ISSN 1070-3632, Russian Journal of General Chemistry, 2007, Vol. 77, No. 3, pp. 371–392. © Pleiades Publishing, Ltd., 2007.
Original Russian Text © A.I. Rusanov, F.M. Kuni, 2007, published in Zhurnal Obshchei Khimii, 2007, Vol. 77, No. 3, pp. 404–426.

On the Theory of the Mechanochemical Sorption-Striction Phenomenon in Nanoporous Bodies with Dispersion Forces

A. I. Rusanov and F. M. Kuni

Mendeleev Center, St. Petersburg State University,
Universitetskaya nab. 7, St. Petersburg, 199034 Russia

Received November 9, 2006

Abstract—The soption-striction phenomenon is a change in the dimensions of a porous body in the course of sorption due to the strain caused by the action of molecular forces. The formulation of the theory of the phenomenon includes the following problems: the statistical-mechanical calculation of the pressure tensor in the pore interior as a function of the pore shape and size; the analysis of the role of surface tension in the mechanical equilibrium condition at the pore wall and producing strain at various mechanisms (physical or chemical) of sorption; the calculation of the body strain within the theory of elasticity. The calculation of the pressure tensor was performed for spherical, cylindrical, and flat (slit-like) pores using asymptotic relations for ordinary dispersion forces (in the context of the nano-scaled pore size) and dispersion forces with electromagnetic retardation (for micropores of larger dimensions), with the pair potential exponents –6 and –7, respectively. The results obtained consider both an initial contraction of a porous body in a vacuum and an additional contraction, if any, or the body expansion on the initial stage of the gas sorption. The exact calculation of strain is given for a cylindrical and spherical pore. The role of surface tension is shown to be reduced, first, to the initial contractive strain of a porous body in a vacuum and, second, to the body dilatation in the course of the gas sorption. A small additional contraction of a porous body on the initial stage of sorption (that, as is shown, cannot be caused by surface tension) is explained by the peculiarities of the sorbate pressure tensor in a pore. The effect is more pronounced the smaller the pore size and the lower the temperature, and is typical for nanoporous bodies. A general consideration based on the Irving–Kirkwood pressure tensor qualitatively confirms the regularities established for any kind of molecular interaction.

DOI: 10.1134/S1070363207030097

I. INTRODUCTION

In view of their large specific area, porous bodies are widely used as sorbents. Besides the study of sorption itself, the sorption-striction phenomenon (i.e. a change in the sorbent volume during sorption) attracted the attention of researchers at least since 1927 [1] and have been multiply discussed in the literature (see, e.g., reviews [2]). In due time, special attention was paid to zeolites [3–7], but both earlier [8–15] and modern investigations [16–21] show the sorption-striction phenomenon to be universal and inherent in any microporous (especially nanoporous) body with any shape of pores. In particular, carbon sorbents with pure dispersion interactions have been studied in detail. Two types of the dependence of the body strain $\Delta\eta$ on the sorption Γ have been established in experiment: (1) a curve with a $\Delta\eta$ minimum when a small sorbent contraction on the initial stage of sorption is replaced by expansion with the growth of sorption; (2) a monotonic increase of $\Delta\eta$ with Γ (Fig. 1). The first type of the dependence is observed at a sufficiently low temperature, while the second is typical for higher temperatures. It was commonly agreed that the phenomenon is related to molecular interactions in a microporous systems.

Concerning theoretical work, we note the first thermodynamic approaches [22, 23] that were restricted by necessity since the thermodynamics of solids was not well developed by that time (see the review [24]). The theory by Serpinski and Yakubov [23] yielded two statements. First, only the dependence of type *1* (Fig. 1) exists in reality. The dependence of type *2* is an artefact due to a great smallness of the minimum depth for some systems. Second, the initial slope of the $\Delta\eta(\Gamma)$ curve is $-\infty$. However, these statements were not corroborated in the newest publication [25]. We can add that they are also disproved in this paper. Realizing the idea of direct relation between intermolecular attractive and repulsive forces and the effects of contraction and expansion of a porous body, Fomkin and Pulin performed a direct calculation of interactions in zeolites using Lennard–

Jones potential with induced electrostatic forces [26]. Basing on the same idea, Ustinov and Do [27] returned to a thermodynamic approach within the functional density method and did calculations for the sorption of nitrogen in slit graphite pores. Another idea (on the counteraction of attraction forces and thermal motion) was considered in [28] where a general consideration was given for explaining sorption-striction. In this communication, we present a more detailed variant of the theory with calculated formulas for the case of dispersion forces.

A theoretical consideration should include solving at least three problems. The first one is the analysis of the pressure tensor inside a nanopore containing a sorbate as dependent on the pore shape and size. The second problem is estimating the role of the surface tension of the pore walls (in case of being non-flat) in the process of strain of a porous body. The solution of the two problems determines forces acting on the bulk phase of a porous body; so that the third problem is naturally formulated as the calculation of strain on the basis of the theory of elasticity (the effects observed are small enough to secure the elastic type of the solid behavior). Solving all the three problems is the goal of this paper.

The pressure tensor inside the pore space will be considered on the basis of the asymptotic statistical-mechanical theory of molecular structure of surface layers in systems with dispersion interactions, formulated on the border of the 60s and 70s of the last century [29–35]. This theory, based on functional expansions relating distribution functions in the surface layer to their values in the bulk, is a rare example of a rigorous statistical-mechanical theory free from models and approximations (such as the Percus–Yevick approximation, the hypernetted chain approximation, the density-functional approach, etc.). The theory is called asymptotic because it describes only the diffuse part of a surface layer far (as compared with atomic dimensions) from the boundary surface between adjacent phases. To calculate the one- and two-particle distribution functions in this region, it is enough to know the asymptotic part of the pair potential, which is rigorously given by the well known expression

$$\varnothing_{ij}(R) = -A_{ij}^{(\lambda)}R^{-\lambda}, \qquad (1)$$

where R is the distance between molecules of sorts i and j, $A_{ij}^{(\lambda)}$ is the interaction constant that is positive and symmetrical with respect to i and j, $\lambda = 6$ for the ordinary van der Waals forces (approximately at $R <$ 20 nm according to experiment) and $\lambda = 7$ for the van der Waals forces with electromagnetic retardation (approximately at $R >$ 80 nm). Finding asymptotic expressions for the one- and two-particle distribution functions in the surface layer was the first step of the theory. The second one was the calculation of the local pressure tensor in the surface layer $\rho(\mathbf{r})$ according to Irving–Kirkwood's definition [36]

$$\rho(\mathbf{r}) = kT\sum_i \rho_i^{(1)}(\mathbf{r})1$$
$$-\frac{1}{2}\sum_{i,j}\int \frac{\mathbf{R}\times\mathbf{R}}{R}\varnothing'_{ij}(R)\int_0^1 \rho_{ij}^{(2)}(\mathbf{r}-\xi\mathbf{R}, \mathbf{r}-\xi\mathbf{R}+\mathbf{R})d\xi, \qquad (2)$$

where k is the Boltzmann constant, T is the temperature, $\rho_i^{(1)}$ and $\rho_{ij}^{(2)}$ are the one- and two-particle distribution functions, 1 is the unit tensor, $\varnothing'_{ij}(R)$ is the derivative of the pair potential of molecular interaction with respect to R (i.e. the interaction force), $\mathbf{R}$ is the vector connecting two interacting molecules and passing through the point $\mathbf{r}$, and $\mathbf{R}\times\mathbf{R}$ is the direct vector product (forming a tensor). The computational scheme for the Irving–Kirkwood pressure tensor is as follows: for each orientation of an elementary unit area at $\mathbf{r}$, only those molecular pairs contribute whose connecting straight line intersects the unit area.

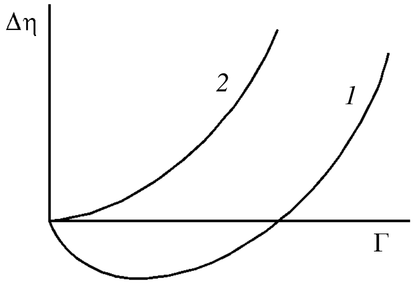

Fig. 1. Two types of the dependence of the porous body strain on sorption.

Passing from surface layers to thin films or narrow slits, we have the situation when the opposite surface layers overlap. The asymptotic theory does work in the middle part of a film or slit and permits the calculation of the pressure tensor in this region. However, the normal component of the pressure tensor is uniform across a film or slit according to the mechanical equilibrium condition, so that the calculation of the normal pressure in the middle means finding it at every point of a system. In this way, the normal pressure of a film is found as a function of the film thickness. Similarly, the pressure tensor can be calculated in the axial part of a thin liquid thread or a cylindrical pore and in the central part of a drop or spherical cavity as a function of the object radius. This time, however, the resultant pressure tensor refers only to the middle of a system.

It is important that expressions of the asymptotic theory contain both the principal (bulk) and corrective (surface) terms. On one side, this produces possibility for estimating the applicability range of the expressions for exact calculations (an example of estimation will be given below). On the other side, considering the case when, due to adsorption, the corrective term becomes equal to or even more than the principal term, is important for qualitative predictions at passing to a nonasymptotic size region. In this presentation, we mainly deal with the initial part of the adsorption isotherm, when adsorption is small and has no influence on the validity of the asymptotic theory.

The asymptotic theory evaluates the pressure tensor in the middle of nanopores of radius smaller than about 10 nm with $\lambda = 6$ and of micropores of radius larger than about 40 nm with $\lambda = 7$. The results of the asymptotic theory are rigorous, even uncertainty related to non-additivity of molecular interactions was overcome by introducing an effective value for the pair interaction constant. However, the asymptotic theory is restricted to the case of dispersion forces. For this reason, we, when concluding, complement estimations of the asymptotic theory with a general consideration in the spirit of [28] to yield at least qualitative explanation of sorption-striction observed for other kinds of forces.

II. ESTIMATIONS OF ASYMPTOTIC THEORY

Let us consider the sorption equilibrium between a gas (phase α) with pressure p and a solid (phase β) containing narrow pores (spherical, cylindrical, or flat) accessible to the gas. Since a small pore cannot contain the bulk phase of a sorbate, the pressure tensor in the middle of the pore is unnecessary isotropic and possesses a structure corresponding to the pore shape. In view of the further application to the calculation of the sorbent volume variation, we are interested in the normal (with respect to the pore walls) component p_N of the pressure tensor. The understanding of p_N is self-evident for flat pores and is associated with the radial principal value $p_N \equiv p_{rr}$ in the cases of spherical and cylindrical symmetry. We subsequently consider below the cases of a spherical, cylindrical, and flat pore.

A. The Case of a Spherical Pore

In reality, spherical cavities in sorbents are connected with channels through which a substance under sorption enters the sorbent interior. For the sake of simplicity, we will ignore the relative role of the channels in calculations. We will regard the cavities to be pure spherical, although it will be assumed that a sorbate has a free access to the cavity interior. One can also say that, in fact, pores of different kinds are simultaneously present in a porous body (for example, spherical cavities are connected with cylindrical pores), but we consider every pore kind separately and begin with a spherical cavity.

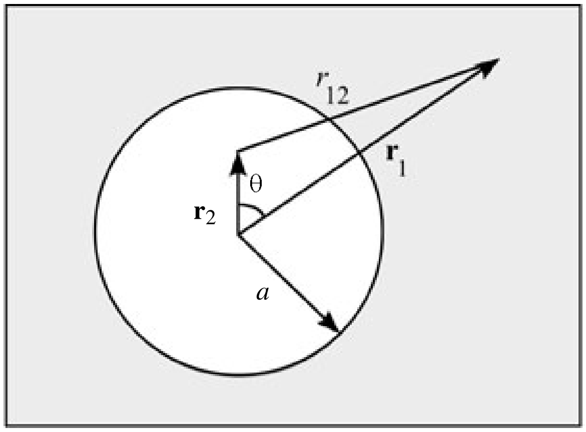

Fig. 2. To the calculation of the dispersion forces field inside a spherical cavity in a condensed phase.

