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Fifty Years of the Theory of the Volume Filling of Micropores

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Fifty years ago Dubinin and Radushkevich (1947) proposed a simple functional relationship between the volume adsorbed in micropores, W, and the adsorption potential, A:

$$W = W_0 \exp(-\kappa A^2) \tag{1}$$

where W_0 represents the maximum volume adsorbed in micropores and κ is the characteristic parameter for a given gas/solid system. The relationship (1), known as the Dubinin-Radushkevich (DR) equation, was the starting point of extensive studies which led Dubinin (1960, 1966, 1975, 1989) to formulate the so-called theory of the volume filling of micropores (TVFM). This equation, together with the well-known Langmuir and BET equations, occupy a central position in the theory of physical adsorption of gases on solids. Later, Dubinin and Astakhov (1971) generalized Eq. (1) by introducing an adjustable exponent n instead of 2. The general form of the DA equation is often written as follows (Dubinin, 1975):

$$W = W_0 \exp\left[-\left(\frac{A}{\beta E_0}\right)^n\right] \tag{2}$$

where the adsorption potential A is defined as the change in the Gibbs free energy taken with minus sign:

$$A = -\Delta G = RT \ln(p_0/p) \tag{3}$$

Above p and p_0 denote respectively the equilibrium pressure and the saturation vapor pressure, β is the similarity (affinity) coefficient (Dubinin, 1975) and E_0 is the so-called characteristic energy. The name of the later parameter is somewhat misleading. Jaroniec and Madey (1989) showed that the parameter E_0 is proportional to the average adsorption potential, i.e., the average value of ΔG.

Although the TVFM theory is often associated with the Polanyi's model of adsorption (Stoeckli, 1993), Bering et al. (1972) argued that some foundations of the Polanyi's model are not applicable inside a micropore with an effective width of several molecular diameters. However, the temperature invariance of the relative adsorption plotted as a function of the adsorption potential, which has been observed for many microporous carbons and is the main consequence of the Polanyi's model, was accepted as the foundation for the TVFM theory (Bakaev and Steele, 1993). The empirical nature of the temperature invariance of $W(A)$ allows only to consider the TVFM theory as a semi-empirical one. Although some theoretical arguments for the DA equation have been published (Jaroniec, 1975; Chen and Yang, 1994), its fully rigorous derivation is probably unachievable. On the other side, the temperature invariance of $W(A)$ was successfully used to obtain analytical equations for the adsorption potential distribution and other thermodynamic functions (Bering et al., 1966, 1972; Jaroniec, 1987; Jaroniec and Madey, 1988; Jaroniec and Choma, 1989).

An important stage in the development of the TVFM theory was determination of the functional dependence between E_0 and the micropore width (Stoeckli, 1974; Dubinin, 1987; Stoeckli et al., 1989; Jaroniec et al., 1990) and assumption that the DA equation represents adsorption in uniform micropores (Stoeckli, 1977; Dubinin and Stoeckli, 1980; Dubinin, 1989). Already in 1965 Izotova and Dubinin postulated that Eq. (1) applies only to adsorption on uniformly microporous solids and proposed a two-term DR equation for solids of bimodal micropore distribution. This postulate allowed to use the DA equation to represent the kernel in the integral equation of adsorption (see references in the review article by Jaroniec and Choma

(1989).) Two most important analytical solutions of this integral were obtained by Dubinin and Stoeckli (1980), Dubinin (1989) for Gaussian micropore distribution and by Jaroniec and Choma (1986) for Gamma distribution. The later micropore distribution lead to much simpler analytical solution than that obtained for Gaussian distribution (Jaroniec and Madey, 1989). In addition, Gaussian distribution needs to be truncated at the zero micropore width in order to satisfy the physical requirements.

Recent achievements (Seaton et al., 1989; Lastoskie et al., 1993; Oliver, 1995) in the modeling of adsorption in micropores using computer simulations and density functional theory (DFT) calculations indicate the concept of the volume filling of micropores postulated by Dubinin is correct. The mechanism of adsorption in micropores differs significantly from the layer-by-layer adsorption, which occurs on flat surfaces. However, the DA equation is not able to represent the stepwise isotherms obtained by computer simulations and DFT calculations in uniform micropores. Therefore, its use as the kernel function in the integral equation of adsorption is questionable. It appears that the DA equation accounts for some effects of surface and structural heterogeneity. Further studies in this direction are required in order to fully understand the applicability of this equation and its limitations.

Fiftieth anniversary of the Dubinin's publication, which laid foundations for the theory of the volume filling of micropores, inspired us to put together the current special issue devoted to "Adsorption in Micropores". This issue contains papers dealing with theoretical as well as experimental studies of adsorption in micropores. A brief overview of the development of TVFM and its foundations are given in the paper by Hutson and Yang. An extension of this theory to adsorption under supercritical conditions is reviewed by Kaneko and Murata. The next paper by Jaroniec et al., provides a critical discussion of simple methods of micropore analysis. Two last papers deal with analysis of the microporous structure of active carbons and coals. Although these contributions do not reflect all important aspects in adsorption on microporous solids and characterization of these solids, at least they indicate the necessity of further studies in this area.

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