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Evaluation of the Energy Distribution Function in Physical Adsorption as the Problem of Laplace Transform. I. Evaluation of the Energy Distribution Function from the Second Gas—Solid Virial Coefficient

Wyznaczanie różniczkowego rozkładu energii adsorpcji jako problem transformaty Laplace'a. I. Wyznaczanie funkcji dystrybucji z drugiego współczynnika wirialnego gaz—ciało stałe

Определение дифференциального распределения энергии адсорбции как проблемы трансформации Лапласа. I. Определение дифференциального распределения энергии адсорбции из второго вириального коэффициента газ—твердое тело

INTRODUCTION

The investigations of heterogeneity of adsorbents are of extremely great importance, for both theoretical and practical reasons. Heterogeneity is responsible for many interesting and important phenomena in physical adsorption [1, 2].

The first problem is to describe quantitatively the adsorbent heterogeneity. When assuming that the adsorbent structure is not perturbed by the presence of adsorbate, such a fully quantitative description is simply the distribution of adsorption energy in the adsorption space. In other words, the function $\varepsilon(r)$ must be known, where ε is the energy of adsorption, and r is the position vector. However, such a function is rather impossible to be evaluated from the experimental data.

When mutual interactions between adsorbate molecules may be neglected, it is sufficient to evaluate only the function $\chi(\varepsilon) = \dfrac{\partial V}{\partial \varepsilon}$ where V is the volume of adsorption space or the number of adsorption sites, depending upon the adsorption model assumed. It results the from

fact that in absence of the mutual interactions, correlation effects in the adsorbate phase may be neglected.

According to our earlier discussion the function $\chi(\varepsilon)$ seems to be a good quantitative description of adsorbent heterogeneity for the majority of adsorption systems investigated in practice. This is probably the reason for which the theoretical investigations of heterogeneity, made so far, concerned the problem of evaluating the function $\chi(\varepsilon)$.

A number of methods have been proposed in order to evaluate $\chi(\varepsilon)$. Apart from calorimetric measurements, all these methods may be divided into two following groups: 1) exploration of the temperature-dependence of adsorption data, 2) exploration of the pressure-dependence of adsorption data. The first possibility is connected with the virial description formalism. In the virial treatment of physical adsorption, the number N of adsorbed molecules is expanded into activity powers [2—5]

$$N = B_{2s} z + B_{3s} z^2 + B_{4s} z^3 + \ldots \tag{1}$$

where z is the absolute activity, and $B_{(l+1)s}$ is the $(l+1)$-th the gas-solid virial coefficient. The virial coefficients are integrals, the integrands of which include the energy distribution $\chi(\varepsilon)$ [2]. The attempts to evaluate $\chi(\varepsilon)$ from the temperature dependence of gas-solid virial coefficients will be discussed in detail in the theoretical section. It will be shown that the evaluation of the function may be reduced to the problem of solving Laplace transform.

THEORETICAL DISCUSSION

In the first part of this paper we shall consider the possibility of evaluating $\chi(\varepsilon)$ from the temperature-dependence of the second gas-solid virial coeficient B_{2s}. As stated above, only such adsorption system is considered, the structure of which may be assumed to be quite inert, and temperature and pressure independent. In such adsorption system B_{2s} is defined as follows:

$$B_{2s} = \int_V \left[\exp\left(-\frac{\varepsilon(\vec{r})}{kT} \right) - 1 \right] d\vec{r} \tag{2}$$

Above $\varepsilon(r)$ is the potential energy field, provided by adsorbent for one single molecule, the center of which is at point r. For practical reasons the volume V is divided into two parts: 1) volume V_s called the volume of the surface phase, where the adsorption takes place; 2) volume V_f,

called the volume of the free gas phase, where the adsorption forces are assumed to be absent, $\varepsilon(r)=0$. With the above notice the integral (2) may be rewritten in the form

$$B_{2s} = \int_{V_S} \exp\left[-\frac{\varepsilon(\vec{r})}{kT}\right] d\vec{r} \qquad (3)$$

