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Abstract

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ON THE QUESTION OF STRUCTURE FORMATION IN DISPERSE SYSTEMS

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The physical chemistry of structure-formation processes in disperse systems was considered in detail by Rehbinder ([1]). At the same time, in studying the properties of a body formed by a disperse system, it is necessary to take into account two types of basic characteristics of the supporting structure—its geometrical and strength characteristics. The geometrical characteristics have been studied in considerable detail ([2,3]). The study of rheological properties and, in particular, strength properties has long been used to clarify the mechanism of structure formation ([4,5]). In a number of investigations a combined study of strength and geometrical characteristics was carried out ([6,7]). In paper ([8]), using the simplest cubic model constructed from chains of spherical particles elongated in three mutually perpendicular directions, the relation between the strength and porosity of catalysts was considered. The formulas derived have general significance and are applicable to disperse structures of various types. The strength of a structural body is expressed through the pore diameter, the density of the solid phase, and the porosity.

The simplest geometrical characteristic of a system is its volume, which is easily measured and from the magnitude of which other structural parameters can be estimated. As a strength characteristic it is convenient to use the limiting shear stress, which is determined by the strength of unit contacts between particles and depends on their number per unit volume. The relation between them is contained in the formulas obtained in ([8]). However, this relation can be obtained by a somewhat simpler and more general route, on a model without restriction of the form of the elementary cells.

The solution of this problem and experimental verification of the result obtained were the aim of the present work. It also proved possible to relate the strength to the degree of modification of the surfaces of the solid phase by long-chain surface-active substances.

Let the system be formed by repeated repetition of one and the same elementary cell, i.e., of some small, not necessarily closed, structural region of constant shape and size. When the volume changes, only the size of the cells changes; their shape is preserved. The basic element of the cell is a certain conditional

edge of mean length, representing a chain composed of n particles of equal diameter D. The system is monodisperse.

Let us denote the number of elementary chains per unit volume by ν; then the number of elementary cells per unit volume is written $\nu\varepsilon$, where ε is the number of elementary cells built from one chain. The total number of chains Z destroyed (under shear) along some section of area 1 cm^2 is proportional to $(\nu\varepsilon)^{2/3}$. Since $(Dn)^3 \sim 1/\nu\varepsilon$, $Z = k/D^2n^2$. If F_k is the strength of one contact, then the strength of the system in the form of the limiting shear stress will be $P_m = ZF_k = kF_k/D^2n^2$. For loose structures, i.e., under the condition $n \gg 1$, the special position of nodal particles may be neglected. In this case the relation $\nu \simeq N/nV_s$ is valid, where N is the number of particles in 1 g of solid phase and V_s is the volume of the system formed by these particles. Since $\nu \sim 1/(Dn)^3$, and $N \sim 1/\rho D^3$ (ρ is the true density of the solid phase), we obtain $n^2 \sim \rho V_s$ and

$$P_m = k' \frac{F_k}{D^2 \rho V_s}. \tag{1}$$

Here k' is a dimensionless coefficient depending on the shape of the particles, the shape of the cells, and the fraction of effective (structural) particles in a chain.

For not very loose structures, the special structural role of nodal particles cannot be disregarded. Therefore the relation determining the number of chains ν per unit volume of the system must be corrected. Instead of the number of particles n arranged along a certain edge (chain) of average length, it is necessary to use the actual average number of particles expended in building each chain of an elementary cell. If the number of nodal particles in each elementary cell is denoted by γ, then $\nu = N/V_s(n-1+\varepsilon\gamma) = N/n[V_s-(1-\varepsilon\gamma)V_s/n]$. As a result, in formula (1), in the denominator, instead of V_s there appears the difference $V_s - V'_m$, where $V'_m = (1-\varepsilon\gamma)V_s/n$.

Numerical substitution into the corresponding expression of the values n, ε, and γ makes it possible to estimate the magnitude of V'_m. For two- to threefold changes in the volume of the system, V'_m deviates from some mean value by no more than 10-15%. If the dispersed phase consists of spherical particles with $\rho = 2.5$, and the model has a cubic form ($\varepsilon = 1/3$ and $\gamma = 1$), the absolute values of V'_m, for a sixfold change in the volume of the system, vary from 0.5 for the densest structures to 0.8 for extremely loose structures. Thus, over a considerable range of observed changes in volumes, the quantity V'_m may be taken as constant. On the other hand, in a real system n cannot be arbitrarily large; beginning with some critical volume V_l ([2]), the continuity, the solidity of the structure of the solid phase is disrupted, the system liquefies, and P_m becomes equal to zero. Thus, formula (1) contains an excess strength P_r, due to the structure which, in accordance with the adopted model, should exist

at $V_s > V_l$, but which in reality is not realized. Taking both corrections into account, formula (1) should be rewritten as

$$P_m = K\frac{F_k}{D^2\rho(V_s - V'_m)} - P_r. \tag{2}$$

The coefficient K may be taken equal to 1.