If an infinite condensed phase contains, in its interior, a cavity of radius a, the phase matter (subscript 1) creates a field of dispersion forces $U(r)$ inside the cavity where $r < a$ is the radial coordinate of the center of mass of a test particle (subscript 2). The simplest estimation of the field looks as follows. If the coordinate of an arbitrary molecule of the condensed phase is $\mathbf{r_1}$ and the test particle coordinate is $\mathbf{r} \equiv \mathbf{r_2}$, their pair potential, according to Eq. (1) (we set $\lambda = 6$ for a small cavity), is

$$\varnothing(r_{12}) = -A_{12}r_{12}^{-6}, \tag{3}$$

where r_{12} is the distance between points $\mathbf{r_1}$ and $\mathbf{r_2}$. This distance is geometrically related to the radial coordinates r_1 and r_2 as

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1r_2\cos\theta, \tag{4}$$

where θ is the angle between the radius-vectors $\mathbf{r_1}$ and $\mathbf{r_2}$ (Fig. 2). If ρ_1 is the molecular number density in the condensed phase, the potential of the field of dispersion forces is

$$U(r_2) = \rho_1\int\limits_{r_2>a} \varnothing(r_{12})d\mathbf{r}_1. \tag{5}$$

It is convenient to perform the integration in the spherical coordinates r_1, θ, φ with reckoning angle θ from the direction $\mathbf{r_2}$ (Fig. 2). Using Eqs. (3) and (4) replaces Eq. (5) by

$$U(r_2) = 2\pi\rho_1A_{12}\int\limits_R^\infty r_1^2dr_1\int\limits_1^{-1} r_1^2 + r_2^2 - 2r_1r_2\cos\theta)^{-3}d(\cos\theta). \tag{6}$$

After performing integration and inverse replacing r_2 by r, we obtain

$$U(r) = -\frac{4}{3}\pi\rho A_{12}\frac{a^3}{(a^2 - r^2)^3}. \tag{7}$$

In particular, Eq. (7) yields for the cavity center

$$U(0) = -\frac{4\pi\rho A_{12}}{3a^3}. \qquad (8)$$

The simplest explanation of the sorbent contraction at the beginning of the sorption process is that first sorbate molecules entering a nanopore occupy the central position and attract the surrounding pore walls. Eq. (7) shows that the central position corresponds to the maximum of the potential energy of a test particle and, therefore, is unstable and cannot be realized. This means that the first entering sorbate molecules will adhere to the pore walls to form an adsorbed monolayer. It is of note that the above potential, Eq. (7), with no repulsive part and calculated for a structureless matter is valid only for the central part of a cavity and cannot be applied to the cavity wall. An adsorbed monolayer forms under the action of contact forces whose potential U_{m} (the bonding energy in the monolayer) is significantly different from Eq. (7). Considering the sorption of a gas, it is typically implied that the molecular number density in the monolayer ρ_2^{m} considerably larger than in the gas bulk density ρ_2 (ρ_2^{m}, otherwise the consideration, as well as the practical application of sorbents, is aimless). The two densities are related to each other by the Boltzmann equation

$$\rho_2^{\mathrm{m}} = \rho_2 \exp\left[-\frac{U_{\mathrm{m}}}{kT}\right]. \qquad (9)$$

For the sake of illustration, let us consider the sorption of benzene on the microporous active carbon. The bonding energy (the work of the bond rupture) of sorption is reported [4] as 21.2×10^3 J mol^{-1}, i.e. $U_{\mathrm{m}} = -21.2 \times 10^3$ J mol^{-1}. Putting this value in Eq. (9) at $T = 293$ K yields $\rho_2^{\mathrm{m}}/\rho_2 \approx 6 \times 10^3$. A similar consideration can be carried out for pores of any shape. Obviously, there will be also unstable the position of a test particle at the axis of a cylindrical pore and at the middle plane of a flat pore.

Simultaneously with the monolayer formation, the pressure tensor changes in the whole interior of the cavity. Using the pair potential (1), the asymptotic theory yields the following expression for the normal component of the pressure tensor at the center of a spherical cavity (where pressure is isotropic) and its vicinity [34, 35]

$$p_{\mathrm{N}} = p - \frac{4\pi\lambda}{3(\lambda-2)(\lambda-3)} a^{-\lambda+3} \sum_{i,j} A_{ij}^{(\lambda)} \left\{ 2^{-\lambda+2}\rho_i^{\beta}\rho_j^{\beta} - \left[2^{-\lambda+3} + \frac{2(\lambda-3)}{\lambda}\right]\rho_i^{\beta}\rho_j^{\alpha} + \left[2^{-\lambda+2} + \frac{2(\lambda-3)}{\lambda}\right]\rho_i^{\alpha}\rho_j^{\alpha} \right\}$$
$$- \frac{4\pi\lambda}{3(\lambda-2)} a^{-\lambda+2} \sum_{i,j} A_{ij}^{(\lambda)} \left\{ 2^{-\lambda+2}\rho_i^{\beta} - \left[2^{-\lambda+2} + \frac{2(\lambda-3)}{\lambda}\right]\rho_i^{\alpha} \right\} \Gamma_j + O(a^{-\lambda+1}), \qquad (10)$$

where pressure p, densities ρ_i, and Gibbs' adsorptions Γ_i refer to a macroscopic system (at $a \to \infty$) and the summation is carried out over all species. Since all statistical-mechanical calculations were made in the grand canonical ensemble, the quantities p_{N} and p in Eq. (10) refer to same values of chemical potentials. This means that p can be understood as the equilibrium outer pressure of a multicomponent gas being in contact with a sorbent. It is also of note that the constants $A_{ij}^{(6)}$ and $A_{ij}^{(7)}$ differ not only in value, but also in dimensionality.

Let us consider the simple case when the phases α and β contain single species not penetrating to each other. We ascribe subscript 1 to the sorbent matter and subscript 2 to the sorbate matter. The subscripts i and j in Eq. (10) now ran values 1 and 2, and, in addition, we have $\rho_1^{\alpha} = 0$ and $\rho_2^{\beta} = 0$. In this situation, we may denote the phase densities as $\rho_1 \equiv \rho_1^{\beta}$ and $\rho_2 \equiv \rho_2^{\mathrm{ox}}$ (the phase superscripts become unnecessary and can be omitted). Correspondingly, Eq. (10) becomes

$$p_{\mathrm{N}} = p - \frac{4\pi\lambda}{3(\lambda-2)(\lambda-3)} a^{-\lambda+3} \left\{ 2^{-\lambda+2} A_{11}^{(\lambda)}\rho_1^2 - \left[2^{-\lambda+3} + \frac{2(\lambda-3)}{\lambda}\right] A_{12}^{(\lambda)}\rho_1\rho_2 + \left[2^{-\lambda+2} + \frac{2(\lambda-3)}{\lambda}\right] A_{22}^{(\lambda)}\rho_2^2 \right\}$$
$$- \frac{4\pi\lambda}{3(\lambda-2)} a^{-\lambda+2} \left\{ 2^{-\lambda+2}\rho_1 (A_{11}^{(\lambda)}\Gamma_1 + A_{12}^{(\lambda)}\Gamma_2) - \left[2^{-\lambda+2} + \frac{2(\lambda-3)}{\lambda}\right] \rho_2 (A_{12}^{(\lambda)}\Gamma_1 + A_{22}^{(\lambda)}\Gamma_2) \right\}. \qquad (11)$$

We now can apply Eq. (11) to the analysis of the pressure behavior inside a pore in the course of the gas sorption. Considering first the initial state in the absence of a sorbate ($p = 0$, $\rho_2 = 0$, $\Gamma_2 = 0$), the normal pressure at the center of a spherical pore is given by the expression

$$p_{N0} = -\frac{2^{-\lambda+4}\pi\lambda \overset{(\lambda)}{A}_{11}\rho_1^2}{3(\lambda-2)(\lambda-3)}\, a^{-\lambda+3}\left[1 + \frac{(\lambda-3)\Gamma_1}{\rho_1 a}\right]. \quad (12)$$

where the additional subscript 0 indicates the absence of a sorbate. The remaining adsorption has the meaning of the solid self-adsorption (a local change of density) induced by the phase force field and surface tension and realized due compressibility. As is known, compressibility is very small for condensed phases. By contrast, stresses arising in the surface layer can be very large (attaining 200 and more bars even for liquids with low surface tension [37]), which makes necessary the estimation of Γ_1. Denoting the surface layer density and thickness as ρ_1^σ and d_1, respectively, and the bulk density as ρ_1, we can represent the self-adsorption as

$$\Gamma_1 = (\rho_1^\alpha - \rho_1)d_1 < 0, \quad (13)$$

where the negative sign corresponds to the solid/vacuum boundary. At a given Γ_1, the value of the density difference in Eq. (13) depends on the d_1 value presumed and is maximum when d_1 is taken for the molecular dimension of the sorbent matter (from this moment, we accept this interpretation of d_1). With this estimation from experimental values of Γ_1 for a number of liquids, the relative decrease of density in the surface layer was found to range within 3–7% (with an exception of water with 15%) [38]. The effect is still smaller for crystals. Direct experimental methods (such as LEED) show a lowered surface density in the first lattice plain and a reduced lattice parameter between the first and second planes, as if the surface layer were really stretched by surface tension. The resulting decrease of surface density is about several percents. Now, returning to Eq. (12) and accounting for the condition $d_1 < a$, we see that the correction term (differing in sign from the principal term) is negligible (confirming the validity range of Eq. (12) down to molecular dimensions in this case). The principal term yields a negative value of the pressure. Thus, $p_{N0} < 0$.

Let now the sorbent come into contact with a gas at a low pressure, so that a small equilibrium amount of the sorbate enters the sorbent pores. Comparing p_N and p_{N0}, we have to answer the principal question: can the difference $p_N - p_{N0}$ be negative? The simplest way of reasoning is the following. We imaginary "freeze" the sorbent structure by setting ρ_1 and Γ_1 constant. Then, subtracting Eq. (12) from Eq. (11), we have

$$\Delta p_N = p + \frac{4\pi\lambda}{3(\lambda-2)(\lambda-3)} a^{-\lambda+3}\left\{\left[2^{-\lambda+3} + \frac{2(\lambda-3)}{\lambda}\right]\overset{(\lambda)}{A}_{12}\rho_1\rho_2 - \left[2^{-\lambda+2} + \frac{2(\lambda-3)}{\lambda}\right]\overset{(\lambda)}{A}_{22}\rho_2^2\right\}$$
$$-\frac{4\pi\lambda}{3(\lambda-2)} a^{-\lambda+2}\left\{2^{-\lambda+2}\overset{(\lambda)}{A}_{12}\rho_1\Gamma_2 - \left[2^{-\lambda+2} + \frac{2(\lambda-3)}{\lambda}\right]\rho_2(\overset{(\lambda)}{A}_{12}\Gamma_1 + \overset{(\lambda)}{A}_{22}\Gamma_2)\right\}. \quad (14)$$

where

$$\Delta p_N \equiv p_N - p_{N0}.$$

In view of smallness of ρ_2 at the initial part of the sorption isotherm, we can neglect the second items in the curly brackets of the principal and correction terms of Eq. (14) to reduce Eq. (14) to the form

$$\Delta p_N \approx p + \frac{4\pi\lambda a^{-\lambda+3}}{3(\lambda-2)(\lambda-3)}\left[2^{-\lambda+3} + \frac{2(\lambda-3)}{\lambda}\right]\overset{(\lambda)}{A}_{12}\rho_1\rho_2 - \frac{4\pi\lambda(2a)^{-\lambda+2}}{3(\lambda-2)}\overset{(\lambda)}{A}_{12}\rho_1\Gamma_2. \quad (15)$$

Equation (15) contains both positive and negative terms, which is a precondition for the sign reversal of the whole expression. In particular, using the ideal gas equation of state

$$p = \rho_2 kT \quad (16)$$

in Eq. (15), we can write the condition $\Delta p_N < 0$ as

$$\frac{\Gamma_2}{\rho_2 a} > \frac{3(\lambda - 2)2^{\lambda-4}kTa^{\lambda-3}}{\pi\lambda A^{(\lambda)}_{12}\rho_1} + \frac{2}{\lambda - 3} + \frac{2^{\lambda-1}}{\lambda}. \tag{17}$$

For nanopores (at $\lambda = 6$) the condition expressed in (17) takes the form

$$\frac{\Gamma_2}{\rho_2 a} > \frac{8kTa^3}{\pi A^{(\sigma)}_{12}\rho_1} + 6. \tag{18}$$

and for micropores (at $\lambda = 7$)

$$\frac{\Gamma_2}{\rho_2 a} > \frac{120kTa^4}{7\pi A^{(7)}_{12}\rho_1} + \frac{135}{14}. \tag{19}$$

Decreasing the pore size and the temperature promotes the fulfillment of these inequalities.

B. The Case of a Cylindrical Pore

For the axial part of a cylindrical pore of radius a, the asymptotic theory yields [32, 35]

$$\begin{aligned} p_{\mathrm{N}} = p - {} & \pi c_\lambda \frac{(\lambda - 5)!!}{(\lambda - 2)!!} a^{-\lambda+3} \sum_{i,j} A^{(\lambda)}_{ij} \left\{ \left[2 - \frac{\lambda - 1}{\lambda - 2}\,(1 - 2^{-\lambda+2})\right] \rho^\alpha_i \rho^\alpha_j - \left[2 - \frac{\lambda - 1}{\lambda - 2}\,(1 - 2^{-\lambda+3})\right] \rho^\alpha_i \rho^\beta_j + \frac{\lambda - 1}{\lambda - 2}\, 2^{-\lambda+2} \rho^\beta_i \rho^\beta_j \right\} \\ & - \pi c_\lambda \frac{(\lambda - 3)!!}{(\lambda - 2)!!} a^{-\lambda+2} \sum_{i,j} A^{(\lambda)}_{ij} \left\{ \frac{\lambda - 1}{\lambda - 2}\, 2^{-\lambda+2} \rho^\beta_i - \left[2 - \frac{\lambda - 1}{\lambda - 2}\,(1 - 2^{-\lambda+2})\right] \rho^\alpha_i \right\} \Gamma_j + O(a^{-\lambda+1}), \end{aligned} \tag{20}$$

where $c_\lambda = \pi$ for even λ and $c_\lambda = 2$ for odd λ (λ is considered as an integer). Accepting the same simplifying assumptions for phases α and β as in the case of a spherical pore, we have

$$\begin{aligned} p_{\mathrm{N}} = p - {} & \pi c_\lambda \frac{(\lambda - 5)!!}{(\lambda - 2)!!} a^{-\lambda+3} \left\{ \frac{\lambda - 1}{\lambda - 2}\, 2^{-\lambda+2} A^{(\lambda)}_{11} \rho_1^2 - \left[2 - \frac{\lambda - 1}{\lambda - 2}\,(1 - 2^{-\lambda+3})\right] A^{(\lambda)}_{12} \rho_1 \rho_2 + \left[2 - \frac{\lambda - 1}{\lambda - 2}\,(1 - 2^{-\lambda+2})\right] A^{(\lambda)}_{22} \rho_2^2 \right\} \\ & - \pi c_\lambda \frac{(\lambda - 3)!!}{(\lambda - 2)!!} a^{-\lambda+2} \left\{ \frac{\lambda - 1}{\lambda - 2}\, 2^{-\lambda+2} \rho_1 (A^{(\lambda)}_{11} \Gamma_1 + A^{(\lambda)}_{12} \Gamma_2) - \left[2 - \frac{\lambda - 1}{\lambda - 2}\,(1 - 2^{-\lambda+2})\right] \rho_2 (A^{(\lambda)}_{12} \Gamma_1 + A^{(\lambda)}_{22} \Gamma_2) \right\}. \end{aligned} \tag{21}$$

Let us apply Eq. (21) to the analysis of the gas sorption in cylindrical pores. In the absence of a gas ($p = 0$, $\rho_2 = 0$, $\Gamma_2 = 0$), Eq. (21) takes the form

$$p_{\mathrm{N}0} = -2^{-\lambda+2} \pi c_\lambda \frac{(\lambda - 1)(\lambda - 5)!!}{(\lambda - 2)(\lambda - 2)!!} A^{(\lambda)}_{11} \rho_1^2 a^{-\lambda+3} \left[1 + \frac{(\lambda - 3)\Gamma_1}{\rho_1 a}\right]. \tag{22}$$

Comparing this result with Eq. (12), we first notice that the ratio of the principal and correction terms is the same for a spherical pore and a cylindrical one. This means that the correction term in Eq. (22) is as relatively small as was estimated for Eq. (12). Second, the negative pressure created by dispersion forces is larger in its absolute value in the spherical case than in the cylindrical case. The normal pressure ratio for these cases is

$$\frac{\overset{\mathrm{s}}{p}_{\mathrm{N}0}}{\overset{\mathrm{c}}{p}_{\mathrm{N}0}} \approx \frac{4\lambda!!}{3c_\lambda(\lambda - 1)!!}, \tag{23}$$

where the superscripts “c” and “s” refer to cylindrical and spherical pores, respectively. The righthand side of Eq. (23) makes about 1.358 at $\lambda = 6$ and about 1.458 at $\lambda = 7$.