The most interesting case is the case of attractive forces. Thus we may write

$$B_{2s} = \int_{-\infty}^{0} \chi(\varepsilon) \exp\left[-\frac{\varepsilon}{kT}\right] d\varepsilon \qquad (4)$$

The above equation may be rewritten as follows:

$$B_{2s} = \int_{0}^{\infty} \chi(\varepsilon') \exp\left[\frac{\varepsilon'}{kT}\right] d\varepsilon' \qquad (5)$$

where $\varepsilon' = -\varepsilon$.

It follows from the above equation that the expression for the second gas-solid virial coefficient is simply Laplace transform of function $\chi(\varepsilon)$ to function B_{2s} $(1/kT)$. Function B_{2s} $(1/kT)$ can be easily found in experimental way, for instance by gas chromatography [6].

Thus the problem of evaluating the distribution function is reduced here to the problem of inversion of Laplace transform, with the transform B_{2s} given in a table form. There exists a number of such methods [7—9]. The kind of the method used will depend on the course of experimental points. In the numerical calculations the experimental results of S a m s et al. [10] concerning the adsorption of argon on graphite P33 have been used. Graphite P33 is usually considered a highly homogenous adsorbent [11]. Therefore its distribution function should be very limited with one sharp maximum. The Laplace transform should be then of exponential type. For such distribution functions two methods of inversion of Laplace transform will be proposed in this paper: 1) an approximate method, when one has a small number of experimental points of B_{2s}; 2) an accurate method, when one has at one's disposal a large number of experimental values of B_{2s}.

1. Approximate method

Let us consider first the case of a fully uniform adsorption space V_s, having an adsorption energy equal to ε_0'. The distribution function $\chi(\varepsilon')$ is in this case simply the delta function $V_s\delta(\varepsilon'-\varepsilon_0')$. The transform B_{2s} will

be then the function $V_s \exp\left(\dfrac{\varepsilon_o'}{kT}\right)$. The nearer to delta functions the

distribution $\chi(\varepsilon')$ the deviations of B_{2s} for the exponential behaviour are smaller. For some small deviations from the exponential behaviour we may write

$$B_{2s}\left(\frac{1}{kT}\right) = \frac{A_1 \exp\left(\frac{\varepsilon_o'}{kT}\right)}{A_2 - \frac{1}{kT}} \tag{6}$$

where the factor $\dfrac{A_2}{A_1} - \dfrac{1}{A_1 kT}$ (correction polynome) describes the small

deviations from the exponential behaviour. Above ε_0', A_1 and A_2 are meanwhile unknown parameters, which can be found, when fitting best eq. (6) with respect to experimental data for B_{2s}. Now the problem of evaluating $\chi(\varepsilon')$ is quite simple. It is known from the literature [8] that the function given by eq. (6) is Laplace transform of the following distribution function

$$\chi(\varepsilon') = \begin{cases} 0 & \text{for } 0 \leqslant \varepsilon' \leqslant \varepsilon_o' \\ A_1 \exp\left[-A_2\left(\varepsilon' - \varepsilon_o'\right)\right] & \text{for } \varepsilon_o' \leqslant \varepsilon \end{cases} \tag{7}$$

The above function fulfils two physical requirements that $\int_0^\infty \chi(\varepsilon')\,d\varepsilon'$

