ACCOUNTING FOR INTERMOLECULAR INTERACTION IN THE STATISTICAL THEORY OF ADSORPTION

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Abstract

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ACCOUNTING FOR INTERMOLECULAR INTERACTION IN THE STATISTICAL THEORY OF ADSORPTION

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I. One of the most important problems in the theory of adsorption is to take into account the interaction of adsorbed particles with one another. Below we consider one of the possible variants of its solution, based on the use of the method of molecular distribution functions. The advantage of this method is that, on the one hand, it allows the potential of pair interaction of particles Φ_{ab} to be included in the initial equations in the most natural way, and, on the other hand, it avoids a crude division of the adsorbed substance into bulk and surface phases. We shall proceed from the Bogolyubov chain of equations for the distribution functions $G_{a_1,\ldots,a_s}$, which, as is known, is an exact analog of the canonical Gibbs distribution ([1]). In particular, for the one-particle function $G_a(z)$, describing the probability of finding a particle of species a at a distance z from the surface of the adsorbent, which occupies the half-space $z < 0$, we have

$$\theta\nabla G_a(z) + G_a(z)\nabla\Phi_a(z) + \int_{z'>0}\sum_{1\le b\le M}\nu_b G_{ab}(\mathbf{r},\mathbf{r}')\nabla\Phi_{ab}(|\mathbf{r}-\mathbf{r}'|)\,d^3r' = 0, \quad (1)$$

where $\theta = kT$; $\Phi_a(z)$ is the energy of a particle of species a in the external field of the adsorbent; ν_a is the number of particles of species a per unit volume far from the interface; M is the number of different species of particles in the system.

Equation (1) is not closed, since in addition to G_a it also contains another distribution function, G_{ab}. This shortcoming can be eliminated by expanding G_a and G_{ab} in series in powers of a small parameter λ and equating the expressions at equal powers of λ. However, such a procedure is unlikely to lead to satisfactory results, since, even if the gas density far from the interface is sufficiently small for it to be possible to construct a small parameter from the quantities characterizing the system, then, at any appreciable adsorption energies Φ_a (and

only this case is of practical interest), the surface density proves to be so large that there can be no question of any small parameters in the adsorption layer. Therefore we proceed differently: we reduce (1) to a certain approximate closed equation with the aid of an approximation of the binary function that correctly describes the behavior of G_{ab} both at small and at large distances.

From the definition of the distribution functions ([1])

$$G_{a_1,\ldots,a_s} = \frac{1}{\Omega}\int e^{U_N/\theta}\, d^3r_{s+1}\ldots d^3r_N, \qquad U_N = \sum_{i=1}^{\infty}\Phi_{a_i} + \sum_{1\le i\le j\le N}\Phi_{a_i a_j} \tag{2}$$

it follows that G_a and G_{ab} can always be represented in the form

$$G_a = \gamma_a g_a, \qquad G_{ab} = \gamma_a\gamma_b\gamma_{ab}g_{ab}, \qquad \text{where } \gamma_a = e^{-\Phi_a/\theta}, \quad \gamma_{ab} = e^{-\Phi_{ab}/\theta}, \tag{3}$$

since in (2) integration over the corresponding coordinates is not performed. The extraction from G_a, G_{ab} of the factors γ_a, γ_{ab} ensures correct-

behavior of these functions at small distances. On the other hand, from the condition of weakening of correlations ([1])

$$G_{ab} \to G_a G_b \quad \text{as } r_{ab}\to\infty \tag{4}$$

it follows that at large distances the correlation function $g_{ab} \to g_a g_b$ (since then $\gamma_{ab} = 1$). Assuming approximately that $g_{ab} = g_a g_b$ at all distances, after substituting (3) into (1) we obtain*

$$\nabla\varphi_a(z) + \int_{z'>0}\sum_{1\le b\le M}\nu_b\gamma_b(z')e^{-\varphi_b(z')}\nabla f_{ab}(|\mathbf{r}-\mathbf{r}'|)\, d^3r' = 0, \tag{5}$$

where $\varphi_a = -\ln g_a$ is the potential of mean force and $f_{ab} = \gamma_{ab} - 1$.

