Physical Chemistry

The extent of the inhomogeneous region at the gas—solid interface

L. G. Shekhovtsova and T. S. Yakubov★

Institute of Physical Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 952 7514

A new approach to the estimation of the extent of the inhomogeneous region during the adsorption of a gas on a planar or slightly curved solid surface is developed. Relationships are derived that enable the corresponding calculations to be made for the case of dispersion interactions of gases with solids. Numerical estimations of the extent of the inhomogeneous region for graphite—helium (neon, argon, krypton, xenon, and methane) systems as a function of temperature are presented.

Key words: adsorption, interface, dispersion interactions, inert gases, methane, graphite.

The notion of adsorption volume is one of the most important characteristics of an adsorption system. Only knowledge of this value makes it possible to calculate the absolute absorption, *i.e.*, the total amount of a substance present in the adsorbed state, from the experimentally measured excess adsorption. All statistical molecular models of adsorption theory are formulated using the notion of absolute adsorption. At the same time, the correct introduction of the notion of adsorption volume into a system in the general case meets known difficulties, which are described in detail in Ref. 1. The main problem can be reduced to the question: can the total number of adsorbed molecules in the inhomogeneous region remain finite, while the field of van der Waals forces of the solid adsorbent formally stretches *ad infinitum*? Based on the fact that the existence of a force field in some region of space is not enough to cause the adsorption phenomenon, we answer this question affirmatively. It is necessary that the field strength cause the adsorbate concentration to change by a value not less than the average equilibrium fluctuation of the concentration of the volume phase at a constant temperature. This approach requires one to specify the volume in which the fluctuation is considered, and the choice of this volume is arbitrary and must be additionally justified in a physical sense.

In this work, an attempt is made to overcome this difficulty by considering the distribution of energy of the molecules in an equilibrium gas phase. The condition can be formulated from which it follows that the adsorption space in which adsorption is observed stretches from the surface of a solid to some finite distance z_0. At very large distances (formally, at an infinite distance from the solid surface) the average kinetic energy (the same as the total energy, E_k) of a molecule of an ideal gas is distributed according to the Maxwell—

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Boltzmann law

$$\eta = 0.6240\sqrt[3]{Q} ,$$

$$dn = W(E_k)dE_k = \frac{2}{\sqrt{\pi(kT)^3}}\exp(-\frac{E_k}{kT})\sqrt{E_k}\,dE_k \quad (1)$$

with the average value $\varepsilon = (3/2)kT$ (see Ref. 2). The mean square deviation from the average energy value is $s = (3/2)^{1/2}kT$.

Let us calculate the fraction p of molecules, whose energy falls within the range $[\varepsilon-s, \varepsilon+s]$.

$$p = \int\limits_{\varepsilon-s}^{\varepsilon+s}\sqrt{x}\,e^{-x}dx = 0.76596, \quad (2)$$

where $x = E/kT$. Therefore, the fraction of molecules, whose energy is beyond the range mentioned, is the following

$$\bar{p} = 1 - p = 0.23404. \quad (3)$$

On the other hand, near the solid surface within the area of an adsorption field, the total energy of the molecules is changed due to the contribution of the potential energy. If the coordinate and impulse parts of the total energy are separated, all of the molecules at a given distance from the solid surface will have the same potential energy. Therefore, the energy distribution function of the molecules that are at some distance z from the solid surface can be written in the form:

$$dn = W(E)dE = \frac{2}{\sqrt{\pi(kT)^3}}\exp(-\frac{E-H}{T})\sqrt{E-H}dE, \quad (4)$$

where H is the potential energy of the interaction of a molecule with the solid surface and E is its total energy. This means that compared to the distribution at an infinitely large distance from the surface, the fraction of molecules with energy lower than some value E^* is increased and the fraction of molecules with energy higher than E^* is decreased by the same value. If the energy for which probability densities (1) and (4) are equal is taken as E^*, the sum of the shaded surface areas in Fig. 1 is called a "distortion" of distribution (1). If the point at which the considered molecule is located approaches the solid surface from infinity, the "distortions" increase from zero to some maximum value, and the value of the "distortion" is unambiguously determined by the potential energy contribution to the total energy of the molecule.

Let us accept that the distance from the solid surface at which the "distortion" of the distribution is equal to the value of 0.23404 specified beforehand (correlation (3)) is the sought-for distance z_0. The "distortion" value is unambiguously determined by the potential energy in expression (4) and calculated by standard Poisson type integrals. The absolute value of H, which is equal to 0.2430 kT, corresponds to this "distortion".

