THE SURFACE DISTRIBUTION FUNCTIONS

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One- and two-body distribution functions in the gas phase are obtained by the generalization of the Kirkwood method in the presence of an external field due to a smoothed solid surface. The numerical calculations of the density distribution function are performed for the case when the particle-surface interaction is 2.5 times stronger than the particle-particle interaction. (This corresponds to the adsorption of methane on silicagel.) The formation of the second adsorption layer is found.

1. Introduction

Among different theories of the physical adsorption [1], the so-called potential theory is one which is free of various additional assumptions concerning mainly the structure of the adsorbed phase. In this theory the substance (gas) is considered as being in the presence of the force field due to the surface of the adsorbent, and the only assumptions here are those about the shapes of potentials of interaction between a pair of particles, and between a particle and the adsorbent.

A theory of this type permits, among others, the *ab initio* calculations to be performed of various distribution functions describing the structure of the adsorbate phase, and may thus be considered as the initial stage of other theories, which require the knowledge of this structure. However, very little so far has been done in this field. Only two methods of obtaining the distribution of particles in the gaseous adsorbate phase are actually known in literature.

The first, proposed by Ono [2], is the McMillan-Mayer method [3] generalized to the presence of an external solid field.

The second due to Kuni [4] consists in the expansion into the generalized Taylor series of the Mayer-Ursell correlation functions, treated as functionals of the functions $\lambda \exp\{-v(z)/kT\}$; λ is here the activity of the adsorbate phase, and $v(z)$ is the external solid surface field.

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Both Ono's and Kuni's methods are based on the assumption that the density change near the solid surface has no influence on the density of the total gas phase. These methods are thus unable to describe the adsorption system when the adsorbed phase volume is comparable with the total gas phase volume, as is the case in the gas chromatography, for example.

We are going to propose in this paper a somewhat different method of the calculation of one- and two-body distribution functions, free of the above-mentioned assumptions, and being the extension of the general Kirkwood treatment of n-body homogeneous distribution functions [5].

2. Theoretical

Define the n-body symmetrical distribution function [5]:

$$\varrho_N^{(n)}(r_1, ..., r_n) = \frac{N!}{(N-n)!} P_N^{(n)}(r_1, ..., r_n), \tag{1}$$

where

$$P_N^{(n)}(r_1, ..., r_n) = \frac{\int_V ... \int \exp\left[\Phi_N(r_1, ..., r_N)/(-kT)\right]dr_{n+1} ... dr_N}{\int_V ... \int \exp\left[\Phi_N(r_1, ..., r_N)/(-kT)\right]dr_1 ... dr_N}. \tag{2}$$

V and Φ are respectively, the volume and the potential energy of the system composed of N identical particles, r_i being the position of the i-th particle.

Define later the n-body symmetrical correlation function $g_N^{(n)}(r_1, ..., r_n)$ as:

$$\varrho_N^{(n)}(r_1, ..., r_n) = \varrho_N^{(1)}(r_1)...\varrho_N^{(1)}(r_n) \cdot g_N^{(n)}(r_1, ..., r_n), \tag{3}$$

and n-body asymmetrical distribution and correlation functions as follows:

$$\varrho_N^{[n]}(r_1, ..., r_n) = \frac{\varrho_N^{(n)}(r_1, ..., r_n)}{\varrho_N^{(n-1)}(r_1, ..., r_{n-1})}, \tag{4}$$

$$g_N^{[n]}(r_1, ..., r_n) = \frac{g_N^{(n)}(r_1, ..., r_n)}{g_N^{(n-1)}(r_1, ..., r_{n-1})}. \tag{5}$$

For our later purposes, the idea of the so-called "potential of average force" $W_N^{(n)}(r_1, ..., r_n)$ will be necessary:

$$\exp\left[W_N^{(n)}(r_1, ..., r_n)/(-kT)\right] = \frac{P_N^{(n)}(r_1, ..., r_n)}{P_N^{(1)}(r_1)...P_N^{(1)}(r_n)}. \tag{6}$$

