

Instytut Chemii UMCS
Zakład Chemii Fizycznej
Kierownik: prof. dr Andrzej Waksmundzki

Władysław RUDZIŃSKI, Jarosław OŚCIK

Density Distribution Functions in Simple Liquids Adsorbed on Solids

Rozkład gęstości w prostych cieczach zaadsorbowanych na ciałach stałych

Распределение плотности в простых жидкостях, адсорбированных на поверхностях
твёрдых тел

GENERAL CONSIDERATIONS

The knowledge of the density distribution functions in the adsorbate phase is of extremely big importance, both in theoretical, and in practical investigations of physical adsorption. The theoretical calculations are the only possibility to obtain this function at the present time, since the problem of its experimental determination still remains unresolved. Because so far no experimental method exists to solve its evaluation.

Recently Kuni [1, 2] has developed the elegant formula for surface distribution functions, using the methods of functional analysis. The Kuni's method would be a very useful one, if it were not limited by the condition, that the method is not applicable for the most interesting region near the solid surface. In this paper we extend the Kuni's theory for the region near the solid surface in the case of liquid adsorbate phases, formed by simple liquids.

Following Kuni we consider the liquid adsorbate phase as a liquid in the presence of an external field due to the solid surface. The basic Kuni's idea is to consider the adsorbate phase; first in the presence of this external solid surface field $\varepsilon(\vec{r})$ (assumed to be of one-particle type) and next in the presence of an "auxiliary" external field $\varepsilon_0(\vec{r})$.

Let $g^{(n)}(\vec{r}_1, \dots, \vec{r}_n)$ and $\bar{g}^{(n)}(\vec{r}_1, \dots, \vec{r}_n)$ are the n -body Mayer-Ursell's correlation functions in the adsorbate phase, being in the presence of the external solid field $\varepsilon(\vec{r})$, and in the presence of the "auxiliary" field $\varepsilon_0(\vec{r})$, respectively. Then the Kuni's method leads to the following expansion:

$$g^{(n)}(\vec{r}_1, \dots, \vec{r}_n) = \left[\exp\left(\frac{-1}{kT}\right) \sum_{i=1}^n \Delta \mathcal{E}(\vec{r}_i) \right] \left\{ g_0^{(n)}(\vec{r}_1, \dots, \vec{r}_n) + \sum_{m=1}^{\infty} \frac{1}{m!} \int \dots \int g_0^{(n+m)} \times \right. \\ \left. \times (\vec{r}_1, \dots, \vec{r}_n, \vec{r}_{n+1}, \dots, \vec{r}_{n+m}) \prod_{i=n+1}^{n+m} \left[\exp\left(\frac{-1}{kT}\right) \Delta \mathcal{E}(\vec{r}_i) - 1 \right] d\vec{r}_{n+1} \dots d\vec{r}_{n+m} \right\} \quad (1)$$

where: V is the volume of the adsorbate phase; next $\Delta \mathcal{E}(\vec{r}) = \mathcal{E}(\vec{r}) - \mathcal{E}_0(\vec{r})$; k and T are the Boltzmann constant and absolute temperature, respectively. The above expansion giving the Mayer-Ursell's correlation functions is simultaneously a kind of expansion for common symmetrical distribution functions $\varrho^{(n)}(\vec{r}_1, \dots, \vec{r}_n)$ because of the simple connections between themselves. For example:

$$g^{(1)}(\vec{r}_1) = \rho^{(1)}(\vec{r}_1) \quad (2)$$

$$g^{(2)}(\vec{r}_1, \vec{r}_2) = \rho^{(2)}(\vec{r}_1, \vec{r}_2) - \rho^{(1)}(\vec{r}_1) \rho^{(1)}(\vec{r}_2) \quad (3)$$

Later, in the case of $\varrho^{(1)}(\vec{r}_1)$ in a liquid adsorbate phase one may neglect in the Kuni's expansion all terms with $n+m > 2$, since three and higher body correlations in liquids contribute in a little measure to the total properties of liquids [3].

