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Regularities of strain in porous bodies

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A phenomenological theory explaining strain caused by surface tension and the pressure tensor of adsorbate in porous bodies is formulated.

A strain of porous bodies in the gas adsorption process has been known for a long time.[1] Modern investigations established particular details of the strain, a slight contraction at the beginning of adsorption (disappearing with the temperature growth) and a subsequent regular expansion for larger adsorbate amounts for various types of porous adsorbents.[2–7] A general phenomenological theory of such phenomena is presented below.

Let us consider a spherical cavity of radius R_1 inside an elastic isotropic solid (phase β) and write the mechanical equilibrium condition at the cavity wall

$$E^{\beta}_{rr}(R_1) = \frac{2\gamma}{R_1} - p^{\alpha}_{rr}(R_1), \tag{1}$$

where $E^{\beta}_{rr}(R_1)$ is the radial component of the stress tensor in the solid at the cavity surface, γ is the surface tension of the solid, $p^{\alpha}_{rr}(R_1)$ is the radial component of the adsorbate pressure tensor, and superscript α refers to the adsorbate phase inside the cavity constructed as a continuation of the state at the cavity centre over the whole cavity space (this method, different from Gibbs' approach, was suggested by Rowlinson and Widom[8]). The right-hand side of equation (1) is obvious to be the force (per unit area) applied to the solid bulk phase on the side of the cavity. As for the outer surface of the solid, it is under the action of the pressure, p, of a gas to be adsorbed. Thus, all forces acting on the solid are determined, and we can proceed to the calculation of strain.

The problem of strain of a hollow ball with inner and outer radii and pressures R_1, R_2 and p_1, p_2, respectively, is very well known in the theory of elasticity.[9] Thus, we can use a ready solution. The radial displacement vector u as a function of the radial spherical coordinate r is

$$u = ar + b/r^2. \tag{2}$$

Constants a and b are defined as

$$a = \frac{p_1\varepsilon - p_2}{1-\varepsilon}\,\frac{1-2\nu}{Y}, \quad b = \frac{R_1^3(p_1 - p_2)}{1-\varepsilon}\,\frac{1+\nu}{2Y}, \tag{3}$$

where $\varepsilon \equiv R_1{}^3/R_2{}^3$ (evidently, $0 < \varepsilon < 1$), Y is the Young modulus, and ν is the Poisson ratio. In particular, the displacement of the pore radius is

$$u(R_1) = R_1\left(a + \frac{p_1 - p_2}{1-\varepsilon}\,\frac{1+\nu}{2Y}\right), \tag{4}$$

and the displacement of the outer radius of the body is

$$u(R_2) = R_2\left(a + \frac{\varepsilon(p_1 - p_2)}{1-\varepsilon}\,\frac{1+\nu}{2Y}\right). \tag{5}$$

The double value of $u(R_2)$ makes the absolute variation of the system linear dimension. The relative variation η is obtained by dividing equation (5) by R_2. Using equation (3), we write the result as

$$\eta \equiv \frac{u(R_2)}{R_2} = p_1\frac{\varepsilon}{1-\varepsilon}\,\frac{3(1-\nu)}{2Y} - p_2\frac{1-2\nu+\varepsilon(1+\nu)/2}{(1+\varepsilon)Y}. \tag{6}$$

We have $p_1 = p^{\alpha}_{rr} - 2\gamma/R_1$ and $p_2 = p$ for the case under consideration, so that equation (6) takes the form

$$\eta = \left(p^{\alpha}_{rr} - \frac{2\gamma}{R_1}\right)\frac{\varepsilon}{1-\varepsilon}\,\frac{3(1-\nu)}{2Y} - p\,\frac{1-2\nu+\varepsilon(1+\nu)/2}{(1+\varepsilon)Y}. \tag{7}$$

Equation (7) is the main result for the case of a spherical cavity. For a more general case of a porous body, η can be interpreted as the body strain (a quantity directly measurable in an experiment) and ε can be understood as the ratio of the cavity volume and the adsorbent volume per one cavity (the adsorbent porosity).