Since far from the interface the adsorbent–adsorbed-substance gas is unperturbed, it is necessary to add to (5) the boundary condition

$$\varphi_a(z)\to 0 \quad \text{as } z\to\infty. \tag{6}$$

After φ_a has been found from (5), (6), the total number of adsorbed particles $N_a^{(ad)}$ can easily be determined from the formula

$$N_a^{(ad)} = \nu_a \int_0^\infty [G_a(z)-1]\,dz \simeq \nu_a \int_0^{h^*} [\gamma_a(z)e^{-\varphi_a(z)}-1]\,dz \simeq \nu_a \int_0^{h^*} e^{-(\Phi_a/\theta+\varphi_a)}\,dz, \tag{7}$$

where h^* is the size of the region within which $G_a(z)$ still differs from 1.

II. As an example, let us consider adsorption of particles on the surface of an ideal wall; for simplicity we shall assume that the adsorption potential Φ_a has a rectangular form, i.e.

$$\Phi_a(z) = \begin{cases} +\infty, & -\infty < z < 0, \\ -\Phi_a^{(0)}, & 0 \le z \le h^*, \\ 0, & h^* < z < \infty; \end{cases} \qquad \gamma_a(z) = \begin{cases} 0, & -\infty < z < 0, \\ \gamma_a^{(0)} = e^{-\Phi_a^{(0)}/\theta}, & 0 \le z \le h^*, \\ 1, & h^* < z < \infty. \end{cases} \tag{8}$$

Suppose that the adsorbed gas consists of a mixture of hard spheres of one and the same diameter r_0, i.e.

$$\Phi_{ab}(r) = \begin{cases} +\infty, & 0 \le r < r_0, \\ 0, & r_0 \le r < \infty; \end{cases}$$

$$f_{ab}(r) = \gamma_{ab} - 1 = e^{-\Phi_{ab}/\theta} - 1 = \begin{cases} -1, & 0 \le r < r_0, \\ 0, & r_0 \le r < \infty. \end{cases} \tag{9}$$

In this case the volume integral entering (5), over the volume occupied by the gas (i.e. over the half-space $z \ge 0$), can be transformed into a one-dimensional one, since the integrand does not depend on the azimuthal angle and since, owing to the stepwise form of the function $f_{ab}(r)$, its gradient is equal to a δ-function. As a result of these transformations, (5) reduces to

$$\varphi_a'(z) = 2\pi \int_{z-r_0}^{z+r_0} \sum_b \nu_b \gamma_b(t) e^{-\varphi_b(t)} (t-z)\,dt. \tag{10}$$

Since the right-hand side of (10) is the same for all sorts of particles, $\varphi_a(z) = \varphi(z)$, i.e. in the present case the potential of mean force does not depend on the index a.** Passing to dimensionless coordinates $x = z/r_0$, $\xi = t/r_0$, $h = h^*/r_0$ and to the dimensionless density $\rho = \pi r_0^3 \nu = 6v_0\nu$, where $\nu = \sum \nu_b$ and $v_0 = \pi r_0^3/6$ is the proper volume of the particles, and taking (8) into account, we—

* This equation differs from the usual superposition equation in that it contains $\nabla f_{ab} = \nabla \gamma_{ab}$ instead of $\nabla \Phi_{ab}$.

** This is a consequence of the fact that we are considering adsorption from a mixture of particles of one diameter.

we write (10) in the form

$$\varphi'(x) = 2\rho \int_{x-1}^{x+1} e^{-\varphi(\xi)}(\xi - x)\, d\xi, \qquad 1 + h < x < \infty; \tag{11_1}$$

$$\varphi'(x) = 2\Gamma \int_{x-1}^{h} e^{-\varphi(\xi)}(\xi - x)\, d\xi + 2\rho \int_{h}^{x+1} e^{-\varphi(\xi)}(\xi - x)\, d\xi, \qquad 1 < x < h + 1; \tag{11_2}$$

$$\varphi'(x) = 2\Gamma \int_{0}^{h} e^{-\varphi(\xi)}(\xi - x)\, d\xi + 2\rho \int_{h}^{x+1} e^{-\varphi(\xi)}(\xi - x)\, d\xi, \qquad 0 < x < 1, \tag{11_3}$$

where

$$\Gamma = \rho \sum_b n_b \gamma_b^{(0)} = \pi r_0^3 \sum_b \nu_b \gamma_b^{(0)}, \qquad n_b = \nu_b / \nu.$$

These equations are valid only if $h < 1$.