Thus, in our case of the density distribution function $\varrho^{(1)}(\vec{r}_1)$ the Kuni's expansion reduces to the following formula:

$$\rho^{(1)}(\vec{r}_1) = \left[\exp \frac{\Delta \mathcal{E}(\vec{r}_1)}{-kT} \right] \left\{ \rho_0^{(1)}(\vec{r}_1) + \int \left[\rho_0^{(2)}(\vec{r}_1, \vec{r}_2) - \rho^{(1)}(\vec{r}_1) \rho^{(1)}(\vec{r}_2) \right] \times \right. \\ \left. \times \left[\exp \left(\frac{\Delta \mathcal{E}(\vec{r}_2)}{-kT} \right) - 1 \right] d\vec{r}_2 \right\} \quad (4)$$

where $\varrho_0^{(n)}(\vec{r}_1, \dots, \vec{r}_n)$ are the common symmetrical distribution functions in the adsorbate phase in the presence of the "auxiliary" external field $\mathcal{E}_0(\vec{r})$. According to the Kuni's method the "auxiliary" external field may be chosen quite arbitrary, but for the practical reason it should be chosen so that the auxiliary correlation functions may be easily evaluated.

In an original procedure developed later by Kuni, it is possible only for the region of the adsorption space, where the reciprocal of the distance from the surface can be considered as a small parameter. In this way only the asymptotical form of these distribution functions has been obtained by Kuni and co-workers. In this paper we are going to propose a new method for calculating the auxiliary field and the auxiliary distribution functions. The method is based on the tunnel theory of dense fluids [4,

5], and is applicable for the whole adsorption space, in particular for the region near the solid surface.

The tunnel theory follows the basic idea of the cell theory that one should divide the whole liquid into subsystems, sufficiently simple to permit calculation of their properties. Thus, the liquid volume is divided into subsystems being hexagonal cylinders (or tunnels), arranged in close-packing. Next, one assumes that each tunnel contains an equal number of molecules. Since each tunnel contains a large number of molecules, it is not necessary to take into account the fluctuations of the number of molecules in each tunnel. The molecules in different tunnels move independently, but only in their own tunnels, the walls of each tunnel being formed by molecules of the neighbouring tunnels.

In using the tunnel model to our purpose, we shall approximate the solid surface by a plane (it will be the plane) and assume the adsorption potential to depend on the distance from the surface (xy plane), only. The above two assumptions are usually made in the majority of publications done in this field so far.

Now consider a hypothetical auxiliary liquid phase, consisting of the same kind of molecules, and being enclosed in the same volume V as our liquid adsorbate phase. Let the density of the auxiliary phase be equal to the density ρ of our adsorbate phase at long distances from the solid surface (in the bulk liquid). We divide the auxiliary phase into the hexagonal tunnels so that the axes of these tunnels should be perpendicular to the plan xy bounding partially the auxiliary phase. Next we suppose the existence of an auxiliary external field $\varepsilon_0(\vec{r})$ acting on the auxiliary phase so that in spite of symmetry lack of interactions near the xy plane, the density should be still equal to ρ through the auxiliary phase. Calculate the auxiliary external field, to use it in the eqn (4).

Following Barker we consider the molecules of neighbouring tunnels as "smeared" uniformly on cylindrical surfaces, whose radiuses and surface densities are tabulated in Barker's papers [2, 3]. Let us calculate the interaction energy $V(\vec{r}_i)$ of molecule at the point $\vec{r}_i$ with the walls of these cylindrical surfaces. To this purpose we transform vector $\vec{r}_i$ to cylindrical coordinates r_i, φ_i, z_i . Following Barker we get:

$$\mathcal{V}(\vec{r}_i) = \mathcal{V}(r_i, z_i) = \sum_{s=1}^{\infty} \int_0^L dz_j \int_0^{2\pi} d\varphi_j R_s \delta_s U(d) \quad (5)$$

where: L is the length of the tunnel; σ_s is the surface density in the s -th cylindrical surface, defined as the ratio of the number of molecules in the s -th cylindrical surface, to this surface area; R_s is the radius of the s -th

cylindrical surface. Next: $d^2 = (z_i - z_j)^2 + R_s^2 + r_i^2 - 2r_i R_s \cos \varphi_j$ and $U(d)$ is the interaction energy between two molecules at the distance d .

