability and magnetic susceptibility of an adsorbate molecule, respectively, and σ_2, α_2 and χ_2 are the diameter, polarizability and magnetic susceptibility of the surface atom of the adsorbent (i.e. carbon), respectively; m is the electron mass; and c is the speed of light.

The potential given by Eq. (1) varies with the distance (z) away from the central plane. Averaging this potential over the available distance within the slit (Fig. 1), and substituting the result into the following equation:
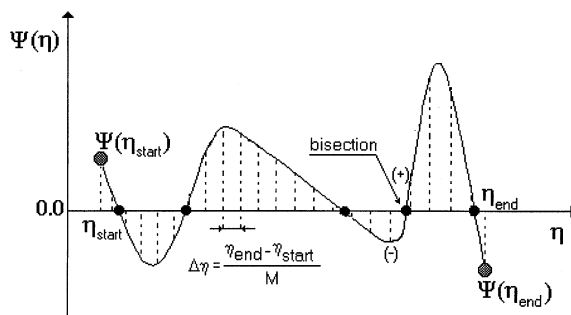

Fig. 3. Strategy applied by DHK program for the detection of all the solutions within the defined range of function changing.

Table 1
Comparative results obtained by Horvath and Suzuki (Fraissard and Conner, 1997) and applying DHK algorithm

Relative pressure	Effective pore diameter (nm)	
	Horvath–Suzuki	DHK
1.46×10^{-7}	0.4	0.3999
6.47×10^{-7}	0.43	0.4300
1.19×10^{-6}	0.46	0.4435
1.05×10^{-5}	0.5	0.5000
1.54×10^{-4}	0.6	0.5999
8.86×10^{-4}	0.7	0.6999
2.95×10^{-3}	0.8	0.8001
2.05×10^{-2}	1.3	1.0819
4.43×10^{-2}	1.5	1.2865
7.59×10^{-2}	3.0	1.5000

$$RT \ln\left(\frac{p}{p_0}\right) = U_0 + P_a \tag{5}$$

where p is the equilibrium pressure and p_0 is the saturation pressure of an adsorbate; R is the universal gas constant; T is the temperature; U_0 is the potential

function describing the adsorbent–adsorbate interaction; and P_a describes the adsorbate–adsorbate–adsorbent interactions, one obtains:

$$RT \ln\left(\frac{p}{p_0}\right) = K\frac{N_1 A_1 + N_2 A_2}{(2\sigma)^4[2d - \sigma_1 - \sigma_2]} \int_{-z^*}^{z^*} \left[\left(\frac{\sigma}{d+z}\right)^{10}\right.$$
$$\left. + \left(\frac{\sigma}{d-z}\right)^{10} - \left(\frac{\sigma}{d+z}\right)^4 - \left(\frac{\sigma}{d-z}\right)^4\right] dz \tag{6}$$

where K is the Avogadro number, and z^* is given by:

$$z^* = d - \frac{(\sigma_1 + \sigma_2)}{2} \tag{7}$$

Integration of Eq. (6) gives:

$$\ln\left(\frac{p}{p_0}\right) - \frac{K}{RT}\frac{N_1 A_1 + N_2 A_2}{\sigma^4[2d - \sigma_1 - \sigma_2]}$$
$$\left[\frac{\sigma^{10}}{9\left(\frac{\sigma_1 + \sigma_2}{2}\right)^9} - \frac{\sigma^4}{3\left(\frac{\sigma_1 + \sigma_2}{2}\right)^3} - \frac{\sigma^{10}}{9\left(2d - \frac{\sigma_1 + \sigma_2}{2}\right)^9}\right.$$
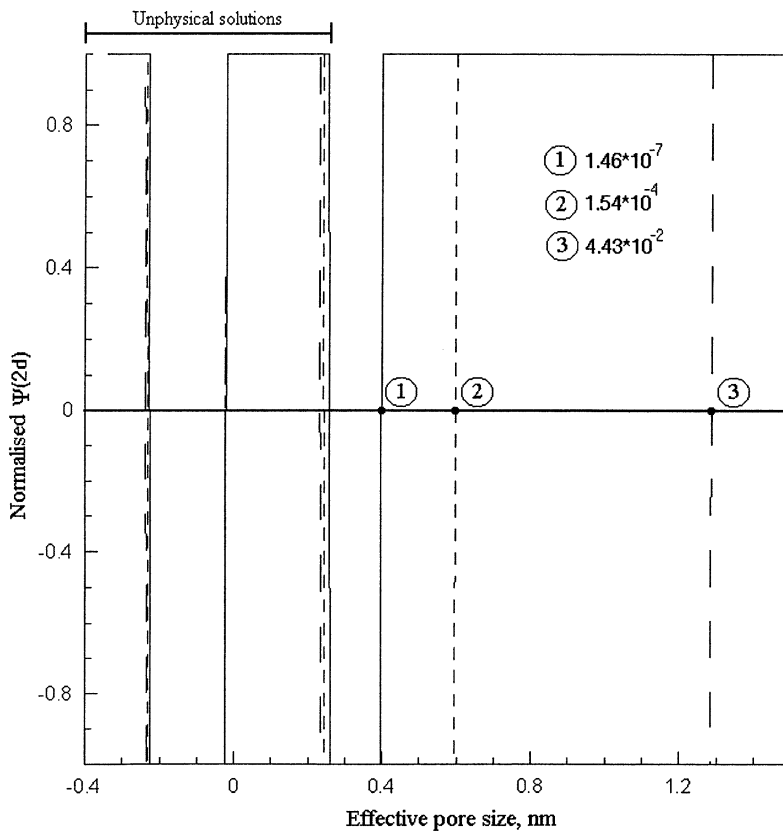$$\left. + \frac{\sigma^4}{3\left(2d - \frac{\sigma_1 + \sigma_2}{2}\right)^3}\right] = 0 \tag{8}$$