By subtracting Eq. (22) from Eq. (21), we found the change ($\Delta p_N \equiv p_N - p_{N0}$) of the normal (radial) pressure near the axis of a cylindrical pore in the course of the starting gas sorption:

$$\Delta p_N = p + \pi c_\lambda \frac{(\lambda-5)!!}{(\lambda-2)!!} a^{-\lambda+3} \left\{ \left[2 - \frac{\lambda-1}{\lambda-2}\left(1 - 2^{-\lambda+3}\right) \right] A_{12}^{(\lambda)} \rho_1 \rho_2 - \left[2 - \frac{\lambda-1}{\lambda-2}\left(1 - 2^{-\lambda+2}\right) \right] A_{22}^{(\lambda)} \rho_2^2 \right\}$$
$$- \pi c_\lambda \frac{(\lambda-3)!!}{(\lambda-2)!!} a^{-\lambda+2} \left\{ \frac{\lambda-1}{\lambda-2} 2^{-\lambda+2} A_{12}^{(\lambda)} \rho_1 \Gamma_2 - \left[2 - \frac{\lambda-1}{\lambda-2}\left(1 - 2^{-\lambda+2}\right) \right] \rho_2 \left(A_{12}^{(\lambda)} \Gamma_1 + A_{22}^{(\lambda)} \Gamma_2\right) \right\}. \qquad (24)$$

At a small density ρ_2, we can neglect the relatively small items on the right-hand side of Eq. (24). Then Eq. (24) is reduced to

$$\Delta p_N \approx p + \pi c_\lambda \frac{(\lambda-5)!!}{(\lambda-2)!!} \left[2 - \frac{\lambda-1}{\lambda-2}\left(1 - 2^{-\lambda+3}\right) \right] a^{-\lambda+3} A_{12}^{(\lambda)} \rho_1 \rho_2 - 2^{-\lambda+2} \pi c_\lambda \frac{(\lambda-1)(\lambda-3)!!}{(\lambda-2)(\lambda-2)!!} a^{-\lambda+2} A_{12}^{(\lambda)} \rho_1 \Gamma_2 . \qquad (25)$$

Using the ideal gas equation of state (16), we can write the condition $\Delta p_N < 0$ as

$$\frac{\Gamma_2}{\rho_2 a} > \frac{2^{\lambda-2}(\lambda-2)(\lambda-2)!!kTa^{\lambda-3}}{\pi c_\lambda (\lambda-1)(\lambda-3)!!A_{12}^{(\lambda)}\rho_1} + \frac{(\lambda-5)!!}{(\lambda-3)!!}\left[2 + \frac{\lambda-3}{\lambda-1} 2^{\lambda-2}\right], \qquad (26)$$

which becomes for nanopores (at $\lambda = 6$)

$$\frac{\Gamma_2}{\rho_2 a} > \frac{512kTa^3}{15\pi^2 A_{12}^{(6)}\rho_1} + \frac{58}{15} \qquad (27)$$

and for wider pores where the forces with electromagnetic retardation act (at $\lambda = 7$)

$$\frac{\Gamma_2}{\rho_2 a} > \frac{25kTa^4}{\pi A_{12}^{(7)}\rho_1} + \frac{35}{6} . \qquad (28)$$

At comparing the condition expressed in (27) and (28) with the corresponding criteria, (18) and (19), for a spherical pore, we should have in mind that, as numerical estimation show, the first item of their right-hand side is mach larger than the second one at ordinary temperatures. Therefore, we have to compare the first items. In this approach, the ratio of the right-hand sides of (26) and (17) is given by the right-hand side of Eq. (23) to produce again 1.358 and 1.458 for $\lambda = 6$ and $\lambda = 7$, respectively. It is seen from here that a pressure decrease in pores of equal radii on the initial stage of the gas sorption is more difficult to attain for cylindrical pores than for spherical ones, although the pressures compared are of the same order of magnitude.

C. The Case of a Flat Pore

We now turn to the case when a pore is a flat slit. In place of the pore radius, we will use the slit width h as the size parameter. The matter inside the slit is an anisotropic nonuniform thin film whose pressure tensor has the normal (p_N) and tangential components. The difference $p_N - p$ named *disjoining pressure* in colloid science, is the central quantity of the theory of thin films and has been multiply estimated in the literature [39]. Accounting for the adsorption of matter on the slit walls was first made in [30] (see also [33]) in statistical-mechanical calculations. With respect to the pair potential shown in Eq. (1), the result obtained can be written as

$$p_N = p - \frac{2\pi}{(\lambda-2)(\lambda-3)} h^{-\lambda+3} \sum_{i,j} A_{ij}^{(\lambda)} \left(\overset{\alpha}{\rho}_i \overset{\alpha}{\rho}_j - 2\overset{\alpha}{\rho}_i \overset{\beta}{\rho}_j + \overset{\beta}{\rho}_i \overset{\beta}{\rho}_j\right) + \frac{4\pi}{\lambda-2} h^{-\lambda+2} \sum_{i,j} A_{ij}^{(\lambda)} \left(\overset{\alpha}{\rho}_i - \overset{\beta}{\rho}_i\right)\Gamma_j. \qquad (29)$$

For the equilibrium system of a one-component sorbent β and a one-component sorbate α ($i, j = 1, 2$; $\rho_1^\alpha = 0$, $\rho_2^\beta = 0$, $\rho_1^\beta \equiv \rho_1$, $\rho_2^\alpha \equiv \rho_2$), Eq. (29) becomes

$$p_\mathrm{N} = p - \frac{2\pi}{(\lambda-2)(\lambda-3)} h^{-\lambda+3} (\overset{(\lambda)}{A}_{11}\rho_1^2 - 2\overset{(\lambda)}{A}_{12}\rho_1\rho_2 + \overset{(\lambda)}{A}_{22}\rho_2^2) + \frac{4\pi}{\lambda-2} h^{-\lambda+2} [\rho_1(\overset{(\lambda)}{A}_{11}\Gamma_1 + \overset{(\lambda)}{A}_{12}\Gamma_2) - \rho_2(\overset{(\lambda)}{A}_{12}\Gamma_1 + \overset{(\lambda)}{A}_{22}\Gamma_2)]. \tag{30}$$

In the absence of a sorbate (when a vacuum is in the slit), Eq. (30) results in

$$p_{\mathrm{N}0} = -\frac{2\pi}{(\lambda-2)(\lambda-3)} h^{-\lambda+3} \overset{(\lambda)}{A}_{11}\rho_1^2 \left[1 + \frac{2(\lambda-3)\Gamma_1}{\rho_1 h}\right] < 0. \tag{31}$$

Having in mind that the width of the slit is an analog of the double pore radius of a spherical or cylindrical pore, we can conclude that the proportion between the principal and correction terms in Eq. (31) is exactly the same as in the above cases of spherical and cylindrical pores. Comparing Eqs. (22) and (31) yields

$$\frac{p_{\mathrm{N}0}^{\mathrm{c}}}{p_{\mathrm{N}0}^{\mathrm{f}}} \approx \frac{c_\lambda(\lambda-1)!!}{4(\lambda-2)!!}. \tag{32}$$

where the superscript "f" belongs to a flat pore. The right-hand side of Eq. (32) numerically is about 1.473 for $\lambda = 6$ and 1.6 for $\lambda = 7$.

By subtracting Eq. (31) from Eq. (30), we obtain the normal pressure difference ($\Delta p_\mathrm{N} \equiv p_\mathrm{N} - p_{\mathrm{N}0}$) in the pore with and without a sorbate:

$$\Delta p_\mathrm{N} = p + \frac{2\pi}{(\lambda-2)(\lambda-3)} h^{-\lambda+3} (2\overset{(\lambda)}{A}_{12}\rho_1\rho_2 - \overset{(\lambda)}{A}_{22}\rho_2) + \frac{4\pi}{\lambda-2} h^{-\lambda+2} [\overset{(\lambda)}{A}_{12}\rho_1\Gamma_2 - \rho_2(\overset{(\lambda)}{A}_{12}\Gamma_1 + \overset{(\lambda)}{A}_{22}\Gamma_2)]. \tag{33}$$

Assuming now the equilibrium gas pressure and the gas density small and neglecting the quantities of the second order of magnitude with respect to ρ_2 (including the product $\rho_2\Gamma_1$ because of the smallness of the self-adsorption of the sorbent), we write Eq. (33) as

$$\Delta p_\mathrm{N} \approx p + \frac{4\pi}{(\lambda-2)(\lambda-3)} h^{-\lambda+3} \overset{(\lambda)}{A}_{12}\rho_1\rho_2 - \frac{4\pi}{\lambda-2} h^{-\lambda+2} \overset{(\lambda)}{A}_{12}\rho_1\Gamma_2. \tag{34}$$

The requirement that, on the initial stage of sorption, the pressure inside the pore becomes still smaller ($\Delta p_\mathrm{N} < 0$), is equivalent to the inequality [written again with using Eq. (16)]

$$\frac{\Gamma_2}{\rho_2 h} > \frac{(\lambda-2)kTh^{\lambda-3}}{4\pi\overset{(\lambda)}{A}_{12}\rho_1} + \frac{1}{\lambda-3}. \tag{35}$$

Equation (35) reads for the ordinary van der Waals forces ($\lambda = 6$)

$$\frac{\Gamma_2}{\rho_2 h} > \frac{kTh^3}{\pi\overset{(6)}{A}_{12}\rho_1} + \frac{1}{3}. \tag{36}$$

and for the van der Waals forces with retardation ($\lambda = 7$)

$$\frac{\Gamma_2}{\rho_2 h} > \frac{5kTh^4}{4\pi\overset{(7)}{A}_{12}\rho_1} + \frac{1}{4}. \tag{37}$$

Comparing two last inequalities with their analogs (27) and (28) for cylindrical pores at $h = 2a$, we find them stronger than in the cylindrical case. The ratio of the first items on the right-hand sides of (35) and (26) coincides with the right-hand side of Eq. (32) to produce again 1.473 for $\lambda = 6$ and 1.6 for $\lambda = 7$. The condition expressed in (35) is satisfied easier the lower the temperature and the slit width.

III. ROLE OF SURFACE TENSION

The term "surface tension" is of multiple meaning. Its primary significance is an excess surface stress, but it can also be thermodynamically defined as the work of formation of unit surface. Gibbs [30] was first to notice that the mechanical (γ) and thermodynamic (σ) definitions of surface tension do not coincide for solids. To make a clear thermodynamic distinction, Gibbs defined γ and σ as the work of formation of unit surface area by stretching an old surface and by creating a new surface (say, by cutting a body), respectively. The principal difference between γ and σ originates from the existence of the chemical potential gradient (even at equilibrium) near the surface of an ideally elastic solid (with no defects in its lattice) due to impossibility of free migration of the lattice particles [31]. The thermodynamic surface tension σ should be positive according to the stability condition, whereas γ can be of any sign, although, according to modern data [16], is preferably positive at the solid–gas interface.

Considering the mechanical state of a porous body, we are naturally interested in the mechanical surface tension γ that is often called "surface stress" in the modern literature (to avoid confusion, we note that some authors replace Gibbs' σ by γ, but we stick close to Gibbs' notation). However, the mechanical surface tension itself is also multiply defined (modern approaches to the surface tension definition have been reviewed recently [24]). For example, the excess surface stress can be taken over the interface volume or over the interface cross-section. In the last case, the local mechanical equilibrium condition at the boundary between phases α and β is invariant to the dividing surface location and can be written in the vector form as [42]

$$\mathbf{p}_N^{\alpha} - \mathbf{p}_N^{\beta} = -\frac{\partial \gamma_1}{\partial l_1} - \frac{\partial \gamma_2}{\partial l_2}, \tag{38}$$

where $\mathbf{p_N}$ is the vector component of the pressure tensor for the normal (to the dividing surface) direction; γ_i is the vector component of the surface tension tensor for the direction i ($i = 1, 2$) on the dividing surface; 1, 2, and $3 \equiv \mathrm{N}$ are the coordinate lines of an orthogonal curvilinear coordinate system diagonalyzing the metric tensor of an interface; l_i is the length of the coordinate line i.