$= $ constans and $\lim\limits_{\varepsilon \to \infty} \chi(\varepsilon') = 0$. This function is not quite correct for small values of ε'. However, the zone V_s exhibiting small values of ε' play a rather negligible role in the total adsorption effect. Our approximate method is similar to the method of S t e e l e [11], who assumed the gaussian distribution in the theoretical description of neon and argon on black pearl BP and on graphite P33. If one considers two surfaces of areas S_{BP} and S_{P33}, then the ratio of the values of B_{2s} for these solids is

$$\frac{B_{2s,BP}}{B_{2s,P33}} = \frac{S_{BP}}{S_{P33}} \exp\left[\frac{1}{2}\left(\frac{u_{BP}}{kT}\right)^2\right] \tag{8}$$

where U_{BP} is the variance of the gaussian distribution for black pearl BP. Since the graphite P33 is assumed to be fully uniform, U_{P33} is taken to be equal to zero. Eq. (8) may be rewritten in the form

$$\ln\left(\frac{B_{2S,BP}}{B_{2S,P33}}\right) = \ln\left(\frac{S_{BP}}{S_{P33}}\right) + \frac{1}{2}\left(\frac{U_{BP}}{kT}\right)^2 \tag{9}$$

Thus the plot $\ln\,(B_{2s,\ BP}/B_{2s\ 33P})$ against $(kT)^{-2}$ should yield a straight

line with the slope equal to $\frac{1}{2}\,U_{BP}^2$. In such a way one gets the

variance which is here the parameter describing the heterogeneity.

Stelle has found that the data for this system, when analyzed in this manner, did indeed give a straight line. The variance obtained from the slope is quite reasonable. It is concluded that the gaussian distribution did seem to be a useful representation for heterogeneity.

In the case of our approximate method, there are three parameters: A_1, A_2, and ε_0', which describe heterogeneity. If the deviations of B_{2s} from experimental behaviour are small, and may be assumed as linear ones, i.e., may be described by the straight line $\frac{A_2}{A_1} - \frac{1}{A_1 kT}$ then the

distribution is given by eq. (7). This distribution is like long-normal distribution.

2. Accurate method

Let us rewrite eq. (5) in the form:

$$B_{2S} = \left[V_S \exp\left(\frac{\varepsilon_1'}{kT}\right)\right] B_{2S}'\left(\frac{1}{kT}\right) \tag{10}$$

where $B_{2s}'(1/kT)$ is a correction function describing the deviations of B_{2s} from the exponential behaviour, due to heterogeneity of the surface. Let us consider B_{2s}' a function of the argument $(-kT)$, and let us write it in the form of a series

$$B_{2S}'(-kT) = \sum_{n=0}^{\infty} d_n'\left(-kT\right)^{n+1} \tag{11}$$

Hence,

$$B_{25} = \exp\left(\frac{\varepsilon_1'}{kT}\right) \sum_{n=0}^{\infty} \alpha_n \left(-kT\right)^{n+1} \tag{12}$$

where $\alpha_n = V_s \alpha'_n$. It is known from the theory of Laplace transforms that when Laplace transform is a product of functions, then the transformed function is a splite of functions. Let, for instance, $f_1(s) \cdot f_2(s)$ be some Laplace transform. Then the transformed function is equal to

$$\int_0^t F_1\left(\tau\right) F_2\left(t-\tau\right) d\tau \tag{13}$$

where $t \geqslant \tau$ and $f_1(s)$, $f_2(s)$ are the following Laplace transforms

$$f_1\left(s\right) = \int_0^{\infty} F_1\left(t\right) \exp\left(-st\right) dt \tag{14}$$

$$f_2\left(s\right) = \int_0^{\infty} F_2\left(t\right) \exp\left(-st\right) dt$$

In our case this law leads to the following results

$$\chi\left(\varepsilon'\right) = \int_0^{\varepsilon} \chi_1\left(\tau\right) \chi_2\left(\varepsilon'-\tau\right) d\tau \tag{15}$$

where

$$\chi_1\left(\tau\right) = \sigma\left(\tau - \varepsilon_1'\right) \tag{16}$$

and

$$\chi_2\left(\tau\right) = \sum_{n=0}^{\infty} \frac{\alpha_n}{n!} \tau^n \tag{17}$$