Fig. 4. Normalized function defined by Eq. (12) for the arbitrarily chosen values of the relative pressure: 1.46×10^{-7}, 1.54×10^{-4}, and 4.43×10^{-2}.
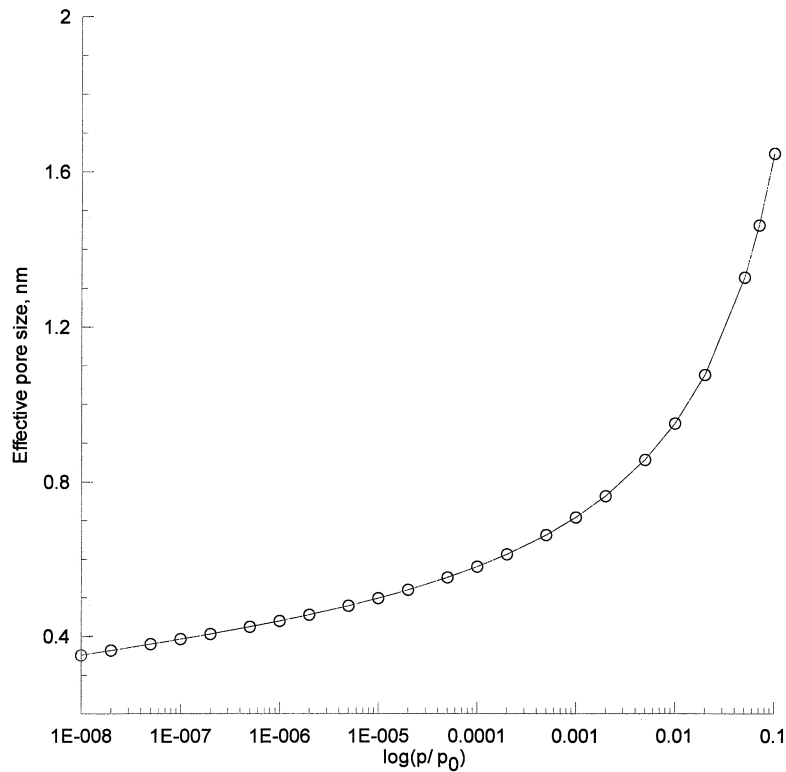
Fig. 5. The results of the calculation of effective pore size: solid line — published by Do (1998); and circles, DHK algorithm.

Eq. (8) connects the gas phase pressure with the effective diameter of the slit-shaped micropore $(2d - \sigma_2)$. Thus, on measuring the adsorption isotherm as a function of reduced pressure, one can derive the relationship between the pore capacity and the effective micropore diameter using Eq. (8). Additionally, the micropore size distribution can be directly obtained from the adsorption data applying the following transform:

$$\Psi(2d) = f\left(\frac{p}{p_0}\right) \tag{9}$$

$$W_{\text{micropore}} = f\left(\frac{p}{p_0}\right) \tag{10}$$

$$\frac{\mathrm{d}}{\mathrm{d}(2d)} W_{\text{micropore}} = \frac{\mathrm{d}}{\mathrm{d}(2d)} \Psi(2d) \tag{11}$$

In the case of the adsorption of nitrogen molecules on the activated carbon, Eq. (8) can be transformed by substituting specific physicochemical constants and the following expression is derived (Horvath and Kawazoe, 1983):

$$\Psi(2d) = \ln\left(\frac{p}{p_0}\right) - \frac{62.38}{2d - 0.64}\left[\frac{1.895 \times 10^{-3}}{(2d - 0.32)^3}\right.$$
$$\left. - \frac{2.7087 \times 10^{-7}}{(2d - 0.32)^9} - 0.05014\right] = 0 \tag{12}$$