From the above definitions we have the following relation between $W_N^{(n)}(r_1, ..., r_n)$ and $g_N^{(n)}(r_1, ..., r_n)$:

$$\exp\left[W_N^{(n)}(r_1, ..., r_n)/(-kT)\right] = g_N^{(n)}(r_1, ...r_n) + 0\left(\frac{1}{N}\right). \tag{7}$$

According to Kirkwood's method [6], we consider the adsorption system with the total potential energy Φ expressed as follows:

$$\Phi = \sum_{i=1}^{N} v(r_i) + \sum_{1 \leqslant j < k}^{N} U(r_j, r_k)\xi_j \cdot \xi_k. \tag{8}$$

$U(r_j, r_k)$ is the interaction energy between j-th and k-th molecule, whereas ξ_l are the so-called "coupling parameters", their values being within the interval $[0, 1]$. ξ_l can be regarded as components of a some n-dimensional vector ξ. Following Kirkwood we differentiate $\varrho_N^{(n)}(r_1, ..., r_n)$ with respect to ξ_1. After some rearrangements, quite identical to those made by Kirkwood we obtain, setting $\xi_1 = \xi, \xi_2 = ... = \xi_N = 1$.

$$kT \ln \frac{\varrho_N^{(n)}(r_1, ..., r_n, \xi)}{\varrho_N^{(n)}(r_1, ..., r_n, 0)} = -\xi \sum_{i=2}^{n} U(r_1, r_i) +$$

$$+ \frac{1}{N} \int_0^\xi d\xi \int_V dr_1 \int_V dr_2 \cdot U(r_1, r_2)\varrho_N^{(2)}(r_1, r_2, \xi) -$$

$$- \int_0^\xi d\xi \int_V dr_{n+1} U(r_1, r_{n+1})\varrho_N^{[n]}(r_1, ..., r_{n+1}, \xi). \tag{9}$$

Following Ono [2] and Kuni [4], we shall now consider the simple case of the one-dimensional surface field depending on the z-coordinate only. With this assumption $\varrho_N^{(n)}(r_1, ..., r_n)$ can be rewritten as follows:

$$\varrho_N^{(n)}(r_1, ..., r_n, 0) = \frac{N}{V*} \exp\left[v(z_1)/(-kT)\right]\varrho_{N-1}^{(n-1)}(r_2, ..., r_n), \tag{10}$$

where

$$V* = \int_V dr \cdot \exp\left[v(z)/(-kT)\right]. \tag{11}$$

Consider now the expression:

$$W_N^{(n)}(r_1, ..., r_n, \xi) - W_{N-1}^{(n-1)}(r_2, ..., r_n) =$$

$$= -kT \ln \frac{\varrho_N^{(n)}(r_1, ..., r_n, \xi)}{\varrho_{N-1}^{(n-1)}(r_2, ..., r_n)} \frac{1}{\varrho_N^{(1)}(r_2, \xi)} \left[\frac{\varrho_{N-1}^{(1)}(r_2)}{\varrho_N^{(1)}(r_2, \xi)} \cdots \frac{\varrho_{N-1}^{(1)}(r_n)}{\varrho_N^{(1)}(r_n, \xi)}\right], \tag{12}$$

and assume that:

$$\frac{\varrho_{N-1}^{(1)}(r_k)}{\varrho_N^{(1)}(r_k, \xi)} \to 1 \text{ for } N \to \infty, \tag{13}$$

because the local density $\varrho_{N-1}^{(1)}(r_k)$ in the system composed of a great number of particles

should be practically unchanged by the addition of one molecule more. Thus:

$$W_N^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n, \xi) - W_{N-1}^{(n-1)}(\mathbf{r}_2, \ldots, \mathbf{r}_n) =$$

$$= -kT \ln \frac{\varrho_N^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n, \xi)}{\varrho_{N-1}^{(n-1)}(\mathbf{r}_2, \ldots, \mathbf{r}_n)} \frac{1}{\varrho_N^{(1)}(\mathbf{r}_1, \xi)} \,. \tag{14}$$