Let us denote by V_∞ the value of V for the distance from the xy plane, where the symmetry lack of interactions may be neglected. Thus, the potential V may be considered as consisting of two parts; V_∞ and ΔV_c , the second of which being due to the symmetry lack of interactions near the xy plane.

$$\mathcal{V}(z_i, r_i) = \mathcal{V}_\infty(r_i) + \Delta \mathcal{V}_c(z_i, r_i) \quad (6)$$

However, the symmetry lack of interactions near the boundary xy arises not only from the symmetry lack of interactions with the cylindrical surfaces, but from the symmetry lack too, in the interactions between the molecules being in the same tunnel. Let us denote the average interactions energy of a considered molecule with all other molecules in the same tunnel by ΔV_T . It is done by the following obvious equation:

$$\Delta \mathcal{V}_T(\vec{r}_i) = \int_{V_T} \mathcal{V}(\vec{r}_i, \vec{r}_j) \rho_0^{(2)}(\vec{r}_i, \vec{r}_j) d\vec{r}_j \quad (7)$$

Above the interaction space V_T is simply the volume of the tunnel.

The function $\rho_0^{(2)}(\vec{r}_i, \vec{r}_j)$ has the following meaning. If there is a molecule at the point $\vec{r}_i$, then the density of molecules at the point $\vec{r}_j$ in the same tunnel is equal to $\rho^{(2)}(\vec{r}_i, \vec{r}_j)$. For our auxiliary phase having the density ρ through the whole space, the following simple relation can be written:

$$\rho_0^{(2)}(\vec{r}_i, \vec{r}_j) = \rho \cdot \rho_0^{(2)}(\vec{r}_i, \vec{r}_j) \quad (8)$$

Evaluating ΔV_c from eqn. (6) and ΔV_T from eqn. (7), we get the required expression for the auxiliary external field.

$$\mathcal{E}_0(\vec{r}_i) = \mathcal{E}_0(z_i, r_i) = - \left[\Delta \mathcal{V}_c(z_i, r_i) + \Delta \mathcal{V}_T(z_i, r_i) \right] \quad (9)$$

The above expression can be inserted into eqn. (4). Now, it is seen that in addition to $\varepsilon_0(\vec{r}_i)$ the two-body distribution function $\rho_0^{(2)}(\vec{r}_i, \vec{r}_j)$ must be known, to use eqn. (4) for our purpose. However, the method of evaluating $\rho_0^{(2)}(\vec{r}_i, \vec{r}_j)$ in the tunnel space has been in detail described in Barker's paper [6].

Now, we have all the functions whose knowledge is required when using eqn. (4). With the assumptions concerning the auxiliary phase the eqn. (4) may be rewritten to the following simpler form:

$$\rho^{(n)}(\vec{r}_i) = \left[\exp \frac{\Delta \mathcal{E}(\vec{r}_i)}{-kT} \right] \left\{ \rho + \int_{V_T} \left[\rho_0^{(2)}(\vec{r}_i, \vec{r}_2) - \rho^2 \right] \left[\exp \left(\frac{\Delta \mathcal{E}(\vec{r}_2)}{-kT} \right) - 1 \right] d\vec{r}_2 \right\} \quad (10)$$

As it should be expected, the density $\varrho^{(1)}(\vec{r}_1)$ in the adsorbed phase is a function of the adsorbate density ϱ in the bulk phase.