Applying Eq. (38) to the pore wall and considering β as a solid phase, we replace $\mathbf{p}_N^{\beta}$ by the stress vector $\mathbf{E_N}$. For the sake of simplicity, we consider surface tension to be isotropic and constant within a small local area, so that the derivatives in Eq. (38) will only produce the surface curvature. Taking the scalar product of Eq. (38) with the normal unit vector and setting $p_N^{\alpha} \equiv p_N$ and $p_N^{\beta} \equiv -E_N$ rewrites Eq. (38) in the Laplace equation form

$$E_N = \gamma c - p_N. \tag{39}$$

where c is the mean surface curvature. Equation (39) shows that surface tension contributes to the solid stress and, hence, to the solid strain unless the surface is flat ($c = 0$ for a flat surface). This means that we should take surface tension into account when calculating strain in the cases of a spherical cavity and a cylindrical pore.

At the pore wall, surface tension as an excess surface stress is composed of two parts on the sides of a solid phase and a sorbate. The notion of "excess" implies the choice of a reference bulk phase. The choice is natural for the solid part of interface since a real solid bulk phase is present. As for the pore interior (where there is no bulk phase), a reference phase can be chosen in a number of ways. According to Gibbs' approach, a reference phase should be of the same nature as the interior content and have the pressure that corresponds to the same values of temperature and chemical potentials as in the pore interior. Another approach was used for small drops by Rowlinson and Widom [27] who obtained a reference phase by extrapolating the isotropic pressure at the drop center to the whole drop volume. The attractiveness of this approach is caused by the reality of pressure, which is especially important if the pressure is needed for the calculation of strain and, in addition, can be easily estimated, e.g., as we did in the preceding section. For this reason, we stick to the approach of Rowlinson and Widom in this paper. At the same time, it should be noted that the contribution to surface tension from the pore interior is typically small as compared with the contribution from the bulk solid. However, not the absolute value, but the change of surface tension in the sorption process is important for our consideration.

Let us discuss the problem of the surface tension variation in the course of sorption. We empathize at once that adsorption differently influences σ and γ (this circumstance was nor taken into account in [25]). For liquids, the problem is easily solved by using the classical Gibbs adsorption equation relating surface tension ($\sigma = \gamma$) to adsorption. A similar relationship for an isotropic solid was derived by Eriksson [43] (later generalized for anisotropic solids [41, 24])

$$d\sigma = (\gamma - \sigma) d\ln A - \Gamma_2 d\mu_2, \tag{40}$$

where A is the surface area (its differential implies stretching the surface) and μ_2 is the sorbate chemical potential. The analysis of equation (40) leads to the relationship [43, 44]

$$\left(\frac{\partial\gamma}{\partial\mu_2}\right) = -\left[\frac{\partial(\Gamma_2 A)}{\partial A}\right]_{\mu_2} = -\Gamma_2\left[1+\left(\frac{\partial\ln\Gamma_2}{\partial\ln A}\right)_{\mu_2}\right], \qquad (41)$$

that relates the mechanical surface tension to the sorbate chemical potential. Since adsorption Γ_2 is an excess of matter per unit surface, the product $\Gamma_2 A$ in Eq. (41) is the sorbate excess for the whole surface.

The estimate of the right-hand side of Eq. (41) depends on the sorption type, which can be nonlocalized (physical) or localized (chemisorption). In the first case, stretching the surface at a fixed sorbate chemical potential (i.e. at a fixed gas pressure if the sorption proceeds from a gaseous phase) can only lead to increasing the total amount of the sorbate on the surface, so that $\partial(\Gamma_2 A)/\partial A > 0$ at $\Gamma_2 > 0$. Correspondingly, we obtain $\partial\gamma/\partial\mu_2 < 0$ from Eq. (41). The initial part of the gas sorption isotherm is characterized by a linear dependence

$$\Gamma_2 = Kp, \qquad (42)$$

where p is the gas pressure and the proportionality coefficient K is known as the Henry constant. The constancy of chemical potential μ_2 means the constancy of p so that putting Eq. (42) in Eq. (41) yields

$$\left(\frac{\partial\gamma}{\partial\mu_2}\right)_A = -K\left[1+\left(\frac{\partial\ln K}{\partial\ln A}\right)_{\mu_2}\right]p \equiv -K'p. \qquad (43)$$

The Henry constant is determined by the sorption potential and should decrease at surface stretching (because of lowering surface density). This means that $(\partial\ln K/\partial\ln A)_{\mu_2} < 0$ and $K' < K$. Assuming the ideal gas behavior ($d\mu_2 = kTd\ln p$) the integration of Eq. (43) on the initial stage of sorption yields

$$\Delta\gamma = -kTK'p. \qquad (44)$$

Introducing the ratio $\ae \equiv K'/K < 1$ and using Eq. (42), Eq. (44) can be written

$$\Delta\gamma = -\ae kT\Gamma_2. \qquad (45)$$

where $kT\Gamma_2$ is well known as the spreading pressure of a sorbate monolayer.

Turning now to the case of chemisorption, we have to consider a specific strong interaction of matter with certain active sites on the solid surface. The total number of active sites on a given surface is fixed and typically does not change during stretching the surface. Therefore, we have $\partial(\Gamma_2 A)/\partial A = 0$. This means, according to Eq. (41), that the mechanical surface tension remains constant in the course of chemisorption ($\Delta\gamma = 0$). It should be emphasized that the localized character of sorption is in a way typical even in the case of physical sorption, which is a consequence of existence of the surface structure and molecules or ions as centers of sorption. As a result, molecules do not move uniformly but jump from one binding position to another (in due time, this mechanism was beautifully described by de Boer [45]).

The estimation of the derivative $(\partial\ln K/\partial\ln A)_{\mu_2}$ in Eq. (43) is closely related to the behavior of the bonding energy U_m as a function of the surface stretching. For the surface of a structureless body (with no density gradient in the solid phase near the boundary surface), the bonding energy U_m is determined by the solid bulk phase density ρ (the matter amount per unit volume) that is inversely proportional to the body volume at a given mass. Relating these quantities to the body area A in the strain process, we have

$$\frac{d\ln U_\mathrm{m}}{d\ln A} = \frac{d\ln\rho}{d\ln A} = -\frac{d\ln V}{d\ln A}. \qquad (46)$$

Calculating $d\ln V/d\ln A$ within the theory of elasticity, the result depends on the type of strain. It is 3/2 for a uniform expansion of a cube or sphere [43] and $(1-2\nu)/(1-\nu)$ at stretching a thin plate [44] or rod. The second variant is preferable [44] since it permits enlarging the surface area by stretching without a change in the body volume (in this case the bonding energy is independent of stretching). At a typical value $\nu = 1/3$, we then have

$$\frac{d\ln U_\mathrm{m}}{d\ln A} = -\frac{1}{2}. \qquad (47)$$

We can relate Γ_2 to U_m with the aid of Eq. (9) by introducing the relationship (valid at $\rho_2^\mathrm{m} \gg \rho_2$, i.e. for the sorption from a gaseous phase) [cf. Eq. (13)]

$$\Gamma_2 = \rho_2^\mathrm{m} d_2. \qquad (48)$$

where d_2 is the monolayer thickness (the molecular dimension of a sorbate). From Eqs. (9) and (48), it follows

$$\left(\frac{d\ln\Gamma_2}{d\ln A}\right)_{\mu_2} = \left(\frac{d\ln K}{d\ln A}\right)_{\mu_2} = -\frac{1}{kT}\frac{dU_\mathrm{m}}{d\ln A}. \qquad (49)$$

Since the right-hand side of Eq. (41) is negative by necessity, the right-hand side of Eq. (49) should be larger than –1. Then, combining Eqs. (47) and (49), we arrive at the condition $U_\mathrm{m}/2kT > -1$ or $|U_\mathrm{m}| < 2kT$, which is an essential restriction on the bonding energy. The result is paradoxical since, naturally, no restriction on the bonding energy is implied. The origin of the paradox is the selfcontradictory model of a compressible but uniform-up-to-the-boundary solid phase with resulting wrong assumption of proportionality between the bonding energy and the bulk density. In a physically self-consistent model, the only case when a solid phase is uniform and does not possess a specific surface layer, is an incompressible phase. According Eq. (46), all the derivatives in Eq. (49) are zeros in this case, and this is the only physically justified conclusion that can be made from the above derivation. In this simple case, we have, from Eqs. (43) and (49), $K = K'$ and $æ = 1$, so that the mechanical surface tension γ, similarly to σ, obeys the ordinary Gibbs adsorption equation.

The problem of the surface curvature effect also arises since Eq. (40) was derived for a flat surface. As the dependence of the mechanical surface tension of the surface curvature was never estimated in the literature, we only can formulate some general arguments. First, the asymptotic theory deals with the adsorption related to a flat surface, and, if we stay within the frames of this theory, we should operate with flat-surface relationships. Second, more generally, Eq. (40) is valid not only for a flat surface, but also for an arbitrary surface provided the surface curvature is fixed. So if one neglects a change in the surface curvature in the course of sorption, Eq. (40) can be applied also to a curved surface. Finally, we estimate not the mechanical surface tension itself, but its variation in the course of sorption. The above statement that both the mechanical and thermodynamic surface tensions can simultaneously follow the Gibbs adsorption equation does not mean that the tensions are close in their values. They can differ greatly, but their variations can be the same.

Let us now discuss the possible role of surface tension in the sorption-striction phenomenon. According to Eq. (39), surface tension will contribute to the porous body strain. At the initial state in a vacuum, at its positive value surface tension contribute to contraction and, at a negative value, to the dilatation of the body. The final state of the body in a vacuum will result from the mutual action of the sorbate pressure tensor and surface tension. Let us see what will happen when the sorption process starts under the condition that the adsorption is positive and the adsorption mechanism is non-localized. In accordance with Eq. (43), surface tension decreases with increasing the sorbate chemical potential. If surface tension is positive, its absolute value will decrease. Since surface tension contributed positively to the initial compression of a porous body, the body begins to expand. If surface tension is negative, its decrease with increasing the sorbate chemical potential means increasing the absolute value of surface tension and the prolongation of the previous action of surface tension, i.e. stretching the sorbent. Thus we arrive at the conclusion that, irrespective of the surface tension sign, its mechanical action on the stage of starting physical sorption is reduced to the body dilatation and, hence, cannot explain the initial contraction observed in experiment.

The case of chemisorption is still simpler because, as it follows from Eq. (41), the mechanical surface tension does not change at all at the beginning of the sorption process. So we can say that surface tension generally contributes to the mechanical state of a porous body, but cannot be responsible for the unusual phenomenon of an additional contraction of the body at starting the sorption process. Consequently, the explanation of this phenomenon can be based only on the behavior of the sorbate pressure tensor and its capability to decreasing the normal pressure when increasing the sorbate chemical potential. The above calculations for dispersion forces show the reality of such behavior at certain conditions. Below, we will confirm this for the general case, but now perform some strain calculations.

IV. CALCULATION OF ELASTIC STRAIN

After obtaining the above results, we can proceed to the calculation of strain within the theory of elasticity (since the strain effects under consideration are small, we confine ourselves with considering only the elastic region of the solid behavior).

A. The Case of Spherical Pores

Let us consider a spherical cavity of radius inside an elastic isotropic solid. The mechanical equilibrium condition at the cavity wall expressed in Eq. (39) takes the form

$$E_N = \frac{2\gamma}{a} - p_N. \tag{50}$$

Equation (50) shows that $p_N - 2\gamma/a$ is an external force (per unit area) acting on the solid (in the direction from the cavity to the body). This force is equilibrated by the stress E_N in the state of mechanical equilibrium and produces strain in the absence of equilibrium.

A certain volume falls on each of many pores in the whole porous body. Assuming radius a to be equal for all the pores and the pores to be distributed uniformly in the body, we will consider this volume also equal for all the pores. We imagine it as the volume of a boll of radius R_2. The boll of radius R_2 has inside a spherical cavity of radius $R_1 \equiv a$ occupied by a pore. The pressure p_1 on the internal surface of the hollow boll surrounding the pore depends on the Laplace pressure in the force balance equation $p_1 = p_N - 2\gamma/a$ according Eq. (50). As for the pressure, p_2, on the external surface of the hollow boll (separated by the distance at least $R_2 - R_1$ from the surfaces of all pores in the body), it is not related to the Laplace pressure. We assume this pressure to coincide with the external pressure p of a gas under sorption acting on the body: $p_2 = p$. There is of no significance that the volumes falling on individual pores in the body do not cover completely the whole volume of the porous body. It is only important that the solid strain in the spherical layer between radii R_1 and R_2 is uniquely determined by the pressures p_1 and p_2, i.e. is independent of what proceeds with the porous body outside this layer.