When the average density of the system $\bar{\varrho} \to 0$, the local density $\varrho_N^{(1)}(\mathbf{r}_k) \to 0$ too. Then from Eq. (9),

$$-kT \ln \frac{\varrho_N^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n, \xi)}{\varrho_N^{(n)}(\mathbf{r}_1, \ldots, \mathbf{r}_n, 0)} \to \xi \sum_{i=2}^{n} U(\mathbf{r}_1, \mathbf{r}_i) \text{ for } \bar{\varrho} \to 0. \tag{15}$$

It follows from Eqs (10) and (14) that:

$$W_N^{(n)}(\mathbf{r}_1, \cdots, \mathbf{r}_n, \xi) - W_{N-1}^{(n-1)}(\mathbf{r}_2, \cdots, \mathbf{r}_n) \to$$

$$\to \xi \sum_{i=2}^{n} U(\mathbf{r}_1, \mathbf{r}_i) - kT \ln \frac{N}{V^*} \frac{\exp\left[v(z_1)/(-kT)\right]}{\varrho_N^{(1)}(\mathbf{r}_1, \xi)} \,. \tag{16}$$

Thus in particular we have:

$$-kT \ln g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \xi) \to \xi U(\mathbf{r}_1, \mathbf{r}_2) - kT \ln \frac{N}{V^*} \frac{\exp\left[v(z_1)/(-kT)\right]}{\varrho_N^{(1)}(\mathbf{r}_1, \xi)} \,, \tag{17}$$

$$-kT \ln g_N^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \xi) \to \xi U(\mathbf{r}_1, \mathbf{r}_2) + \xi U(\mathbf{r}_1, \mathbf{r}_3) +$$

$$+ U(\mathbf{r}_2, \mathbf{r}_3) - kT \ln \frac{N}{V^*} \frac{\exp\left[v(z_1)/(-kT)\right]}{\varrho_N^{(1)}(\mathbf{r}_1, \xi)} \,. \tag{18}$$

This is the so-called "zeroth order approximation" for the correlation functions. This approximation is to be used in the integrals of the right-hand side of Eq. (9). In particular for $n = 2$ we get:

$$-kT \ln g_N^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \xi) = kT \ln \frac{V^*}{N} \frac{\varrho_N^{(1)}(\mathbf{r}_1, \xi)}{\exp\left[v(z_1)/(-kT)\right]} + \xi U(\mathbf{r}_1, \mathbf{r}_2) -$$

$$- \frac{1}{N} \int_0^\xi d\xi \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 U(\mathbf{r}_1, \mathbf{r}_2) \frac{N}{V^*} \exp\left[\frac{\xi U(\mathbf{r}_1, \mathbf{r}_2) + v(z_1)}{-kT}\right] +$$

$$+ \int_0^\xi d\xi \int_V d\mathbf{r}_3 U(\mathbf{r}_1, \mathbf{r}_3) \varrho_N^{(1)}(\mathbf{r}_3, \xi) \exp\left[\frac{U(\mathbf{r}_2, \mathbf{r}_3) + \xi U(\mathbf{r}_1, \mathbf{r}_3)}{-kT}\right]. \tag{19}$$

We assume further, that in the right-hand side of Eq. (19) $\varrho_N^{(1)}(\mathbf{r}_k, \xi)$ does not depend on ξ when integrating with respect to ξ. The above assumptions are consistent with the

limit in Eq. (13). Integrating with respect to ξ, and putting $\xi = 1$ we get:

$$\ln g^{(2)}(r_1, r_2) = \frac{U(r_1, r_2)}{-kT} - \ln \frac{V^* \varrho^{(1)}(r_1)}{N \exp [v(z_1)/(-kT)]} -$$

$$- \iint_V \frac{\varrho^{(1)}(r_2)}{V^*} \exp [v(z_1)/(-kT)] \left\{ \exp \left[\frac{U(r_1, r_2)}{-kT} \right] - 1 \right\} dr_1 dr_2 +$$

$$+ \int_V g^{(1)}(r_3) \exp \left[\frac{U(r_2, r_3)}{-kT} \right] \left\{ \exp \left[\frac{U(r_1, r_3)}{-kT} \right] - 1 \right\} dr_3. \tag{20}$$