APPROXIMATE MODEL

In this section we shall apply the eqn. (10) to hard-sphere fluid, being in the presence of an external field which is defined as follows:

$$\mathcal{E}(\vec{r}_i) = \mathcal{E}(z_i) = \begin{cases} +\infty & \text{for } 0 \leq z < a \\ \varepsilon_{\min} & \text{for } a \leq z < b \\ 0 & \text{for } b \leq z < +\infty \end{cases} \quad (11)$$

It is well-known that the hard-sphere fluid is a good approximation for many liquids having the slow-collision diameter equal to the particle diameter of this hard-sphere fluid. Next, it is known that the function in eqn. (11) with suitable chosen parameters; a , b , $\varepsilon_{\min}$ is a good approximation for majority of adsorption potentials. In addition, the application of hard-core interactions in theoretical descriptions of the properties of fluids, leads to extremely simple results. For this reason we expect to get simple formulas for $\varrho^{(1)}(\vec{r}_1)$ in our adsorbate phase, when considering it as a hard-sphere fluid in the presence of the external field from eqn. (11). Next, we shall later assume:

$$U(d) = \begin{cases} +\infty & \text{for } 0 \leq d < D \\ 0 & \text{for } D \leq d < +\infty \end{cases} \quad (12)$$

Above D is the slow-collision diameter.

In the case of the hard-sphere fluid, the interactions of a considered molecule with all cylindrical surfaces are equal to zero, except for the interactions with the first nearest cylindrical surface. This interaction is described as follows:

$$\mathcal{V}(z_i, \vec{r}_i) = \begin{cases} 0 & \text{for } 0 \leq r_i < (R-D) \\ +\infty & \text{for } (R-D) \leq r_i < +\infty \end{cases} \quad (13)$$

Here R is the radius of the first cylindrical surface, its value being connected with the density ϱ of the adsorbate [4].

$$R = \left(\frac{2}{\rho\sqrt{3}} \right)^{\frac{1}{3}} \quad (14)$$

For really existing fluids (liquids) D is about 90% of R . ($R=1, 11D$ for liquid argon in 84°K [6]). It justifies our next approximation that,

$$U(d) = U(|z_i - z_j|) = \begin{cases} +\infty & \text{for } 0 \leq |z_i - z_j| < D \\ 0 & \text{for } D \leq |z_i - z_j| < +\infty \end{cases} \quad (15)$$

Next, we approximate the function $\varphi_0^{(2)}(\vec{r}_i, \vec{r}_j)$ by the following one:

$$\rho_0^{(2)}(\vec{r}_i, \vec{r}_j) = \rho_0^{(2)}(z_i, z_j) = \begin{cases} 0 & \text{for } 0 \leq |z_i - z_j| < D \\ \rho^2 & \text{for } D \leq |z_i - z_j| < +\infty \end{cases} \quad (16)$$

For a variety of practical situations D is much higher than $(b-a)$. In the case of gas-solid adsorption system of carbon tetrachloride adsorbed on graphit, the value $(b-a)$ found by us was about 10^{-9} cm. We shall therefore assume $(b-a) \ll D$. Next, for majority adsorption systems $D > a$. For example $D = 3,4$ Å, and $a = 2,9$ Å for argon on carbon black [7, 8]. Thus, we shall later assume $D > a$. With these all above assumptions eqn. (4) yields:

1. for $0 \leq z < a$

$$\rho^{(1)}(\vec{r}) = 0$$

2. for $a \leq z < b$

$$\rho^{(1)}(\vec{r}) = \left[\exp \frac{\varepsilon_{\min}}{-kT} \right] \left[\rho + \rho^2 a A_T - \rho^2 (b-a) A_T \exp \frac{\varepsilon_{\min}}{-kT} \right]$$

3. for $b \leq z < a+D$

$$\rho^{(1)}(\vec{r}) = \rho + \rho^2 (a-z) A_T - \rho^2 (b-a) A_T \exp \frac{\varepsilon_{\min}}{-kT} \quad (17)$$

4. for $a+D \leq z < b+D$

$$\rho^{(1)}(\vec{r}) = \rho + \rho^2 (D-z+b) A_T \exp \frac{\varepsilon_{\min}}{-kT}$$

5. for $b+D \leq z < +\infty$

$$\rho^{(1)}(\vec{r}) = \rho$$

Above A_T is the free cross-sectional area of the tunnel being equal to $\pi(R-D)^2$.