The resulting system can be solved analytically under the condition that the degree of coverage of the adsorption layer is not very large.* Then, without much error, in the region $x > h + 1$ one may neglect the influence of the wall by putting $\varphi(x) = 0$. It is easy to verify that in this case equation (11_1) will be identically satisfied everywhere except in the interval $1 + h < x < 2 + h$, which, however, we shall neglect. In addition, if at least one of the $\gamma_a^0 \gg 1$, then, for a not very large degree of filling of the monolayer, the inequality $\Phi_a^{(0)}/\theta \gg 1$** will always hold and, consequently, $\sum n_b \gamma_b^{(0)} e^{-\varphi(x)} \gg 1$. Therefore in ($11_2$) and ($11_3$) the terms not containing Γ may be neglected, as a result of which we obtain

$$\varphi'(x) = \varphi(x) = 0, \qquad 1 + h < x < \infty; \tag{12_1}$$

$$\varphi'(x) = 2\Gamma \int_{x-1}^{h} e^{-\varphi(\xi)}(\xi - x)\, d\xi, \qquad 1 < x < h + 1; \tag{12_2}$$

$$\varphi'(x) = 2\Gamma \int_{0}^{h} e^{-\varphi(\xi)}(\xi - x)\, d\xi, \qquad 0 < x < 1. \tag{12_3}$$

Let us denote the following constants by α, β, δ:

$$\alpha = \Gamma \int_0^h e^{-\varphi(\xi)}\, d\xi, \qquad \beta = \Gamma \int_0^h \xi e^{-\varphi(\xi)}\, d\xi, \qquad \delta = \Gamma \int_0^h \xi e^{-\varphi(\xi)}\, d\xi. \quad (13)$$

It is easy to note that after this (12_3) takes the form $\varphi' = 2(\beta - \alpha x)$, or

$$\varphi(1) - \varphi(x) = \int_x^1 \varphi'(x)\, dx = \alpha x^2 - 2\beta x - (\alpha - 2\beta), \qquad 0 < x < 1. \quad (14)$$

The integration constant $\varphi(1)$ appearing here can be found from (12_2). Taking into account that $\varphi(1+h) = 0$ (see (12_1)), after integration by parts we obtain

$$\int_1^{1+h} \varphi'(x)\, dx = -\varphi(1) = \int_1^{1+h} dx \cdot 2\Gamma \int_{x-1}^h e^{-\varphi(\xi)}(\xi - x)\, d\xi = \delta - 2\beta. \quad (15)$$

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* It must be borne in mind that at high degrees of filling the original equation (5) itself, in all probability, becomes inaccurate.

** Indeed, the potential of the mean force describes the influence of all the other particles of the system on the given one. Therefore, when the degree of filling of the monolayer is so small that in it the interaction of the particles with one another can be neglected, $\varphi = 0$, and adsorption is described by the usual formula of Boltzmann $N^{(ad)} = h\nu\gamma^{(0)}$ (see (7)). Conversely, when the degree of filling of the monolayer is large and $N^{(ad)} = N_{\max}^{(ad)} \approx r_0^{-2}$, then from (7), rewritten in the form $N^{(ad)}/N_{\max}^{(ad)} \approx (h/\pi r_0)\exp[\Phi^{(ad)}/\theta - \varphi]$, it follows that $\varphi \approx -\Phi^{(ad)}/\theta + \ln(\rho h/\pi r_0^2) \approx -\Phi^{(ad)}/\theta$ and $\gamma e^{-\varphi} = 1$. Therefore the quantity $\gamma^{(0)}e^{-\varphi}$ lies within the limits $\gamma^{(0)} \gg \gamma_0 e^{-\varphi} \gg 1$.