It is easy to check that for $v(z) \rightarrow 0$, the above equation becomes the well-known equation for the correlation function $^0g^{(2)}(r_1, r_2)$ in the free gas phase, equal to:

$$^0g^{(2)}(r_1, r_2) = - \frac{U(r_1, r_2)}{kT} +$$

$$+ \varrho \int \left\{ \exp \left[- \frac{U(r_1, r_2)}{kT} \right] - 1 \right\} \left\{ \exp \left[- \frac{U(r_2, r_3)}{kT} \right] - 1 \right\} dr_3. \tag{21}$$

Thus, if the density distribution function $\varrho^{(1)}(r_k)$ were known, the function $\varrho^{(2)}(r_1, r_2)$ would be easily calculated from Eq. (3). The problem of the practical utility of Eq. (20) will be discussed in the next Section of this work. Here we would like to call attention to the lack of symmetry in the Eq. (20).

This lack of symmetry is a kind of approximation which can be expressed as follows. The deviation from the behaviour of a "quasi-ideal" adsorbate phase (*i.e.*, the phase for which $U = 0$ and $v \neq 0$), expressed by the ratio $\varrho_q^{(1)}(r_k)/\varrho^{(1)}(r_k)$ ($\varrho_q^{(1)}$ being the density of the "quasi-ideal" phase), is the same throughout the adsorbate phase. It arises from the fact that the parameter ξ_1 in differentiating Eq. (1) was chosen quite arbitrarily. Since the parameter ξ_2 may be used as well, the simple symmetrization procedure seems to be applicable:

$$^sg^{(2)}(r_1, r_2) = \tfrac{1}{2} [g^{(2)}(r_1, r_2) + g^{(2)}(r_2, r_1)]; \tag{22}$$

$^sg^{(2)}(r_1, r_2)$ is the fully symmetrical correlation function, and $g^{(2)}(r_2, r_1)$ is the function taken from (20) when the positions of the molecules 1 and 2 are exchanged.

3. Numerical results and discussion

It is seen from Eq. (20) that the knowledge of $\varrho^{(1)}(r_1)$ is necessary for the calculation of $g^{(2)}(r_1, r_2)$. The method of solution will be the method of successive approximations for distribution and correlation functions. In the zeroth order approximation we assume $\varrho^{(1)}(r_1)$ in the right-hand side of Eq. (20) to be the density $\varrho_q^{(1)}(r_1)$ of the "quasi-ideal" adsorbate gas phase (*i.e.* the phase for which $U(r_i, r_j) = 0$ and $v = v(z_i)$).

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In this way we obtain the zeroth order approximation for $g^{(2)}(r_1, r_2)$, and the zeroth order approximation for $\varrho^2(r_1, r_2)$ (by using the zeroth order approximation for $g^{(2)}(r_1, r_2)$ and for $\varrho^{(1)}(r_1)$ in Eq. (3)).

Next, using the zeroth order approximation for $\varrho^{(2)}(r_1, r_2)$ we calculate the first order approximation for $\varrho^{(1)}(r_1)$ from the following obvious relation:

$$\varrho^{(1)}(r_1) = \frac{1}{N-1} \int_V \varrho^{(2)}(r_1, r_2) dr_2. \tag{23}$$

We use in the right-hand side of Eq. (20) the first order approximation for $\varrho^{(1)}(r_1)$ to calculate the first order approximation for $g^{(2)}(r_1, r_2)$. The method for calculating higher order approximations in now evident.

To illustrate the above method, the numerical evaluations of the first approximation for $\varrho^{(1)}(r_1)$ have been performed. Before presenting details of these calculations, we would like to point out a certain property of Eq. (20).