Let us denote by N the number of adsorbed molecules (the nett Gibbses adsorption). Then:

$$N = \frac{2S}{\sqrt{3}R^3} \int_V \left[\rho^{(1)}(\vec{r}) - \rho \right] d\vec{r} = \frac{2S}{\sqrt{3}R} \left[\alpha(T)\rho + \beta(T)\rho^2 \right] \quad (18)$$

Above S is the adsorbent area, and

$$\alpha(T) = A_r(b-a) \left[\exp\left(\frac{\epsilon_{\min}}{-kT}\right) - 1 \right] \quad (19)$$

In the above equation we shall approximate the value, since for the

$$\left[\exp\left(\frac{\epsilon_{\min}}{-kT}\right) - 1 \right] \text{ by } \exp\frac{\epsilon_{\min}}{-kT}$$

majority of adsorption systems the last value is about 10^5 at room temperatures. Next:

$$\begin{aligned} \beta(T) = & a(b-a)A_r \left[\exp\frac{\epsilon_{\min}}{-kT} \right] - (b-a)^2 A_r \left[\exp\frac{2\epsilon_{\min}}{-kT} \right] + a(a+D-b)A_r - \\ & - (b-a)(a+D-b)A_r \left[\exp\frac{\epsilon_{\min}}{-kT} \right] - \left[\frac{(a+D)^2}{2} - \frac{b^2}{2} \right] A_r + (D+b)(b-a)A_r \left[\exp\frac{\epsilon_{\min}}{-kT} \right] - \\ & - \left[\frac{(b+D)^2}{2} - \frac{(a+D)^2}{2} \right] A_r \left[\exp\frac{\epsilon_{\min}}{-kT} \right] \end{aligned} \quad (20)$$

From the experimental plot $\frac{N\sqrt{3R^2}}{2S}$ against ϱ one can get both α , and β . Let us insert eqn. (19) into eqn. (20), found in the temperature T_n .

$$\beta(T_n) = \alpha(T_n) \left[2b - \frac{\alpha(T_n)}{A_r} - \frac{(b+D)^2}{2(b-a)} + \frac{(a+D)^2}{2(b-a)} \right] + a(a+D-b)A_r - \left[\frac{(b+D)^2}{2} - \frac{(a+D)^2}{2} \right] A_r \quad (21)$$

By plotting $\frac{N\sqrt{3R^2}}{2S}$ against ϱ in a number of temperatures one gets the same number of different equations of type (21). From these equations one can evaluate the parameters: a , b , $\epsilon_{\min}$, D , S , by means of the method of the smallest areas.

For many liquids whose molecules have not spherical symmetry, the hard-sphere model may be used by introducing the concept of "effective slow-collision diameter", and "effective adsorption potential". These are the appropriate potentials, averaged over all coordinates describing the state of molecule, except for the center of mass. Here by comparing the effective slow-collision diameter in the adsorbed, and in the bulk phase, one may extract additional interesting informations about the adsorption model.

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STRESZCZENIE

W pracy dokonano próby rozszerzenia teorii Kuniego funkcji dystrybucji w fazach powierzchniowych celem opisania obszaru leżącego blisko powierzchni ciała stałego. Z tego względu zaaplikowano pewne idee z teorii tunelowej Barkera opisującej gęste płyny.

РЕЗЮМЕ

Путем расширения теории поверхностных функций распределения Куни, авторы пытаются описать распределение плотности вблизи поверхности твердого тела. Для этой цели применяются некоторые идеи теории Баркера, описывающей плотные жидкости.