If a body of the shape of a hollow ball has the inner and outer radii and pressures R_1, R_2 and p_1, p_2, respectively, the radial displacement vector u as a function of the radial spherical coordinate r under the mechanical equilibrium condition is [46]

$$u(r) = \frac{(p_1\varphi - p_2)(1 - 2\nu)}{(1 - \varphi)Y} r + \frac{R_1^3(p_1 - p_2)(1 + \nu)}{2(1 - \varphi)Y} r^{-2}, \tag{51}$$

where $\varphi \equiv R_1^3/R_2^3$ is the cavity volume fraction ($0 < \varphi < 1$), Y is the Young modulus ($Y > 0$), and ν is the Poisson ratio ($0 \le \nu \le 0.5$, the value 0.5 corresponding to the incompressibility of a solid). In particular, the displacement of the inner radius is

$$u(R_1) = R_1 \left[\frac{(p_1\varphi - p_2)(1 - 2\nu)}{(1 - \varphi)Y} + \frac{(p_1 - p_2)(1 + \nu)}{2(1 - \varphi)Y}\right], \tag{52}$$

and the displacement of the outer radius of the body is

$$u(R_2) = R_2 \left[\frac{(p_1\varphi - p_2)(1 - 2\nu)}{(1 - \varphi)Y} + \frac{\varphi(p_1 - p_2)(1 + \nu)}{2(1 - \varphi)Y}\right]. \tag{53}$$

Equations (52) and (53) show that both inner and outer radii are capable of changing even at an incompressible solid phase (when $\nu = 0.5$). The relative variation, η, of radius R_2 is obtained by dividing Eq. (53) by R_2:

$$\eta \equiv \frac{u(R_2)}{R_2} = \frac{3\varphi(1 - \nu)}{2(1 - \varphi)Y} p_1 - \frac{1 - 2\nu + \varphi(1 + \nu)/2}{(1 - \varphi)Y} p_2. \tag{54}$$

Let us apply Eq. (54) to the case of a spherical cavity of radius a in a porous body. We have to set $R_1 = a$, $p_2 = p$, and, according to Eq. (50), $p_1 = p_N - 2\gamma/a$, so that Eq. (54) becomes

$$\eta = \frac{3\varphi(1 - \nu)}{2(1 - \varphi)Y}\left(p_N - \frac{2\gamma}{a}\right) - \frac{1 - 2\nu + \varphi(1 + \nu)/2}{(1 - \varphi)Y} p. \tag{55}$$

Equation (55) characterizes the mechanical state of the body. According to Eqs. (54) and (55), the quantity η will be the same for all the pores at equal R_2 and φ. Then η will also represent the relative variation of the linear size of the whole porous body (directly measured in experiment) with an arbitrary number of pores, and φ can be understood as the porosity of such a body. Thus, the theory accounts for the multiplicity of pores, although their mutual influence is not considered (such consideration would be an extremely difficult problem).

According to formulas in [46], in the case of a spherical pore we have

$$p_{rr}\big|_{r = R_2} = p_2,$$

$$p_{\theta\theta}\big|_{r = R_2} = p_{\varphi\varphi}\big|_{r = R_2}$$

$$= \frac{p_2(2R_2^3 + R_1^3) - 3p_1R_1^3}{2(R_2^3 - R_1^3)} \equiv \frac{p_2(2 + \varphi) - 3p_1\varphi}{2(1 - \varphi)},$$

where r, θ, φ are spherical coordinates (to avoid confusion, note that symbol φ as a coordinate is only used in a subscript, letter φ still designates porosity). If the restrictions hold $\varphi \ll 1$, $3\varphi|p_1| \ll (2 + \varphi)p_2$ (the larger R_2 and smaller φ at a given R_1 the larger can be an allowable value of $|p_1|$ at a given value of $p_2 > 0$), the pressure tensor in a solid on the spherical surface of radius R_2 will be practically isotropic and corresponding the uniform bulk pressure p_2. It is natural to expect the pressure tensor also to remain isotropic outside the spherical surfaces of radius R_2, i.e. at a still larger distance from pores. Herewith, pressure p_2 will have the sense of the external pressure p of a gas under sorption on the whole porous body (due to macroscopic dimensions of the body, its surface curvature is negligible and, hence, do not produce a pressure jump). In this way, the condition $p_2 = p$ is justified.

As for the asymptotic theory, Eq. (10) was derived in [34, 35] under the assumption that a body is continuous and does not contain pores outside a spherical pore of radius $R_1 \equiv a$, i.e. at $r > R_1$ where r is the distance from the pore center. In our case, however, there are other spherical pores in the region $r > 2R_2 - R_1$. To secure the applicability of Eq. (10) with the earlier understanding of p as an external pressure, the following restrictions can be shown to obey

$$\left(\frac{2R_2 - R_1}{R_1}\right)^{\lambda-3} \gg 1,$$
$$\left(\frac{2R_2 - R_1}{R_1}\right)^{\lambda-2} \gg 1.$$

For this it is practically enough at $\lambda = 6$ and $\lambda = 7$ that R_2 exceeds R_1 at least 1.5 times, i.e. that the condition $\varphi \equiv R_1^3/R_2^3 < 8/27$ is fulfilled. That R_2 should markedly exceed R_1 is seen from the fact that only then pressure p_2 can markedly differ from pressure p_1 an be equal to the external pressure p of a gas under sorption.

Passing to the analysis of Eq. (55), we first consider a porous body in a vacuum. At the zero gas pressure ($p = 0$), Eq. (55) yields

$$\eta_0 = \frac{3\varphi(1-\nu)}{2(1-\varphi)Y}\left(p_{N_0} - \frac{2\gamma_0}{a}\right). \tag{56}$$

Using Eq. (52), we also can calculate the pore radius a_0 in a vacuum as

$$a_0 = a\left[1 + \frac{2\varphi(1-2\nu) + 1 + \nu}{2(1-\varphi)Y}\left(p_{N_0} - \frac{2\gamma_0}{a}\right)\right], \tag{57}$$

where $a_0 - a \equiv u(R_1)$ has been taken into account. As is seen from Eqs. (56) and (57), the body possesses a certain vacuum strain due to the normal pressure and surface tension action, the effect being more pronounced the larger porosity and the smaller the Young modulus and the pore size. Since $p_{N_0} < 0$ in a vacuum according to Eq. (12), the pressure and surface tension act in the same direction in the typical case when $\gamma > 0$. This yields $\eta_0 < 0$ and $a_0 < a$, and we may conclude that every porous body in a vacuum is typically in the state of self-contraction. Strictly speaking, however, γ can be of any sign depending on the nature and the prehistory of a sample, so that the type of strain will generally result from the competition of the pressure and surface tension terms of Eqs. (56) and (57) in the case of a negative surface tension. Since the γ value is difficult of access, we can estimate the effect of surface tension by maximum. We set $\gamma \sim 1$ N/m and $a \sim 1$ nm, take the elasticity modulus $Y \sim 10^{11}$ Pa, the typical Poisson ratio value $\nu = 1/3$, and accept $\varphi = 0.2$. This yields the surface tension contribution to η_0 as about –0.005. However, there is also a contribution to η_0 from p_{N_0}.

Let us see what will happen when the first gas portion enters the cavity interior. Since the strain effects under consideration are small, we may calculate the additional strain by simple subtracting Eq. (56) from Eq. (55) to give

$$\Delta\eta = \frac{3\varphi(1-\nu)}{2(1-\varphi)Y}\left(\Delta p_N - \frac{2\Delta\gamma}{a}\right) - \frac{1 - 2\nu + \varphi(1+\nu)/2}{(1-\varphi)Y}\,p, \tag{58}$$

where $\Delta\eta \equiv \eta - \eta_0$, $\Delta p_N \equiv p_N - p_{N0}$, and $\Delta\gamma \equiv \gamma - \gamma_0$. Using the results of Section II, we can estimate the right-hand side of Eq. (58) for the case of dispersion forces. For the sake of brevity, we write Eq. (15) in the form

$$\Delta p_N \approx p + \overset{(\lambda)}{b}_{1s}\overset{(\lambda)}{A}_{12}\rho_1\rho_2 a^{-\lambda+3} - \overset{(\lambda)}{b}_{2s}\overset{(\lambda)}{A}_{12}\rho_1\Gamma_2 a^{-\lambda+2}, \tag{59}$$

where $b_{ks}^{(\lambda)}$ ($k = 1, 2$) are the numerical coefficients of Eq. (15):

$$b_{1s}^{(\lambda)} \equiv \frac{4\pi\lambda}{3(\lambda-2)(\lambda-3)}\left[2^{-\lambda+3} + \frac{2(\lambda-3)}{\lambda}\right],$$
$$b_{2s}^{(\lambda)} \equiv \frac{4\pi\lambda 2^{-\lambda+2}}{3(\lambda-2)}. \tag{60}$$

(in particular, $b_{1s}^{(6)} = 3\pi/4$, $b_{2s}^{(6)} = \pi/8$, $b_{1s}^{(7)} = 9\pi/16$ and $b_{2s}^{(7)} = 7\pi/120$). Putting Eq. (59) in Eq. (58) yields

$$\Delta\eta = -\frac{1-2\nu}{Y}p + \frac{3\varphi(1-\nu)}{2(1-\varphi)Y} \times \left(\overset{(\lambda)}{b}_{1s}\overset{(\lambda)}{A}_{12}\rho_1\rho_2 a^{-\lambda+3} - \overset{(\lambda)}{b}_{2s}\overset{(\lambda)}{A}_{12}\rho_1\Gamma_2 a^{-\lambda+2} - \frac{2\Delta\gamma}{a}\right). \tag{61}$$

There are four terms on the right-hand side of Eq. (61). In contrast with Eq. (15), the first term is negative, which mirrors the contracting action of the outer pressure. This term is related to the compressibility of the bulk solid phase and disappears for an incompressible solid (when $\nu = 0.5$). Three other terms are related to the shear strain. The second term is positive and the third one negative in accordance with Eq. (59). Since $\Delta\gamma = 0$ in the case of chemisorption and $\Delta\gamma < 0$ in the case of physical sorption, the last term in Eq. (61), if any, is positive and supplements the second term. The presence of terms of opposite signs is a precondition for the occurrence of both a positive and negative additional strain of a porous body at the initial stage of sorption, depending on the particular values of the equation parameters.

Let us see what parameters are responsible for the condition $\Delta\eta < 0$. The role of porosity φ is seen at once. When the solid phase is compressible ($\nu < 0.5$) and the porosity is small, $\Delta\eta$ is negative because the contribution of all other terms on the right-hand side of Eq. (61), except the first one, becomes negligible at $\varphi \to 0$. The case of high porosity is more complicated. As is seen from Eq. (61), the sign of $\Delta\eta$ is determined irrespective of the Young modulus value. The negative sign of $\Delta\eta$ corresponds to the condition

$$g_s p + \frac{b_{2s}^{(\lambda)} A_{12}^{(\lambda)} \rho_1 \Gamma_2}{a^{\lambda-2}} > \frac{b_{1s}^{(\lambda)} A_{12}^{(\lambda)} \rho_1 \rho_2}{a^{\lambda-3}} - \frac{2\Delta\gamma}{a}, \qquad (62)$$

where we have introduced the nonnegative coefficient $g_s \equiv g_s(\varphi, \nu)$ originated from the theory of elasticity:

$$g_s \equiv \frac{2(1-\varphi)(1-2\nu)}{3\varphi(1-\nu)}. \qquad (63)$$

The first term in the inequality (62) is zero for an incompressible solid phase. So we can temporarily omit this term keeping in mind that if the condition (62) is satisfied without the first term, it will be satisfied a fortiori with this term. Then we consider the case when the interaction constant $A_{12}^{(\lambda)}$ is as large as to allow us to neglect also the last term in (62). This permits us to consider jointly the case of the physical sorption with a strong interaction and the case of chemisorption when the last term is zero exactly (because of the condition $\Delta\gamma = 0$ shown in Section III). With two remaining terms, the inequality (62) is reduced to the condition

$$\frac{\Gamma_2}{\rho_2 a} > \frac{b_{1s}^{(\lambda)}}{b_{2s}^{(\lambda)}}, \qquad (64)$$

the right-hand side being 6 for $\lambda = 6$ and $135/14 \approx 9.64$ for $\lambda = 7$. The coefficient values and that fact that a is considerably larger at $\lambda = 7$ than at $\lambda = 6$ show that the realization of the condition $\Delta\eta < 0$ is more probable for nanopores. Putting Eqs. (9) and (48) rearranges the inequality (64) to the form

$$\frac{a}{d_2} < \frac{b_{2s}^{(\lambda)}}{b_{1s}^{(\lambda)}} \exp\left[-\frac{U_m}{kT}\right], \qquad (65)$$

that predicts the fulfillment of the condition $\Delta\eta < 0$ to secure by increasing the energy of interaction of a sorbate with a sorbent and decreasing the temperature and the pore size. In the above example with the sorption of benzene by the active carbon, we have from (65) $a/d_2 < 10^3$, which shows that the condition $\Delta\eta < 0$ is easily attained for nanopores.

Turning now to the case of physical sorption with a moderate interaction and using Eq. (45), we can rewrite (62) as

$$g_s p + \frac{b_{2s}^{(\lambda)} A_{12}^{(\lambda)} \rho_1 \Gamma_2}{a^{\lambda-2}} > \frac{b_{1s}^{(\lambda)} A_{12}^{(\lambda)} \rho_1 \rho_2}{a^{\lambda-3}} + \frac{2æ kT\Gamma_2}{a}. \qquad (66)$$

The first term promotes the fulfillment of the condition $\Delta\eta < 0$, whereas the last term acts in the opposite direction. A high significance of the last term is seen from the fact that the first term vanishes ($g_s = 0$) in the case of an incompressible solid phase. In contrast, the last term increases because æ = 1 due to the constancy of density of an incompressible solid phase. It is also great the compensatory role of the last term with respect to the second term since the major contributor of the second term, adsorption Γ_2 is also contained in the last term. We illustrate this with the example of graphite [37] at $\lambda = 6$ when, for the carbon–carbon interaction $A_{12}^{(\lambda)} = 4\varepsilon d^6$ (ε and d are the Lennard-Jones potential constants) with $\varepsilon = 28k$ K and $d = 3.4 \times 10^{-10}$ m. Using these values and the graphite density at $\rho_1 d^3 \sim 0.5$ the second term can be larger than the last one at $(d/a)^3$ exceeding about $0.1T$ (where T is a dimensionless quantity numerically equal to temperature). Even for sizable sorbate molecules with $A_{12}^{(6)}$ larger by the order of magnitude than in the above example, the second term maintains its dominant role only in the vicinity of the absolute zero of temperature. The matter stands differently at ordinary temperatures. Using Eq. (60), we see that the ratio of the last term to the competing second term in Eq. (66) exceeds the quantity $2æ kTa^{\lambda-3}/A_{12}^{(\lambda)}\rho_1$. According to the remarks after Eqs. (27) and (28), at ordinary temperatures there is the strong inequality

$$\frac{kTa^{\lambda-3}}{A_{12}^{(\lambda)}\rho_1} >> 1,$$

where $\lambda = 6$ or $\lambda = 7$. Then the last term dominates over the second term in Eq. (66) at ordinary temperatures (provided parameter æ is not too small). The variation of parameters ν and æ can change the situation, but we come to the general conclusion that the contribution of the surface tension of a solid is capable to reverse the condition $\Delta\eta < 0$ already at ordinary temperatures.