It is evident that the form of Eq. (20) allows for taking into account the third order interactions between adsorbate molecules and the solid surface in the form of Sinanoglu's term [7].

These third order interactions are interactions between two adsorbate molecules, perturbed by the presence of solid surface. Our numerical calculations are of an illustrative character, hence some simplifying assumptions concerning the interaction potentials have been introduced. First we assume the interactions between the pairs of adsorbate molecules to be unperturbed by the presence of solid, and to have the form of Lennard-Jones potentials:

$$U(r_i, r_j) = 4\varepsilon_a \left[\left(\frac{\delta_a}{r_i - r_j} \right)^{12} - \left(\frac{\delta_a}{r_i - r_j} \right)^6 \right]. \tag{24}$$

Further we consider the adsorption potential $v(r_i)$ as being of the form of Lennard-Jones potential too, with suitably chosen parameters ε_p and δ_p;

$$v(r_i) = 4\varepsilon_p \left[\left(\frac{\delta_p}{z_i} \right)^{12} - \left(\frac{\delta_p}{z_i} \right)^6 \right], \tag{25}$$

though in many cases of adsorption systems the [9–6] type potentials seem to be more adequate [8–10].

We have chosen for our calculations the values $\frac{\varepsilon_a}{k} = 400°K$ and $\frac{\varepsilon_p}{k} = 1000°K$. These values should describe for example the adsorption of methane by some kind of silicagels. Later δ_a and δ_p were assumed to be equal, and have been chosen as a unit.

The calculations were performed using the ODRA-1204 computer for the surface phase lying between the solid surface and the surface $z = 4$ (in our units). Since these calculations are rather lengthy, the first order approximations have been computed only for $\varrho^{(1)}(r_1)$. The results are shown in Fig. 1. The dashed line shows the density $\varrho_q^{(1)}(r_1)$ of the "quasi-

-ideal" gas phase $\left(U = 0, \dfrac{\varepsilon_p}{k} = 1000°K \right)$, as a function of the distance z from the surface.

The continuous line gives the density of the real adsorbate phase $\left(\dfrac{\varepsilon_a}{k} = 400°K, \right.$

$\dfrac{\varepsilon_p}{k} = 1000°K \left. \right)$. Higher order approximations were not computed. One sees at once that there is a rather remarkable difference between the adsorption of the "quasi-ideal" and real gas phase.

First of all two peaks appear in the case of the real gas phase, which seems to correspond to earlier assumptions [11] about the formation of the second adsorption layer in the adsorbate phase.
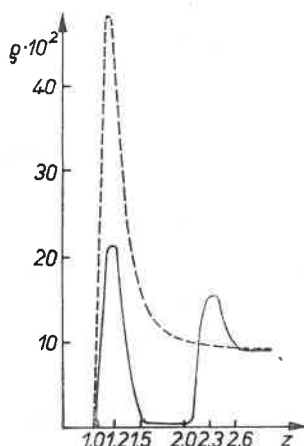

Fig. 1. The dashed line shows the density $\varrho_q^{(1)}(r_1)$ of the "quasi-ideal" gas phase $\left(U = 0, \dfrac{\varepsilon_p}{k} = 1000°K \right)$ as a function of the distance z from the surface. The continuous line gives the density of the real adsorbate phase

Moreover, the maximum of the first peak in the case of the real phase is at the distance $z = 1.2$, instead of $z = 1.1$ as is in the case of the "quasi-ideal" phase.

The greatest difference is between the net Gibbs' adsorption in these two cases. It is seen that the net Gibbs' adsorption decreases considerably for the real adsorbate phase in comparison with that "quasi-ideal" one. This effect seems to be connected with the repulsion in the adsorbate phase, and attraction with the free gas phase.

There exists no possibility of comparing our numerical results with experimental data, since the problem of the experimental determination of $\varrho^{(1)}(r_1)$ has not been solved so far.

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