Substituting (15) into 14), we obtain

$$\varphi(x) = -\alpha x^2 + 2\beta x + \alpha - \delta, \qquad 0 < x < 1. \quad (16)$$

The constants α, β, and δ entering here can be found from a system of three transcendental equations obtained after substituting (16) into (13). In particular, integrating by parts the equation

$$\beta = \Gamma \int_0^h x e^{-\varphi(x)}\, dx,$$

we transform it to the form

$$\beta = \frac{\Gamma}{2\alpha}\left(e^{\alpha h^2 - 2\beta h} - 1\right) + \beta,$$

whence it follows that $\alpha h = 2\beta$, and

$$\varphi(x) = -\alpha x(x-h) + \alpha - \delta, \qquad 0 < x < 1. \tag{17}$$

In the case of small Γ and h (always less than 1), the potential $\varphi(x)$ changes little in the region $(0, 1+h)$. Therefore in the equations

$$\alpha = \Gamma \int_0^h e^{-\varphi(x)}\, dx, \qquad \delta = \Gamma \int_0^h x e^{-\varphi(x)}\, dx$$

the exponentials may be replaced by $1 - \varphi(x)$, as a result of which they take the form

$$\alpha = \Gamma \int_0^h e^{\alpha x(x-h) - (\alpha - \delta)}\, dx = \Gamma h \left(1 - \frac{\alpha h^2}{6} - \alpha + \delta\right), \tag{18}$$

$$\delta = \Gamma \int_0^h x^2 e^{\alpha x(x-h) - (\alpha - \delta)}\, dx = \Gamma h \left(\frac{h^2}{3} - \frac{h^4}{20}\alpha - \frac{h^2}{3}\alpha + \frac{h^2}{3}\delta\right). \tag{19}$$

Solving this system, we obtain

$$\alpha = h\Gamma / \left[1 + (h - {}^1\!/_6 h^3)\Gamma - {}^1\!/_{180} h^6 \Gamma^2\right] \approx h\Gamma / \left[1 + (h - {}^1\!/_6 h^3)\Gamma\right]. \tag{20}$$

Since, according to (7), the number of adsorbed particles is

$$N_a^{(ad)} \simeq \gamma_a \gamma_a^{(0)} r_0 \int_0^h e^{-\varphi(x)}\, dx = n_a \gamma_a^{(0)} / \pi r_0^2 \sum_b n_b \gamma_b^{(0)},$$

then finally

$$N_a^{(ad)} = h^* \gamma_a^{(0)} \gamma_a \Bigg/ \left[1 + v_0 \left(\frac{h^*}{r_0}\right)^3 \left[6\left(\frac{r_0}{h}\right)^2 - 1\right] \sum_b \gamma_b \gamma_b^{(0)}\right] = A\gamma_a \Bigg/ \left[1 + B \sum_b \gamma_b \gamma_b^{(0)}\right]. \tag{21}$$

This is the well-known expression for the adsorption isotherm from a mixture of gases, which is the simplest generalization of the Langmuir isotherm ([2]).

Let us make one comment concerning the solution obtained. Usually, in deriving the Langmuir isotherm, one does not take into account the presence of the

intermediate region $\{h, 1+h\}$, located between the adsorption layer $\{0, h\}$ and the bulk phase $\{1+h, \infty\}$, assuming that in it, as in the bulk phase, $\varphi = 0$. As is seen from (17), this means that it is usually assumed that $\alpha = \delta$. In this case it follows from (18) that $\alpha = h\Gamma/(1+{}^1\!/_6 h^3\Gamma)$, which, for example, at $h = {}^1\!/_2$, gives $\alpha = 0.5\Gamma/(1+{}^1\!/_{48}\Gamma)$, whereas from (21) it follows that $\alpha = 0.5\Gamma/(1+{}^{23}\!/_{48}\Gamma)$. The difference obtained is so large that it cannot in any way be neglected. In other words, the dimensions of the "perturbed" region at those concentrations at which the deviation from the Boltzmann isotherm becomes appreciable are

$$H \approx h^* + r \approx {}^3\!/_2 r_0 \approx 4 \div 6 \text{ Å},$$

and by no means

$$H \approx h^* \approx r_0/2 \approx 1\text{-}2 \text{ Å},$$

as is usually assumed. The reason for this is simple: spheres whose centers are in the adsorption layer $\{0, h^*\}$, by their "sides" occupy a certain volume of the intermediate region and thereby partially screen vacant sites in the adsorption layer from molecules arriving from the bulk phase.

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[1] N. N. Bogolyubov, *Problems of Dynamical Theory in Statistical Physics*, Moscow, 1946.
[2] S. Brunauer, *Adsorption of Gases and Vapors*, 1, IL, 1948.

Note: Figure translations are in progress. See original paper for figures.