B. The Case of Cylindrical Pores

In the case of cylindrical pores of equal radius a, the mechanical equilibrium condition at the pore wall following from Eq. (39) is

$$E_{\mathrm{N}} = \frac{\gamma}{a} - p_{\mathrm{N}}, \tag{67}$$

so that $p_{\mathrm{N}} - \gamma/a$ is an external force (per unit area) acting on the isotropic solid (in the direction from the pore to the solid), and the gas pressure p is also an external force. The arguments, formulated in the preceding section concerning the volumes falling on each of the pores in the whole porous body, are also easily applicable to the case of cylindrical pores. Then finding the strain is very close to the standard problem of the theory of elasticity on a pipe with different pressures inside and outside. A pipe with a significant wall thickness is just a solid with a single through pore. So we can again use a ready solution for our purpose.

Let us remind the solution for a pipe with the internal and external radii and pressures R_1, R_2 and p_1, p_2, respectively. The radial displacement u as a function of the radial coordinate r is [46]

$$u(r) = \frac{(p_1\varphi - p_2)(1+\nu)(1-2\nu)}{(1-\varphi)Y}\, r + \frac{R_1^2(p_1 - p_2)(1+\nu)}{(1-\varphi)Y}\, r^{-1}, \tag{68}$$

where the pore volume fraction is now defined as $\varphi \equiv R_1^2/R_2^2$ $(0 < \varphi < 1)$, Y is again the Young modulus, and ν is the Poisson ratio. In particular, the displacements of the inner and outer radii are

$$u(R_1) = R_1 \left[\frac{(p_1\varphi - p_2)(1+\nu)(1-2\nu)}{(1-\varphi)Y} + \frac{(p_1 - p_2)(1+\nu)}{(1-\varphi)Y} \right], \tag{69}$$

$$u(R_2) = R_2 \left[\frac{(p_1\varphi - p_2)(1+\nu)(1-2\nu)}{(1-\varphi)Y} + \frac{\varphi\,(p_1 - p_2)(1+\nu)}{(1-\varphi)Y} \right]. \tag{70}$$

The relative variation, η, of radius R_2 is found by dividing Eq. (70) by R_2:

$$\eta \equiv \frac{u(R_2)}{R_2} = \frac{(1+\nu)}{(1-\varphi)Y}\,[2\varphi(1-\nu)p_1 - (1 - 2\nu + \varphi)p_2]. \tag{71}$$

In our case, $R_1 = a$, $p_1 = p_{\mathrm{N}} - \gamma/a$, and $p_2 = p$ so that Eq. (71) takes the form

$$\eta = \frac{2\varphi(1-\nu^2)}{(1-\varphi)Y}\left(p_{\mathrm{N}} - \frac{\gamma}{a}\right) - \frac{(1+\nu)(1-2\nu+\varphi)}{(1-\varphi)Y}\,p. \tag{72}$$

Equation (72) is the main result for a cylindrical pore. At equality of R_2 and φ in all the pores, the quantity η will be also equal according to Eqs. (71) and (72). Then η represents the relative variation of the linear size of the whole porous body directly measurable in experiment and φ is the body porosity. Here the theory also accounts for the multiplicity of pores (without their mutual influence).

According to formulas in [46], in the case of a cylindrical pore we have

$$p_{rr}\big|_{r=R_2} = p_2,$$

$$p_{\varphi\varphi}\big|_{r=R_2} = \frac{p_2(R_2^2 + R_1^2) - 2p_1R_1^2}{R_2^2 - R_1^2} \equiv \frac{p_2(2+\varphi) - 2p_1\varphi}{1-\varphi},$$

$$p_{zz}\big|_{r=R_2} = 2\nu\,\frac{p_2R_2^2 - 2p_1R_1^2}{R_2^2 - R_1^2} \equiv 2\nu\,\frac{p_2 - 2p_1\varphi}{1-\varphi},$$

where r, φ, z are cylindrical coordinates. If the restrictions are fulfilled $\varphi \ll 1$, $2\varphi|p_1| \ll (1+\varphi)p_2$ (the larger R_2 and smaller φ at a given R_1 the larger can be an allowable value of $|p_1|$ at a given value of $p_2 > 0$) and, in addition, the Poisson ratio ν is close to 0.5 (the solid phase is slightly compressible), then, as in the case of spherical pores, it is natural to expect $p_2 = p$. In this way, this inequality is justified.

As for the asymptotic theory, Eq. (20) was obtained in [32, 35] under the assumption that the body

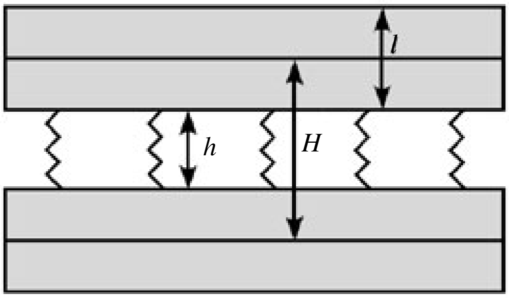

Fig. 3. The elementary cell of a porous body with flat slit-like pores.

does not contain pores outside a cylindrical pore of radius $R_1 \equiv a$ i.e. at $r > R_1$, where r is the distance from the pore axis. In our case, however, there are other cylindrical pores in the body region $r > 2R_2 - R_1$. To make Eq. (20) valid again with understanding p as the external pressure of a gas under sorption, it is practically enough at $\lambda = 6$ and $\lambda = 7$ that (see the reasoning in the case of spherical pores) R_2 exceeds R_1 at least 1.5 times, i.e. the condition $\varphi \equiv R_1^3/R_2^3 <$ 4/9 is fulfilled. Although the restriction on the ratio R_2/R_1 remains the same as in the case of spherical pores, the restriction on φ becomes a bit weaker.

For the initial state of a sorbent in a vacuum, Eq. (72) yields

$$\eta_0 = \frac{2\varphi(1-\nu^2)}{(1-\varphi)Y}\left(p_{\mathrm{N}_0} - \frac{\gamma_0}{a}\right). \tag{73}$$

From Eq. (69) we also can calculate the pore radius a_0 in a vacuum:

$$a_0 = a\left\{1 + \frac{(1+\nu)[1+\varphi(1-2\nu)]}{(1-\varphi)Y}\left(p_{\mathrm{N}_0} - \frac{\gamma_0}{a}\right)\right\}. \tag{74}$$

where $a_0 - a \equiv u(R_1)$ has been taken into account. It is seen from Eqs. (73) and (74) that the surface tension of pores contributes to the initial strain of a sorbent. As it follows from Eq. (22), the pressure p_{N_0} is negative in the absence of a sorbate and, in accordance with Eq. (73), produces a contracting action on the sorbent as a whole. For a more typical positive value of surface tension, the capillary term in Eq. (73) yields a negative contribution, so that surface tension enhances the action of p_{N_0} to produce still larger contraction. If, however, $\gamma < 0$, the capillary effect acts in the opposite direction. Comparing Eqs. (56) and (73) at equal porosities and equal with accounting for Eq. (23), yields a larger value of the coefficient for a cylindrical pore but a larger absolute value of the pressure tensor and capillary pressure multiplier for a spherical pore. As a result, the strain of a porous body turns to be of the same order of magnitude for both of the pore shapes.

By subtracting Eq. (73) from Eq. (72), we obtain

$$\Delta\eta = \frac{2\varphi(1-\nu^2)}{(1-\varphi)Y}\left(\Delta p_{\mathrm{N}} - \frac{\Delta\gamma}{a}\right) - \frac{(1+\nu)(1-2\nu+\varphi)}{(1-\varphi)Y}p. \tag{75}$$

According to Eq. (25), we can represent the expression for Δp_{N} in the case of dispersion forces as

$$\Delta p_{\mathrm{N}} \approx p + b_{1\mathrm{c}}^{(\lambda)} A_{12}^{(\lambda)} \rho_1\rho_2 a^{-\lambda+3} - b_{2\mathrm{c}}^{(\lambda)} A_{12}^{(\lambda)} \rho_1\Gamma_2 a^{-\lambda+2}, \tag{76}$$

with

$$b_{1\mathrm{c}}^{(\lambda)} = \pi c_\lambda \frac{(\lambda-5)!!}{(\lambda-2)!!}\left[2 - \frac{\lambda-1}{\lambda-2}(1-2^{-\lambda+3})\right],$$

$$b_{2\mathrm{c}}^{(\lambda)} = 2^{-\lambda+2}\pi c_\lambda \frac{(\lambda-1)!!}{(\lambda-2)(\lambda-2)!!} \tag{77}$$

(in particular, $b_{1\mathrm{c}}^{(6)} = 29\pi^2/256$, $b_{2\mathrm{c}}^{(6)} = 15\pi^2/512$, $b_{1\mathrm{c}}^{(7)} = 7\pi/30$, and $b_{2\mathrm{c}}^{(7)} = \pi/5$). Putting Eq. (76) in Eq. (75) yields

$$\Delta\eta = -\frac{(1+\nu)(1-2\nu)}{Y}p + \frac{2\varphi(1-\nu^2)}{(1-\varphi)Y} \times\left(b_{1\mathrm{c}}^{(\lambda)} A_{12}^{(\lambda)} \rho_1\rho_2 a^{-\lambda+3} - b_{2\mathrm{c}}^{(\lambda)} A_{12}^{(\lambda)} \rho_1\Gamma_2 a^{-\lambda+2} - \frac{\Delta\gamma}{a}\right). \tag{78}$$

Since Eq. (78) is of the same appearance as Eq. (61) and differs only in the coefficient values, the above analysis of Eq. (61) is easily carried over to Eq. (78). The negative sign of $\Delta\eta$ corresponds to the condition [cf. (62)]

$$g_{\mathrm{c}}p + \frac{b_{2\mathrm{c}}^{(\lambda)} A_{12}^{(\lambda)} \rho_1\Gamma_2}{a^{\lambda-2}} > \frac{b_{1\mathrm{c}}^{(\lambda)} A_{12}^{(\lambda)} \rho_1\rho_2}{a^{\lambda-3}} - \frac{\Delta\gamma}{a}, \tag{79}$$

where

$$g_{\mathrm{c}} \equiv \frac{(1-\varphi)(1-2\nu)}{2\varphi(1-\nu)} \quad \left(= \frac{3}{4}g_{\mathrm{s}}\right). \tag{80}$$

If the first and last terms in Eq. (79) are small, the inequality (79) is reduced to the condition

$$\frac{\Gamma_2}{\rho_2 a} > \frac{b_{1\mathrm{c}}^{(\lambda)}}{b_{2\mathrm{c}}^{(\lambda)}}. \tag{81}$$

The right-hand side of Eq. (81) amounts to 58/15 ≈ 3.867 for $\lambda = 6$ and 175/30 ≈ 5.833 for $\lambda = 7$, which is about by third smaller than the right-hand side of the inequality (64). Thus we can conclude that, comparing cylindrical and spherical pores of the same radius, the condition $\Delta\eta < 0$ is attained easier in the cylindrical case and with a larger probability for nanopores. Concerning the role of the temperature following from the ratio Γ_2/ρ_2, all said above for spherical pores is applicable to the case of cylindrical pores. A temperature decrease promotes the fulfillment of the inequality (81).

Turning to estimating the role of the surface tension, we use Eq. (45) to rewrite the inequality (79) as

$$g_c p + \frac{\overset{(\lambda)}{b}_{2c}\overset{(\lambda)}{A}_{12}\rho_1\Gamma_2}{a^{\lambda-2}} > \frac{\overset{(\lambda)}{b}_{1c}\overset{(\lambda)}{A}_{12}\rho_1\rho_2}{a^{\lambda-3}} + \frac{\text{æ}kT\Gamma_2}{a}. \qquad (82)$$

The surface tension term is now half as much as compared with the case of spherical pores, the inequality (66). However, repeating the arguments at discussing the inequality (66), we can say that the surface tension term remains sufficiently large to be capable of inversing the inequality (82) already at ordinary temperatures.

C. The Case of Flat Pores

The case of flat pores looks to be the simplest of the three cases, but the problem requires a more detailed formulation. The matter is that, in contrast with a cylindrical pore, a flat pore in a body cannot be through-going (otherwise the body will split into two parts) and cannot be considered as infinite. In other words, the boundary conditions at the slit edges are needed, but they can be formulated in many different ways. In addition, the wall of a closed pore with a flat-parallel part cannot be a surface of constant mean curvature and forfeits its conformity in the course of the normal strain.