3. Numerical considerations

From numerical point of view, we want to solve the nonlinear equation defined by Eq. (12). Different methods have been proposed to solve the equations of this type. The most popular of them are bisection, falsi, and Newton's methods (Press et al., 1992). Thus the program was written using Turbo Pascal v.7.0. From practical point of view, we consider three general classes of functions proposed in the DHK program (they are shown in Fig. 2). In the case of the first class of function, it is impossible to solve the nonlinear equation in the defined range because the function does not change a sign. The second class of functions is characterized by two solutions. In this case, the solution obtained is strictly dependent on the defined range. The third class of functions is the most complicated one because it is characterized by a number of solutions in the defined range. In this case, special procedures must be applied to find all the solutions and, moreover, to choose the appropriate one. The strategy of DHK program is presented in Fig. 3. The first step is dividing the defined range of the function into subintervals. In the second step, the sign change in all the subintervals is explored. Obviously, when the change of a sign is detected, the bisection method (Press et al., 1992) is used to find zero with the defined accuracy.
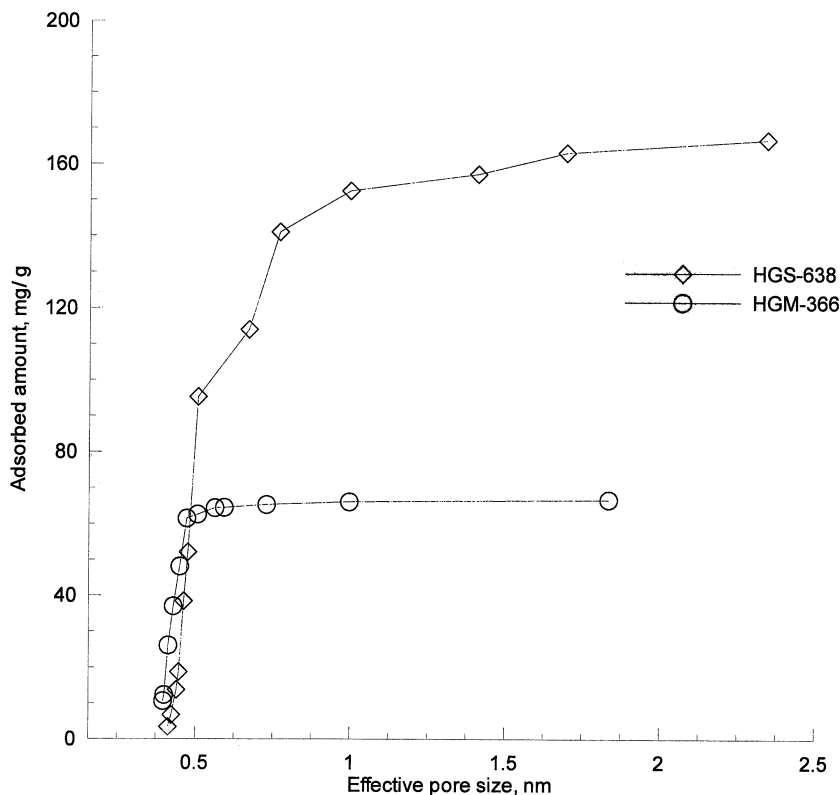
Fig. 6. Cumulative micropore size distribution obtained using DHK algorithm applying the data published by Horvath and Kawazoe (1983).

4. Results and discussion

In the first step, a DHK algorithm is used for the determination of the effective pore sizes for arbitrarily chosen relative pressures. The results are compared with those published by Horvath and Suzuki (Fraissard and Conner, 1997). From Table 1 it can be seen that in most of the cases an excellent agreement exists, however, some values of the effective pore sizes obtained in the current study are different from those evaluated in Horvath and Suzuki computations (in our opinion, the differences are caused by the Editor's mistakes). In Fig. 4, the results of the computations for an arbitrarily chosen relative pressure, for the defined range of function Eq. (12), are presented. Notice that four solutions are detected by DHK program, but only the last one can be accepted for all the cases (only one possesses a physical meaning). In Fig. 5, the results of the calculations published by Do (1998) are compared with those obtained by DHK program. Good agreement between both algorithms is observed.

Finally, to show the ability of the presented procedure for experimental data description, in Fig. 6 the cumulative pore-size distributions, calculated by DHK program, are shown. The data of nitrogen adsorption on two microporous carbons were taken from Horvath and Kawazoe's original paper (Horvath and Kawazoe, 1983). The distributions obtained are practically identical with those calculated by Horvath and Kawazoe.

5. Conclusions

The DHK program presented can be successfully applied for the determination of effective pore-size distributions from the low-temperature (77.5 K) nitrogen adsorption isotherm.

6. Program availability

The listing of this program is available upon request.

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