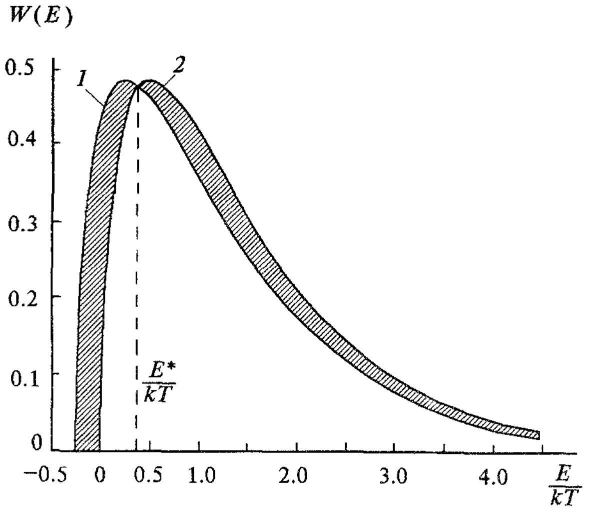

Fig. 1. Density of the total energy distribution of molecules near a surface (*1*) and at an infinite distance from the surface (*2*).

The dependence of the adsorption potential of the solid state (ψ) on distance (z) for the case of dispersion interactions can be presented in the form[3]

$$-\psi(z) = \iiint\frac{C_6}{R_i^6}MdV = \frac{\pi M C_6}{6}\cdot\frac{1}{z^3} = \frac{C_6}{z^3}, \quad (5)$$

where C_6 is the constant of pair-wise interaction (*i.e.*, attraction, because repulsion at distances greater than the diameter of the adsorbed molecule can be neglected), which can be calculated, *e.g.*, from the Kirkwood—Muller formula; R_i is the distance from the center of the adsorbed molecule to the center of the i-th atom of the solid state; M is the number of adsorbed atoms per unit volume; the integration in (1) is performed over the whole infinite half-space of the solid state V; C_3 is the constant of the attraction of an adsorbate to an adsorbent. The relation between the C_6 and C_3 constants for the case when the solid surface is non-planar, and is therefore more complicated, can be found in Ref. 3.

Thus, setting the potential energy ψ equal to 0.2430 kT, we obtain

$$C_3/z_0^3 = 0.2430\ kT. \quad (6)$$

If the dimensionless variables $\eta = z_0/\sigma$ and $Q = C_3/(kT\sigma^3)$ are introduced, correlation (6) takes the form

$$\eta = 0.6240\sqrt[3]{Q} , \quad (7)$$

where σ is the diameter of the adsorbing molecules. The corresponding parameter of the Lennard—Johns potential for adsorbate atoms is chosen as σ.

Eqs. (6) and (7) are used to calculate the extent of the inhomogeneous region at the graphite—inert gas and graphite—methane interfaces at various temperatures in

Table 1. Calculated values of the extent of the inhomogeneous region and the dimensionless attraction constant at the graphite—gas interface

Adsorbate	σ/nm	T/K	Q	η	z_0/nm
Helium	0.2576	77.35	1.99319	2.017	0.5195
		300	0.51391	1.284	0.3306
Neon	0.2789	77.35	3.92628	2.528	0.7051
		300	1.01233	1.609	0.4488
Argon	0.3418	77.35	7.13341	3.085	1.0544
		300	1.83923	1.963	0.6711
Krypton	0.3610	77.35	7.94751	3.198	1.1545
		300	2.04913	2.035	0.7348
Xenon	0.4055	77.35	9.04191	3.338	1.3538
		300	2.33131	2.125	0.8616
Methane	0.3812	77.35	7.71839	3.167	1.2072
		300	1.99006	2.016	0.7684

the region of the ideal gas state of an adsorbate. The constants of the dispersion interaction of the adsorbate molecules with the surface of graphite are taken from Ref. 4. The results of the calculations are listed in Table 1. The calculations show that the widths of the adsorption layers are within one to three diameters of the adsorbate molecules in a sufficiently wide temperature range. To calculate the volume of the adsorption space for an uncovered surface, the value z_0 should be multiplied by the adsorbent surface area found, for example, by the BET (Brunauer—Emmett—Teller) method.

It should be mentioned that knowledge of the value z_0 allows one to make a reasonable estimation of the upper values of the characteristic linear size l of the gap-like micropores in which the adsorption field is sufficiently strong: $l \leq 2z_0$.

In conclusion it should be indicated that if the equilibrium gas phase is non-ideal, the contribution of the average energy of interparticle interaction to the total average energy of a particle should be taken into account in formula (4). The average energy of interparticle interaction is a function of the density of the adsorbing gas and, hence, a function of the distance of the considered particle from the solid surface.

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