Eq. (17) follows from the following law: It is known from the theory of Laplace transforms that if the function $f(s)$ can be expanded into the series

$$f_{(s)} = \sum_{n=0}^{\infty} \frac{\alpha_n}{s^{n+1}} \tag{18}$$

convergent for $|s| > R$, then the following expansion is valid

$$F(t) = \sum_{n=0}^{\infty} \frac{a_n}{n!} \, t^n \qquad (19)$$

Next, it is easy to check that the series $\sum_{n=0}^{\infty} a_n (-kT)^{n+1}$ $(-kT)^{n+1}$

is Laplace transform of the series $\sum_{n=0}^{\infty} \frac{a_n}{n!} (\varepsilon' - \varepsilon_1')^n$. From eqs. (15—19)

we get

$$\chi(\varepsilon') = \int_0^{\varepsilon'} \delta(\tau - \varepsilon_1') \sum_{n=0}^{\infty} \frac{a_n}{n!} (\varepsilon - \tau)^n d\tau \qquad (20)$$

and hence

$$\chi(\varepsilon') = \sum_{n=0}^{\infty} \frac{a_n}{n!} (\varepsilon' - \varepsilon_1)^n \qquad (21)$$

It follows from the experiment that function $\sum_{n=0}^{\infty} a_n (-kT)^{n+1}$ is quickly

convergent, especiallly at higher temperatures. Since $(-kT)$ is rather a large value for moderate and higher temperatures, the coefficients a_n's must very quickly tend towards zero, with the subscript n increasing. This makes it possible to truncate the series in eq. (11) after some power of $(-kT)$, and to find the coefficients a_n, using the best-fit procedure. In this way we obtain the coefficients in the expansion for the energy distribution function, given by eq. (21). Let us additionally notice that the series (21) is even more rapidly convergent than series in eq. (11), because of the factor $1/n!$. It should be emphasized that eqs. (18) and (19) are valid only for some class of functions which fulfil the additional requirement that.

$$|F(t)| < C \exp\left(c|t|\right) \qquad (22)$$

This additional requirement is always fulfilled, which follows from the

fact that $\lim\limits_{\varepsilon \to \infty} \chi(\varepsilon') = 0$.

NUMERICAL RESULTS AND DISCUSSION

As was mentioned above, the experimental results of S a m s et. al. [10] will be used here in the calculations of the energy distribution function $\chi(\varepsilon')$. They concern adsorption of argon on highly graphitized carbon P33 (2700). These experimental data have been applied for two reasons: First, they are the most accurate experimental results for B_{2s} reported so far in literature. Second, graphite P33 (2700) is considered to be a highly homogeneous adsorbent. Therefore, the possibility of quantitative detecting its heterogeneity by means of our methods, would be a good reference for these methods. The experimental data for B_{2s} were rather numerous, and, therefore, it was possible to apply them to the accurate method in order to calculate $\chi(\varepsilon')$.

The calculations were performed on the computer ODRA-1204 in the UMCS Department of Numerical Calculations. The results are shown in Figure 1. The dashed line denotes the function $\chi(\varepsilon')$, obtained by trunca-
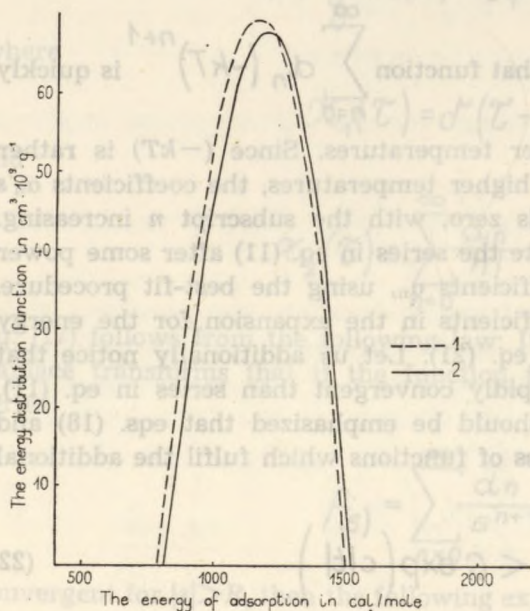