If, however, we assume that the opposite pore walls of a flat pore are connected by elastic bridges [27] (Fig. 3), the situation is profoundly simplified. In such a model, a flat pore can be infinite. Let us consider a periodical lamellar structure of a solid with parallel slit-like pores and select its elementary cell of thickness H. If h is the slit width and l is the thickness of the solid layer between neighboring slits, it is evident the relationship (Fig. 3).

$$H = h + l. \qquad (83)$$

The body porosity is characterized by the quantity $\varphi \equiv h/H$ $(0 < \varphi < 1)$ in this case. Let us see what forces, capable of inducing strain, act in the system. According to Eq. (39), surface tension becomes out of play in the case of a flat surface, and the normal stress in the solid phase is equal, by its absolute value, to the external pressure p $(E_N = -p_N = -p)$ under the equilibrium condition. Inside the slit, its opposite surfaces are pushed apart by the disjoining pressure $p_N - p$ but sustended by the stress of the bridges strings E'_N (considered, for the sake of simplicity, as not concentrated but smoothed on the unit surface area). Since, however, their resultant action is to be reduced to the pressure p under the mechanical equilibrium condition, the relationship holds

$$p_N - E'_N = p. \qquad (84)$$

Equation (84) determines the bridges stress as $p_N - p$ (i.e. exactly as the disjoining pressure in the slit) and permits its calculation. In accordance with the Hook law, the bridges strain is found as

$$\frac{\delta h}{h} = \frac{p_N - p}{Y'}, \qquad (85)$$

where Y' is the Young modulus of bridges. As for the bulk phase of the solid, it is under the pressure p and undergoes the strain

$$\frac{\delta l}{l} = \frac{p}{Y} \qquad (86)$$

(Y is the Young modulus of the solid phase). Accounting for Eqs. (83), (85), and (86), the total strain of a porous body, measured in experiment, is given by the equation

$$\eta \equiv \frac{\delta H}{H} = \frac{\varphi(p_N - p)}{Y'} - \frac{(1-\varphi)p}{Y}. \qquad (87)$$

It is of note that, in the case of flat pores, there is no restriction from above on the quantity $\varphi \equiv h/H$ stronger then the initial restriction $\varphi < 1$.

In the absence of pores $(\varphi = 0)$ or for rigid bridges $(Y' = \infty)$ it remains in Eq. (87) only the second term describing the trivial contraction of the body under the action of the external pressure. If, however, the solid phase is incompressible $(Y = \infty)$, it conversely remains only the first term (the approach used in [27]). For a sorbent in a vacuum $(p = 0)$ Eq. (87) is simplified to the form

$$\eta_0 = \frac{\varphi p_{N_0}}{Y'} \qquad (88)$$

and, because of $p_{N_0} < 0$ [see (31)], indicates the sorbent contraction. An additional strain in the course of beginning sorption is found as the difference of Eqs. (87) and (88):

$$\Delta\eta = \frac{\varphi(\Delta p_N - p)}{Y'} - \frac{(1-\varphi)p}{Y}. \qquad (89)$$

In the case of dispersion forces the pressure increment Δp_N is given by Eq. (34) that, for the sake of brevity, can be written in the form

$$\Delta p_N - p \approx \overset{(\lambda)}{b}_{1f} h^{-\lambda+3} \overset{(\lambda)}{A}_{12} \rho_1 \rho_2 - \overset{(\lambda)}{b}_{2f} h^{-\lambda+2} \overset{(\lambda)}{A}_{12} \rho_1 \Gamma_2, \quad (90)$$

where

$$\overset{(\lambda)}{b}_{1f} \equiv \frac{4\pi}{(\lambda - 2)(\lambda - 3)}, \quad \overset{(\lambda)}{b}_{2f} \equiv \frac{4\pi}{\lambda - 2}, \quad (91)$$

(in particular, $b_{1f}^{(6)} = \pi/3$, $b_{2f}^{(6)} = \pi$, $b_{1f}^{(7)} = \pi/5$, and $b_{2f}^{(7)} = 4\pi/5$). Putting Eq. (90) in Eq. (89) leads to the result

$$\Delta\eta = -\frac{1 - \varphi}{Y} p + \frac{\varphi}{Y'} \left(\overset{(\lambda)}{b}_{1f} \overset{(\lambda)}{A}_{12} \rho_1 \rho_2 h^{-\lambda+3} - \overset{(\lambda)}{b}_{2f} \overset{(\lambda)}{A}_{12} \rho_1 \Gamma_2 h^{-\lambda+2}\right). \quad (92)$$

The contributions of the first and second terms on the right-hand side of Eq. (92) depend on the value of the body porosity and the ratio of the two modules standing in Eq. (92). The case is the most interesting when the porosity is high (φ can be as close to unity as possible in the case of flat pores) and the bridges Young modulus Y' is significantly smaller than the bulk modulus Y. Then the first item in Eq. (92) can be omitted, and the requirement $\Delta\eta < 0$ is equivalent to the inequality

$$\frac{\Gamma_2}{\rho_2 h} > \frac{\overset{(\lambda)}{b}_{1f}}{\overset{(\lambda)}{b}_{2f}} = \frac{1}{\lambda - 3}. \quad (93)$$

In contrast with the analogous criterion, Eq. (35), for the normal pressure inside a flat pore, the quantity on the right-hand side of Eq. (93) is constant, and the condition expressed in (93) is fulfilled still easier than that in (35). The temperature does not stand explicitly in Eq. (93), but strongly influences (as also the slit width) the value of the left-hand side of Eq. (93). The higher temperature and smaller the slit width, the easier is attained the inequality (93). For the ordinary van der Waals forces ($\lambda = 6$), Eq. (93) is written as

$$\frac{\Gamma_2}{\rho_2 h} > \frac{1}{3}, \quad (94)$$

and, for the van der Waals forces with retardation ($\lambda = 7$), as

$$\frac{\Gamma_2}{\rho_2 h} > \frac{1}{4}. \quad (95)$$

Comparing the two last inequalities with the condition (81) for cylindrical pores at $h = 2a$, we see the right-hand sides of (94) and (95) to be considerably (by several times) smaller than in the cylindrical case. This means that the effect of additional contraction is observable with higher probability for a sorbent with flat pores than for a sorbent with cylindrical pores. If, in addition, the relative smallness of the modulus Y' is taken into account, the effect should be more pronounced for the case of flat pores, as it is just exhibited by experiment.

V. GENERAL REMARKS AND CONCLUSIONS

Let us discuss when the inequalities $\Delta p_N > 0$ and $\Delta\eta > 0$ can act on the initial stage of sorption. Naturally, the answer to this question is reverse to the above answer to the main question whether the quantities Δp_N and $\Delta\eta$ can be negative on the initial stage of sorption. We begin with the case of spherical pores. In the right-hand side of Eq. (15) for Δp_N, the asymptotically principal terms at a large a are the positive second term and, in the order of hierarchy, the negative third term. It follows already from here (and from $p \geq 0$) that $\Delta p_N > 0$ at a large a. Passing to the consideration of $\Delta\eta$ and confining with the case of physical sorption, we set $\Delta\gamma = -æ kT\Gamma_2$ [see Eq. (45)]. Herewith, asymptotically main terms on the right-hand side of Eq. (61) for $\Delta\eta$ will be the positive last term and, subsequently in the hierarchy, the positive second and the negative next-to-last terms.

If a is not too large, Γ_2 is large, φ is not too small, and, in addition, the strong inequality [noted at ordinary temperature after Eqs. (27) and (28)]

$$\frac{kTa^{\lambda-3}}{\overset{(\lambda)}{A}_{12} \rho_1} >> 1, \quad (96)$$

acts, the positive last term on the right-hand side of Eq. (61) will exceed both the negative first and the negative next-to-last terms. Then it will be $\Delta\eta > 0$. Just the dominant role of the last term on the right-hand side of Eq. (61) lead in Section 3 to the conclusion about the possibility of the reversal of the condition $\Delta\eta < 0$ already at ordinary temperatures.

A similar picture is observed in the case of cylindrical pores. For this reason, we turn to the case of flat pores. On the right-hand side of Eq. (34) for Δp_N, the asymptotically main terms at a large h are the positive second term and, in the order of hierarchy, the negative third term. From here(and from $p \geq 0$), it already follows that $\Delta p_N > 0$ at a large h. Passing to the consideration of $\Delta\eta$, the asymptotically main terms at a large h on the right-hand side of Eq. (92) for δ_i will be the positive second term and, in the order of hierarchy, the negative third term. If h is not too large, φ is not too small, and, in addition, $Y' << Y$ the positive second term will exceed the negative first term on the right-hand side of Eq. (92). Then it will be $\Delta\eta > 0$.

After the finish of the initial stage of sorption when pressure p and, especially, adsorption Γ_2 will increase considerably, the quantities Δp_N and $\Delta\eta$ will become considerably larger and, consequently, definitely positive. To prove the said, one has to consider the rigorous relationships: Eq. (14) in place of Eq. (15) in the case of spherical pores, Eq. (24) in place of Eq. (25) in the case of cylindrical pores, and, finally, Eq. (33) in place of Eq. (34) in the case of flat pores. Naturally, this would mean heavy workload in this research.

Since the above calculations were performed for dispersion forces, we have to consider possible arguments for the general case. As a matter of fact, such arguments have been already formulated in [28] as following. Let us return to the general definition of the pressure tensor given in Eq. (2) where the pair interaction $\varnothing'_{ij}(R)$ can be of any nature. The principal feature of the pressure tensor is that it is composed of a positive kinetic part [the first term in Eq. (2)] and a typically negative force part (the second term) sometimes termed molecular pressure. The first part in independent of direction and is numerically equal to the pressure of an ideal gas at a given local density. As applied to liquids, this quantity is of a colossal value. However, since the difference between the first and second terms should be the ordinary hydrostatic pressure, one has to accept that the second (force) term is also huge in its absolute value. Therefore, the hydrostatic pressure in liquids is a difference of two very large quantities according to Eq. (2).

Let us apply Eq. (2) to the interior of a cylindrical pore as an example. First of all, we compare the normal and tangential components, p_N and p_T, of the pressure tensor. In accordance with Eq. (2), the kinetic part is same for both the components, but the force term is much larger in absolute value for p_N than for p_T. This is caused by the geometry and the calculation method: the unit surface perpendicular to the pore wall is more oriented to the free space than to matter. Therefore, the pressure tensor component p_N is initially smaller (with accounting for the sign) than the component p_T, and there are more chances for pressure to become negative. How could it be attained in practice? There are two ways to do this as it is seen from the structure of the kinetic part of the pressure tensor. The first way is lowering temperature. The kinetic part is absent at all, and the whole pressure tensor is negative at the absolute zero of temperature (except the case of highest densities when the repulsive forces come to action). It is clear that pressure p_N can become negative at lowering temperature whereas pressure p_T still remains positive. The second way is lowering the sorbate molecular concentration in the middle of the pore space, i.e. molecular localization (by means of chemisorption or physical adsorption) on the pore walls. This way is determined by the sorbent ability, the sorbent chemical composition and the presence of active centers. Note that the role of temperature also remains important for this mechanism since, as is known, temperature can transform a sorbate from a localized to a non-localized state.

We now retrace how the state of a microporous sorbent changes in the course of sorption. We begin with the limiting case when a gas is still absent, and a sorbent is in a vacuum. Then, the middle of a pore is empty ($\rho_i^{(1)} = 0$) and, according to Eq. (2), the kinetic part of the pressure tensor is canceled, i.e. the pressure tensor is negative as a whole (as at the zero temperature). Herewith, as was reasoned above, the normal component of the pressure tensor is much stronger that the tangential one, which will cause the pore contraction and, as a consequence, the contraction of the whole sorbent. Thus, a sorbent typically is in a compressed state still before it is used. What can force it to contract still more when sorption begins? We can imagine that the first molecules penetrated into a pore are attracted by the pore walls. Then there will be again no molecules in the middle of the pore (the pore remains empty), whereas the attractive part of the pressure tensor is enhanced by the gas molecules sorbed. This will just cause an additional contraction of pores and the sorbent as a whole.

The probability of such event is higher, the lower is the temperature and the larger is the number and quality (the bond energy) of sorption active centers that operate in the first turn. Therefore, the above event can happen not with any porous body and not at any temperature. However, if it has happened, it turns be a short episode. As the gas chemical potential increases and the gas molecules continue penetrating into the pore, the sorbate density in the pore middle increases. Correspondingly, the kinetic part of the pressure tensor increases and attains giant values when the density approaches its value in a liquid phase. In the course of growth of the kinetic part, there subsequently occurs the sign reversal first for the tangential pressure and later for the normal pressure. As it has just happened, the expansion of pores and the dilatation of a sorbent as a whole begin and proceed in the whole rest range of pressure p, unless pressure p is leveled with the pressure inside the pores (provided a sample is not destroyed earlier). The above justification of a small sorbent contraction on the initial stage of sorption, based on Eq. (2), is easily applicable to pores of any geometrical shape.

The theory presented explains all the features of the sorption-striction phenomenon registered by experiment: the possibility of both of the dependence types shown in Fig. 1 and, in particular, no restriction on the initial slope for $\Delta\eta$; an increasing probability of the negative slope with decreasing temperature; the role of the nanoscale pore size for observing the phenomenon at all. Some numerical estimations has been carried out for the case of dispersion forces, but the phenomenon itself has been shown to be of a universal character.

Let us now discuss some horizons and other methods of calculation. For a long time, neither theory nor experiment was ready for quantitative comparison: theory operated with a restricted set of pore types, and experiment dealt with too complicated structures. The aim was a qualitative physical explanation of the main features of the sorption-striction phenomenon, and this aim has been attained. Further theoretical progress includes the study of pores of various shapes. Among them, a wedge-like pore is of general significance, whose pressure tensor and definition of disjoining pressure have been introduced recently [48]. Concerning alternative methods of calculation, the density-functional theory (DFT) and computer simulation, the Monte Carlo (MC) and molecular dynamics (MD) methods can be mentioned.