Passing to the analysis of equation (7), we first consider a porous body in a vacuum. At zero pressure ($p = 0$), equation (7) yields

$$\eta = \left(p_{rr}^{\alpha} - \frac{2\gamma}{R_1}\right)\frac{\varepsilon}{1-\varepsilon}\frac{3(1-\nu)}{2Y}. \qquad (8)$$

As is seen in equation (8), the body possesses a certain vacuum strain, and the capillary effect due to surface tension and surface curvature plays a certain role in this effect. Although γ is mostly positive for solids, it can be of any sign depending on the nature and the history of a sample. According to equation (8), the capillary contribution to η is negative (the body is compressed) if $\gamma > 0$ and positive (the body is stretched) if $\gamma < 0$. Naturally, the effect is small. To estimate the effect by a maximum, we set $\gamma \sim 1$ N m^{-1} and $R \sim 1$ nm, take a low elasticity modulus $Y \sim 10^{10}$ Pa, accept $\varepsilon = 0.1$ and neglect ν. This yields a capillary contribution to η of about –0.03.

Allowing a gas to enter the vacuum chamber, the gas adsorption begins on the cavity walls to cause a change in surface tension. The estimation of this effect is not simple. The matter is that, for solids, the mechanical (γ) and thermodynamic (σ, which is surface free energy in a one-component system) definitions of surface tension as the work of formation of a unit surface area, do not coincide. For an isotropic solid, the generalised Gibbs adsorption isotherm is[10]

$$\mathrm{d}\sigma = (\gamma - \sigma)\mathrm{d}\ln A - \Gamma\mathrm{d}\mu, \qquad (9)$$

where A is the surface area and Γ and μ are the adsorption and chemical potential of the adsorbate, respectively. The analysis of equation (9) leads to the relationship[10,11]

$$\left(\frac{\partial\gamma}{\partial\mu}\right)_A = -\left[\frac{\partial(\Gamma A)}{\partial A}\right]_\mu, \qquad (10)$$

which relates the mechanical surface tension to the adsorbate chemical potential. The product ΓA is the adsorbate excess for the whole surface. The estimate of the right-hand side of equation (10) depends on the adsorption type, which can be non-localised (physical) or localised (chemisorption). In the former case, stretching the surface at a fixed adsorbate chemical potential (*i.e.* at a fixed gas pressure) can only lead to an increase in the total amount of the adsorbate on the surface, so that $\partial(\Gamma A)/\partial A > 0$ at $\Gamma > 0$. Correspondingly, we obtain $\partial\gamma/\partial\mu < 0$ from equation (10). Concerning the quantitative estimate of the right-hand side of equation (10), we mean the adsorption potential and the Henry coefficient to decrease at the surface stretching. For this reason, the surface area increase yields the adsorbate increment in a lower proportion. In the case of chemisorption when the number of active centres does not change at all at surface stretching, we have $\partial(\Gamma\mathrm{A})/\partial A = 0$. This means, according to equation (10), that surface tension remains constant in the course of chemisorption.

We now apply equation (10) to the cavity surface in the case of non-localised positive adsorption, when surface tension decreases with increasing the adsorbate chemical potential. If surface tension is positive, its absolute value will decrease. Since surface tension contributed to the initial compression of the adsorbent, and that effect is now partly cancelled, the adsorbent begins to expand. If surface tension is negative, its decrease with increasing the adsorbate chemical potential means increasing the absolute value of surface tension and the prolongation of the previous action of surface tension, *i.e.*, stretching the adsorbent. Thus, we arrive at a conclusion that, irrespective of the surface tension sign, its mechanical action is reduced to the adsorbent dilatation and, hence, cannot explain the initial contraction observed in an experiment.

We now turn to pressure p_{rr}^{α} in equation (7). To explain the adsorbent contraction by the action of this pressure, p_{rr}^{α} should take a negative value. To discuss this possibility, we write a general expression of statistical mechanics for the local pressure tensor $\hat{p}$ in a multicomponent liquid[12]

$$\hat{p}(\mathbf{r}) = kT\sum_i \rho_i^{(1)}(\mathbf{r})\hat{1} - \frac{1}{2}\sum_{i,j}\int \frac{\mathbf{R}\times\mathbf{R}}{R}\varnothing'_{ij}(R)\mathrm{d}\mathbf{R}\int_0^1 \rho_{ij}^{(2)}(\mathbf{r} - \xi\mathbf{R}, \mathbf{r} - \xi\mathbf{R} + \mathbf{R})\mathrm{d}\xi, \quad (11)$$