Fig. 1. The energy distribution function for adsorption system argon on graphite P33 2700; 1 — the function $\chi(\varepsilon')$ obtained by truncation of the series

$$\sum_{n=0}^{\infty} \frac{d_n}{n!} \left(\varepsilon' - \varepsilon_1'\right)^n$$

after the fifth term, 2 — the function $\chi(\varepsilon')$, obtained by truncation after the sixth term

tion of the series $\sum_{n=0}^{\infty} a_n \left(-kT\right)^{n+1}$, after the fifth term, whereas the

solid line denotes $\chi(\varepsilon')$, obtained by truncation after the sixth term. The differences seem to be rather small.

Later, it is seen from Fig. 1, that contrary to the assumption made by S t e e l e [11], the graphite P33 is not a highly homogeneous adsorbent.

We would like to emphasize a basic advantage of the accurate method proposed here, in comparison with the methods used by S t e e l e [11], R o s s and O l i v i e r [1], H o o r y and P r a u s n i t z [12], H o n i g [13]. In their investigations of adsorbent heterogeneity, the analytical form of $\chi(\varepsilon')$ has been assumed a priori, whereas in our accurate method the form $\chi(\varepsilon')$ results from the calculations performed.

REFERENCES

1. There exists a number of monographs, in which one can find an exhaustive review of the problem of heterogeneity. These are:
   (a) Solid Surfaces and the Gas-Solid Interface. American Chemical Society, Applied Publications. Washington 1961, 62—67.
   (b) Y o u n g D. M., C r o w e l l A. D.: Physical Adsorption of Gases, Chapter VII, Butterwoths. London 1962.
   (c) R o s s S. R., O l i v e r J. P.: On Physical Adsorption. Chapter IV. J. Willey, New York 1964.
2. P i e r o t t i R. A., T h o m a s H. E.: Physical Adsorption: The Interaction of Gases with Solids. Chapter IV. J. Willey, New York 1971.
3. O n o S.: J. Phys. Soc. Japan 6, 10 (1951).
4. B a r k e r J. A., E v e r e t t D. H.: Trans. Faraday Soc. 58, 1608 (1962).
5. A b d a l a h A. A., B a k r i M. M.: J. Chem. Phys. 57, 667 (1972).
6. R u d z i ń s k i W., S u p r y n o w i c z Z., R a y s s J.: J. Chromatogr. 66, 1 (1972).
7. W i d d e r D. V.: The Laplace Transform. Princeton Univ. Press., 1946.
8. D o e t s c h G.: Anleitung zum Praktischen Gebrauch der Laplace Transformation. R. Oldenburg, München 1961.
9. P a p o u l i s A.: Quarterly Appl. Mathem. 14, 405 (1957).
10. S a m s J. R., C o n s t a b a r i s G., H a l s e y G. D.: J. Chem. Phys. 36, 1334 (1962).
11. S t e e l e W. A.: J. Phys. Chem. 67, 2016 (1963).
12. H o o r y S., P r a u s n i t z J. M.: Surface Sci. 6, 377 (1967).
13. H o n i g J. M.: Ann. N. Y. Acad. Sci. 58, 741 (1954).

S T R E S Z C Z E N I E

Zagadnienie ilościowej charakterystyki niejednorodności adsorbentów przedstawione zostało w oparciu o wirialny formalizm opisu zjawiska adsorpcji. Wykazano, że problem znalezienia funkcji rozkładu energii adsorpcji z matematycznego punktu

widzenia jest problemem rozwiązania transformaty Laplace'a. W pierwszej części autorzy podają sposób na wyznaczenie funkcji dystrybucji z drugiego współczynnika wirialnego gaz—ciało stałe.

Р Е З Ю М Е

В работе доказано, что с математической точки зрения проблема определения дифференциального распределения энергии адсорбции является проблемой трансформации Лапласа. Указан новый метод определения дифференциального распределения энергии адсорбции.