The aim of the DFT is finding the spatial matter distribution from minimizing the free energy (or grand potential in case of the grand canonical ensemble) functional in a non-uniform equilibrium system. The rigorous local formulation of the DFT presumes the local free energy (grand potential) density to be a function of not only local matter density, but also its gradients of all orders. Since only lower order gradients can be really taken into account [van der Waals confined himself by the (squared) first gradient], it follows that any real variant of the DFT is an approximation. The nonlocal formulation of the DFT operates with a local smoothed density. Several variants of smoothing were suggested [49–54], among which Tarazona's approach [49, 50] remains most popular. In the 90s, this improved variant of the DFT were multiply used for studying adsorption [55–63], and this is natural since adsorption is just the problem of spatial distribution of matter. The DFT produces the total distribution of a sorbate (say, the radial and longitudinal distribution of the sorbate density in a cylindrical pore [63]) and is capable of calculating adsorption, which is unattainable for the asymptotic theory. The knowledge of the one-particle distribution function is enough for calculating adsorption but not enough for calculating the pressure tensor, when, according to Eq. (2), both the one- and two-particle distribution functions are needed. As was shown by Schmidt [59], the pair correlation function for an adsorption system can also be found from the DFT. This means that, in principle, the calculation of the pressure tensor from Eq. (2) is also possible within the frames of the DFT. Another route was suggested by Napari and Laaksonen [64] for calculating the disjoining pressure of a wetting film. The relation of the disjoining pressure to the DFT was also discussed by Henderson [65]. It seems, however, that the DFT has not yet been applied for calculating the pressure tensor inside cylindrical and spherical pores.

Computer simulation is unable to yield results in an analytical form and is not predestinated for creating theories. However, computer simulation is very useful for checking theories since a numerical experiment can be organized just for the model used in constructing a certain theory. Both MC and MD methods were used for studying adsorption systems. The majority of investigations (historically reviewed by Steele [66], see also [67–71]) were restricted to the adsorption calculation, but some [72–82] including those issuing from the author's were involved in estimating forces, which is equivalent to the calculation of the pressure tensor. The procedure of calculation of the pressure tensor is sufficiently simple in MD and does not require the two-particle distribution function since the integral in Eq. (2) is replaced by direct summation of pair forces. The simulation data obtained typically refer to very narrow (of several molecular diameters) flat slit-like pores and can be qualified as complimentary to the asymptotic theory. For such narrow slits, the specific kind of behavior with pronounced oscillations with the slit width was found not only for the local density, but also for the pressure tensor [68]. No data seem to exist for cylindrical pores and spherical cavities. The spherical case is rather difficult for computer simulation. In our day [70], we were the first to apply MD for calculating the pressure tensor in a small cluster and simulating the dependence of surface tension on the cluster size on the basis of Eq. (2) (a possible alternative interpretation of the result was discussed recently). Because of importance for the nucleation theory, such calculations were repeated by many authors up to the present time periodically producing contradictory results even in the dependence sign. One of possible causes of discrepancies can be different ways of truncation of the pair potential. We now may conclude that neither the DFT nor the computer simulation methods have been prepared at this stage for solving the problems raised in this paper. However, these methods develop and promise progress in the future.

ACKNOWLEDGMENTS

The work was supported by the program "Leading scientific schools of Russian Federation" (project no. NSh-4241.2006.3).

REFERENCES

1. Meehan, F.T., *Proc. Roy. Soc. (A),* 1927, vol. 115, p. 199.
2. *The Solid–Gas Interface,* Flood, E.A., Ed., New York: Dekker, 1967, vols. 1, 2.
3. Kononyuk, V.F., Sarakhov, A.I., and Dubinin, M.M., *Russ. Chem. Bull.,* 1972, vol. 21, p. 1637.
4. Rimmer, D.L. and McIntosh R., *Canad. J. Chem.,* 1974, vol. 52, p. 3699.
5. Radeke, K.H. and Peters, H., *Z. Chem.,* 1975, vol. 10, p. 414.
6. Bering, B.P., Krasil'nikova, O.K., and Serpinski, V.V., *Dokl. Akad. Nauk SSSR,* 1976, vol. 231, p. 373.
7. Krasil'nikova, O.K., Sarakhov, A.I., and Dubinin, M.M., *Russ. Chem. Bull.,* 1977, vol. 26, p. 1359.
8. Bangham, D.H. and Fakhoury, N., *Proc. Roy. Soc. (A),* 1930, vol. 130, p. 81.
9. Bangham, D.H., Fakhoury, N., and Mohamed, A.F., *Proc. Roy. Soc. (A),* 1932, vol. 138, p. 162.
10. Bangham, D.H., Fakhoury, N., and Mohamed, A.F., *Proc. Roy. Soc. (A),* 1934, vol. 147, p. 152.
11. Bangham, D.H. and Razouk, R.I., *Proc. Roy. Soc. (A),* 1938, vol. 166, p. 572.
12. Haines, R.S. and McIntosh, R., *J. Chem. Phys.,* 1947, vol. 15, p. 28.
13. Dacey, J.R., Frohnsdorff, G.J.C., and Gallagher, J.T., *Carbon,* 1964, vol. 2, p. 41.
14. Razouk, R.I., Saleeb, F.Z., and Said, F.S., *Carbon,* 1968, vol. 6, p. 561.
15. Dacey, J.R. and Evans, M.J.B., *Carbon,* 1971, vol. 9, p. 579.
16. Tvardovski, A.V., Fomkin, A.A., Tarasevich, Yu.I., Polyakova, I.G., Serpinski, V.V., and Guseva I.M., *J. Colloid Interface Sci.,* 1994, vol. 164, p. 114.
17. Tvardovski, A.V., Fomkin, A.A., Tarasevich, Yu.I., and Zhukova, A.I., *J. Colloid Interface Sci.,* 1997, vol. 191, p. 117.
18. Tvardovski, A.V., Fomkin, A.A., Tarasevich, Yu.I., and Zhukova, A.I., *J. Colloid Interface Sci.,* 1999, vol. 212, p. 426.
19. Fomkin, A.A., Regent, N.I., and Sinitsyn, V.A., *Russ. Chem. Bull.,* 2000, vol. 49, p. 1012.
20. Tvardovski, A.V., Fomkin, A.A., Tarasevich, Yu.I., and Zhukova, A.I., *J. Colloid Interface Sci.,* 2001, vol. 241, p. 297.
21. Yakovlev, V.Yu., Fomkin, A.A., and Tvardovski, A.V., *J. Colloid Interface Sci.,* 2003, vol. 268, p. 33.
22. Berezin, G.I. and Kozlov, A.A., *Dokl. Akad. Nauk SSSR,* 1980, vol. 253, p. 373.
23. Serpinski, V.V. and Yakubov, T., *Russ. Chem. Bull.,* 1981, vol. 30, p. 54.
24. Rusanov, A.I., *Surf. Sci. Rep.,* 2005, vol. 58, p. 111.
25. Jakubov, T.S. and Mainwaring, D.E., *Phys. Chem. Chem. Phys.,* 2002, vol. 4, p. 5678.
26. Fomkin, A.A. and Pulin, A.L., *Russ. Chem. Bull.,* 1999, vol. 48, p. 1887.
27. Ustinov, E.A. and Do, D.D., *Carbon,* 2006, vol. 44, p. 2652.
28. Rusanov, A.I., *Russ. J. Gen. Chem.,* 2006, vol. 76, p. 5.
29. Kuni, F.M. and Rusanov, A.I., *Phys. Lett.,* 1967, vol. 25A, p. 577.
30. Kuni, F.M., Rusanov, A.I., and Brodskaya, E.N., *Kolloid. Zh.,* 1969, vol. 31, p. 860.
31. Kuni, F.M. and Rusanov, A.I., *Kolloid. Zh.,* 1970, vol. 32, p. 232.
32. Brodskaya, E.N., Kuni, F.M., and Rusanov, A.I., *Kolloid. Zh.,* 1971, vol. 33, p. 23.
33. Rusanov, A.I. and Kuni, F.M., *Kolloid. Zh.,* 1971, vol. 33, p. 121.
34. Kuni, F.M. and Rusanov, A.I., *Kolloid. Zh.,* 1971, vol. 33, p. 238.
35. Kuni, F.M. and Rusanov, A.I., *Fizicheskaya adsorbtsiya iz mnogokomponentnykh faz* (Physical Adsorption from Multicomponent Phases), Dubinin, M.M. and Serpinsky, V.V., Eds., Moscow: Nauka, 1972.
36. Irving, J.H. and Kirkwood, J.G., *J. Chem. Phys.,* 1950, vol. 18, p. 817.
37. Rowlinson, J. and Widom, B., *Molecular Theory of Capillarity,* Oxford: Clarendon, 1982.
38. Rusanov, A.I., *Phasengleichgewichte und Grenzflaechenerscheinungen,* Berlin: Akademie, 1978.
39. Derjaguin, B.V., Churaev, N.V., and Muller, V.M., *Surface Forces,* New York: Consultants Bureau, 1987.
40. Gibbs, J.W., *The Scientific Papers,* New York: Longmans, 1928, p. 315.
41. Rusanov, A.I., *J. Colloid Interface Sci.,* 1978, vol. 63, p. 330.
42. Rusanov, A.I. and Shchekin, A.K., *Colloids Surf.,* 2001, vol. 192, p. 357.

43. Eriksson, J.C., *Surf. Sci.,* 1969, vol. 14, p. 221.
44. Halsey, G., *Surf. Sci.,* 1978, vol. 72, p. 1.
45. de Boer, J.H., *The Dynamic Character of Adsorption,* Oxford: Clarendon, 1953.
46. Landau, L.D. and Lifshitz, E.M., *Theory of Elasticity,* Oxford: Pergamon, 1970.
47. Maurer, S., Mersmann, A. and Peukert, W., *Chem. Eng. Sci.,* 2001, vol. 56, p. 3443.
48. Rusanov, A.I. and Shchekin, A.K., *Mol. Phys.,* 2005, vol. 103, p. 2911.
49. Tarazona, P., *Phys. Rev., A,* 1985, vol. 31, p. 2672.
50. Tarazona, P., Marconi, U.M.B., and Evans, R., *Mol. Phys.,* 1987, vol. 60, p. 573.
51. Rosenfeld, Y., *Phys. Rev. Lett.,* 1989, vol. 63, p. 980.
52. Kierlik, E. and Rosinberg, M.L., *Phys. Rev., A,* 1990, vol. 42, p. 3382; *Phys. Rev., A,* 1991, vol. 44, p. 5025.
53. Denton, A.R. and Ashcroft, N.W., *Phys. Rev., A,* 1991, vol. 44, p. 8242.
54. Patra, C. and Ghosh, S., *Phys. Rev., E,* 1993, vol. 47, p. 4088; *Phys. Rev., E,* 1993, vol. 48, p. 1154.
55. Lastoskie, C., Gubbins. K.E., and Quirke, N., *J. Phys. Chem.,* 1993, vol. 97, p. 4786.
56. Lastoskie, C., Gubbins, K.E., and Quirke, N., *Langmuir,* 1993, vol. 9, p. 2693.
57. Olivier, J., *J. Porous Materials,* 1995, vol. 2, p. 9.
58. Ravikovitch, P.I., Vishnyakov, A., and Neimark, A.V., *Phys. Rev., E,* 2001, vol. 64, p. 011602.
59. Schmidt, M., *Phys. Rev., E,* 2002, vol. 66, p. 041108.
60. Ustinov, E.A. and Do, D.D., *J. Chem. Phys.,* 2004, vol. 120, p. 9769.
61. Ustinov, E.A., Do, D.D., and Jaroniec, M., *Appl. Surf. Sci.,* 2005, vol. 252, pp. 548, 1013.
62. Ustinov, E.A., Do, D.D., and Jaroniec, M., *J. Phys. Chem., B,* 2005, vol. 109, p. 11653.
63. Ustinov, E.A. and Do, D.D., *Adsorption,* 2005, vol. 11, p. 455.
64. Napari, I. and Laaksonen, A., *J. Chem. Phys.,* 2002, vol. 119, p. 10363.
65. Henderson, J.R., *Phys. Rev., E,* 2005, vol. 72, p. 051602.
66. Steele, W., *Appl. Surf. Sci.,* 2002, vol. 196, p. 3.
67. Vishnyakov, A. and Neimark, A.V., *J. Chem. Phys.,* 2003, vol. 119, p. 9755.
68. Gelb, L.D., *Mol. Phys.,* 2002, vol. 100, p. 2049.
69. Coasne, B. and Pellenq. R.J.-M., *J. Chem. Phys.,* 2004, vol. 120, p. 2913.
70. Kuchta, B., Llewellyn, P., Denoyel, R., and Firlej, L., *Colloids Surf., A,* 2004, vol. 241, p. 137.
71. Neimark, A.V. and Vishnyakov, A., *J. Chem. Phys.,* 2005, vol. 122, p. 234108.
72. Snook, I.K. and van Megen, W., *J. Chem. Phys.,* 1980, vol. 72, p. 2907.
73. Magda, J.J., Tirrell, M., and Davis, H.T., *J. Chem. Phys.,* 1985, vol. 83, p. 1888.
74. Somers, S.A., McCormick, A.V., and Davis, H.T., *J. Chem. Phys.,* 1993, vol. 99, p. 9890.
75. Balbuena, P.B., Berry, D., and Gubbins, K.E., *J. Chem. Phys.,* 1993, vol. 97, p. 937.
76. Schoen, M., Gruhn, Th., and Diestler, D.J., *J. Chem. Phys.,* 1998, vol. 109, p. 301.
77. Hayashi, T., Pertsin, A.J., and Grunze, M., *J. Chem. Phys.,* 2002, vol. 117, p. 6271.
78. Pertsin, A.J. and Grunze, M., *J. Chem. Phys.,* 2003, vol. 118, p. 8004.
79. Vishnyakov, A.M., Piotrovskaya, E.M., and Brodskaya, E.N., *Russ. J. Phys. Chem.,* 1999, vol. 73, p. 519.
80. Sizov, V.V., Piotrovskaya, E.M., and Brodskaya, E.N., *Colloid J.,* 2003, vol. 65, p. 772.
81. Zakharov, V.V., Brodskaya, E.N., and Laaksonen, A., *Langmuir,* 2001, vol. 17, p. 4443.
82. Semashko, O.V. and Brodskaya, E.N., *Colloid J.,* 2004, vol. 66, p. 80.