PHYSICAL BASIS UNDERLYING THE THEORY OF
POLYMOLCULAR ADSORPTION FILMS AND OF
CAPILLARY CONDENSATION OF POLAR LIQUIDS.
II. DETERMINING THE ADSORPTION POTENTIAL OF A
MODEL WHICH APPROXIMATES THE STRUCTURE OF
FINE DISPERSIONS

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An analysis is made of the conditions under which polar molecules are adsorbed at surfaces
of finite dimensions. On the basis of the nonuniformity of the electric-field topography of
an adsorbent surface, an expression is derived for the adsorption potential and suitable for
thermodynamic calculations of surface phenomena.

The adsorption potential \( \varphi \) will be defined as the work of adsorption forces in moving an adsorbate
molecule from infinity to the interface between adsorption film and adsorbate vapor. This work is numeri-
cally equal to the excess potential energy \( \Delta \varphi \) of the given molecule in the adsorbent field, but has the
opposite sign.

A quantitative determination of \( \varphi \) is rather difficult and the problem has not yet been solved com-
pletely, mainly because the expressions for the potentials of molecular adsorbent—adsorbate and adsorbate
—adsorbent interaction have not been completely developed while there are no test data available on the state
of adsorbed molecules and their complexes [1]. Furthermore, the residual nonhomogeneity of a solid sur-
face not only makes it difficult to calculate the adsorption potential of a given substance but also has a large
effect on the repeatability of adsorption test data. For this reason, the determinations of the adsorption
potential reported in the technical literature [2-5] apply mainly to models of pure substances with homo-
geneous surfaces.

Thus, the adsorption potential of polydisperse substances, which are considered in this study, can be
calculated only approximately and the problem reduces to the correct choice of a model which will best re-
represent the actual adsorbent. According to the test data in [6, 7] pertaining to surface properties of vari-
ous substances (silica gel, wood pulp, cereals), at the surfaces of these substances there exist certain
active groups (for example, dipolar H—O-radicals). The surface of such a sorbent resembles a dipole
lattice. Since the electric-field topography of such a surface is nonuniform [8, 9], and also since it is geo-
metrically not homogeneous (due to granules, notches, fractures, and inclusions), hence the lattice is of
finite size and forms a systematic domain structure of pores and gaps. The problem of determining the
adsorption potential of such a model can be reduced, approximately, to that of calculating the potential
energy of interaction between a polar sorbate molecule and a finite surface of a dipole lattice in the sorb-
ent, the latter carrying similarly oriented dipoles of hydroxyl groups.

In the light of the preceding discussion, the potential energy of an elastic sorbate dipole in the domain
field consists of the electrostatic energy due to both dipole—dipole and inductive interaction as well as of the
energy due to dispersive interaction.* If the potential energy outside the field is assumed equal to zero, then by
definition

*The forces of dipole—quadrupole and of quadrupole—quadrupole interaction as well as the forces of sorb-
ent—sorbate repulsion are all disregarded here, inasmuch as in our case the thickness of a polymolecular
adsorption film is much greater than the intermolecular distances.

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We will now examine the field intensity due to a single domain, as a function of the distance $z$ from this domain, and a mere qualitative analysis of the problem will allow us to draw the following conclusions:

1. At sufficiently great distances $z$ the field may be regarded as the field due to dipoles uniformly "spread" over a finite small area.

2. As $z$ decreases, the magnitude of the field intensity becomes appreciably affected by the discreteness of the dipoles.

Evidently, a field due to a domain depends on the two said factors: the boundary effect and the discreteness of dipoles:

$$E_0 = E_{or} + E_{dg}.$$  

The $E_{or}$ component of field intensity associates with the strong bond between a monolayer and the adsorbent surface, while the $E_{or}$ component (together with the dispersive component) associates with the far-range effect of intermolecular interaction forces during polymolecular adsorption.

In the general case $E_0$ can be calculated as the sum of the field intensities due to all dipoles in the lattice [10]:

$$E_0 = \frac{1}{4\pi e_0} \sum \frac{m_r}{R^3} (\vec{r}_0 \cos \beta + \vec{p}_0 \sin \beta).$$  

For the purpose of this analysis, however, it is preferable to derive a functional relation for $E_0(x, y, z)$. We, therefore, revert to formula (2) and consider both components separately. We find the field potential at any arbitrary point $M(x_0, y_0, z_0)$ due to a plane square domain whose side is $2a$ and whose area is covered by uniformly distributed charges with the surface density $\sigma_r$. The potential due to a single dipole is

$$\psi = \frac{m_r \cos \beta}{4\pi e_0 R^2}.$$  

Since $R^2 = z_0^2 + (x-x_0)^2 + (y-y_0)^2$ and $\cos \beta = z_0 / R$, hence

$$\psi = \frac{m_r x_0}{4\pi e_0 [z_0^2 + (x-x_0)^2 + (y-y_0)^2]^{3/2}},$$  

or in differential form

$$d\psi = \frac{\sigma_r x_0 dxdy}{4\pi e_0 [z_0^2 + (x-x_0)^2 + (y-y_0)^2]^{3/2}}.$$

The field potential due to the entire area is

$$\psi_r = \frac{\sigma_r x_0}{4\pi e_0} \int_{-a}^{a} \int_{-a}^{a} \frac{dxdy}{[z_0^2 + (x-x_0)^2 + (y-y_0)^2]^{1/2}}.$$  

An evaluation of the integral in (7) yields

$$\psi_r = \frac{\sigma_r}{4\pi e_0} \left\{ \arctg \frac{(a + x_0) (a + y_0)}{z_0 [z_0^2 + (a + x_0)^2 + (a + y_0)^2]^{1/2}} + \arctg \frac{(a - x_0) (a - y_0)}{z_0 [z_0^2 + (a - x_0)^2 + (a - y_0)^2]^{1/2}} + \arctg \frac{(a + x_0) (a - y_0)}{z_0 [z_0^2 + (a + x_0)^2 + (a - y_0)^2]^{1/2}} + \arctg \frac{(a - x_0) (a + y_0)}{z_0 [z_0^2 + (a - x_0)^2 + (a + y_0)^2]^{1/2}} \right\}. $$  

With the aid of Eq. (8) we find the field intensity at the center point $M(0, 0, z)$:

$$E_{or} = -\nabla \psi = \frac{2a^2 \sigma_r}{(a^2 + z^2)(2a^2 + z^2)^{1/2} e_0}.$$  

If the additional field due to the mirror image of the dipole lattice [10] is also taken into account, then we have

$$E_{or} = \frac{2a^2 \sigma_r}{\pi e_0} \left\{ \frac{1}{(a^2 + z^2)(2a^2 + z^2)^{1/2}} + \frac{e_r - 1}{e_r + 1} \frac{1}{[a^2 + (z + L)^2](2a^2 + (z + L)^2)^{1/2}} \right\}.$$  

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