where $\rho_i^{(1)}(\mathbf{r})$ and $\rho_{ij}^{(2)}(\mathbf{r})$ are one- and two-particle distribution functions, $\varnothing'_{ij}(R)$ is the derivative of the pair potential of molecular interaction (*i.e.*, the interaction force), **R** is the vector connecting two interacting molecules and passing through the point **r**, the subscripts i and j refer to components (we have, at least, two components, an adsorbate and an adsorbent). The computational procedure for the Irving–Kirkwood pressure tensor (11) is as follows: for each orientation of the elementary unit area, only those molecular pairs contribute whose connecting straight line intersects the unit area. The main feature of the pressure tensor is that it has been composed of a positive kinetic part [the first term in (11)] and a negative force part (the second term) sometimes called the molecular pressure. The first part is independent of direction and is numerically equal to the pressure of an ideal gas at a given local density. This is a giant quantity for liquids under ordinary conditions, and, since the difference between the first and second terms in equation (11) is an ordinary hydrostatic pressure, we have to accept that the second term is also huge. Thus, according to equation (11), hydrostatic pressure in liquids is a difference of two very large quantities.

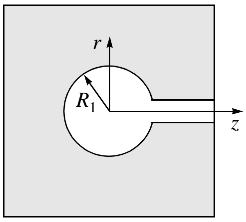

Figure 1 A spherical cavity in a porous body.

Let us apply equation (11) to the cavity interior. We now have to detail the cavity configuration by the fact that the cavity should be connected with the outer space by a certain kind of channel (Figure 1). This creates a cylindrical symmetry with the z axis and makes it possible to discriminate between the pressure tensor components p_{rr} and p_{zz}. In accordance with equation (11), their kinetic parts are identical, but the force part is larger for p_{rr} than for p_{zz}. This is related to the geometry and the computational scheme: the unit area perpendicular to the z axis is more directed to the less dense space than to matter. Therefore, pressure p_{rr} is initially smaller than p_{zz} and has more chances to become negative. From the structure of the kinetic part of the pressure tensor, there are only two ways to attain negative values for p_{rr}. The first way is lowering the temperature. The kinetic part is absent at all and the whole pressure tensor is negative at zero temperature. Hence, by lowering the temperature, pressure p_{rr} can become negative while p_{zz} still remains positive. The second way is lowering the concentration of adsorbate molecules inside the cavity, *i.e.*, their localization (chemisorption). This way is determined by the adsorbent characteristics and chemical composition and the presence of active centres on the cavity surface. However, the role of temperature is also important in this case since the temperature lowering can transform non-localised adsorption into localised one.

Thus, we have found conditions when pressure p_{rr}^{α} can be negative. Putting now a negative value of p_{rr}^{α} in equation (7), we see, first of all, that p_{rr}^{α} also participates in the initial adsorbent contraction. As for the additional contraction on the first stage of adsorption, it can be explained as follows. Let us imagine that first adsorbate molecules, entering the cavity space, are captured by chemisorption centres to be completely localised at the cavity wall. Then, the adsorbate concentration at the cavity centre is maintained to be zero, and the same is to be said about the kinetic part of the pressure tensor. By contrast, the force tensor part (which is negative) is enlarged due to the molecules adsorbed to induce an additional contraction of the whole porous body.

We only have to discuss the possible compensatory role of surface tension γ in the course of adsorption. This problem is simply resolved. As was shown above, surface tension does not change in the case of chemisorption. The negative term γ/R has already done its job. Now, a new negative increment, p^{α}_{rr}, is added and leads to the extra (and last) contraction of the adsorbent. However, this lasts not a long time. As the chemical potential and concentration of the adsorbate in the cavity interior increase and the chemisorption centres are exhausted, the kinetic part of the pressure tensor increases to induce an increase in p^{α}_{rr}. Eventually, p^{α}_{rr} passes to positive values and causes (this time, together with surface tension) the expansion of the adsorbent.

The above explanation of a little contraction of an adsorbent at the initial stage of adsorption based on equation (11) is easily applicable to other geometrical shapes of cavities in porous bodies. Similar arguments can be formulated for cylindrical and flat pores. If the cavity is a flat slit in a solid, and the z axis is directed perpendicularly to the slit walls, the pressure tensor component p^{α}_{zz} will play the role of p^{α}_{rr} in the above consideration (the difference $p^{\alpha}_{zz} - p$ is called the disjoining pressure in colloid science). In this way, it explained the initial contraction sometimes observed for laminar silicates of the montmorillonite type.[3,4] We may conclude that the above theory based on equations (7) and (11) yields a qualitative explanation of all mechanochemical effects observed for porous bodies.

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