When applied to real systems, relation (2) must contain a functional dependence on the polydispersity of the structure-forming phase. At present it is not yet possible to take the nature and parameters of such a dependence into account with sufficient rigor. We shall therefore note only that, for polydisperse systems, as they are compressed, the reduction of a certain part of the volume becomes increasingly difficult because of the appearance of incompressible structural islands formed by large particles.

At the same time, small particles in the intermediate, free space continue to repack relatively easily. Thus, compression of the structure and a change in the number of contacts occur in a certain free volume $(V_s - V''_m)$, where V''_m is a function of the volume V_s and of the polydispersity of the solid phase. Similar phenomena may arise because of inhomogeneities in packing. This effect, to a first approximation, can be allowed for by replacing V''_m by some average idle volume $\overline{V''_m}$, which remains unchanged when the system is compressed. It is clear that for a real system the absolute value of the "volumetric" correction increases; consequently, in the denominator of formula (2), instead of V'_m one must substitute $V_m (= V'_m + \overline{V''_m})$.

Figure 1 reproduces experimental data from work [9] for an aqueous suspension of quartz having an average particle diameter of $5.5\,\mu$, and the curve $P_m = f(V_s)$ calculated from formula (2). The average force of interaction between the particles proved to be equal to $(2) \cdot 10^{-5}$ dyn.

Figure 2 presents our experimental data on determining the strength of xylol suspensions of quartz with an average particle diameter of $2\,\mu$. As can be seen, in this case as well formula (2) describes well the dependence of P_m on V_s.

The interaction force proved to be equal to $(3) \cdot 10^{-5}$ dyn. It is of interest to note that, in order of magnitude, both quantities agree well with the values of the interaction forces arising in point contacts of solid bodies, according to experimental measurements [10] and theoretical estimates [8].

In modifying the hydrophilic surface of particles of the solid phase with long-chain surfactants [11,12], the nature of the surface and the interaction force between particles change. In the absence of peptization, the change in the interaction force can formally be taken into account by adopting a scheme according to which, upon modification, two types of regions are formed on the surface: one type giving the maximum possible interaction, the other—minimal or even zero interaction. In some cases such a scheme may have a real physical meaning. Thus, in works [12,13] the macromosaic structure of the surface of quartz

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

modified with long-chain amines was indicated. A change in the degree of modification (surface coverage) $\alpha = A/A_m$, where A is the adsorption under the given conditions and A_m is the maximum adsorption, will change the ratio between lyophilic and lyophobic regions and, consequently, the number of contacts of different kinds. This makes it possible to write the strength of the system P_m as a function of α.

Fig. 1. Dependence of the strength P_m of sediments of quartz suspensions in water on their specific volume V_s (according to data [9]). The solid curve was calculated by formula 2.

If the number of heterogeneous regions on each particle is large, then the probability that two particles collide at lyophobic regions is equal to $(1-\alpha)^2$.

Fig. 2. Dependence of the strength P_m of sediments of quartz suspensions in xylene on their specific volume V_s. The solid curve was calculated by formula (2).

Assuming that every collision at lyophobic regions leads to coagulation and to the formation of strong contacts, and that the probability of contact formation does not depend on the presence of already existing contacts, the fraction of lyophobic, strong contacts in the volume may be taken as equal to the probability of their occurrence, $(1-\alpha)^2$. In the thin layer of suspension adjacent to the shear plane, in which destruction of the structure takes place, the fraction of strong contacts is $(1-\alpha)^{4/3}$. Since the strength of contacts formed when two lyophilic regions and a lyophilic and a lyophobic region meet is practically equal to zero, formula (2) for the case under consideration may be rewritten as

$$P_m = K\frac{F_k(1-\alpha)^{4/3}}{D^2\rho(V_s - V_m)} - P_r. \tag{3}$$

It is easy to see that, with the usually observed course of change of the volume V_s as the solid phase is modified [13,14], in our case the quantity $(V_s - V_m)$, which is illustrated by curves 1 in Figs. 3 and 4, the function P_m of α has a maximum, since the factor $(1-\alpha)^{4/3}$ changes relatively little with α, almost linearly, whereas the volume of the system and, consequently, $(V_s - V_m)$, decreases very sharply up to $\alpha \approx 0.4$, and after $\alpha \approx 0.5$ remains practically constant. If the volume of the system at $\alpha = 0$ is denoted by V_0, then the quotient $\dfrac{(1-\alpha)^{4/3}}{V_s/V_0}$

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

will characterize, in relative units, the dependence of P_m on α. When the function V_s of α has the form indicated above, the expected course of the change in stren-

···in relative units is represented by curve 2 (Fig. 3). Figure 4 presents the results of measuring the strength of quartz suspensions in xylol, modified with octadecylamine, and the volumes of the sediments as functions of α.

Fig. 3. Schematic representation of the relationship between the degree of surface coverage α, the change in the volume of the system V_s, and its strength in accordance with formula (3)

Fig. 4. Dependence of the strength P_m of sediments of quartz suspensions in xylol on the degree of coverage of the particle surface α with octadecylamine and the change in the volume V_s

Comparison of Figs. 3 and 4 shows that formula (3) correctly reflects the relationship between the strength and the degree of modification of the surface of the solid phase. The physical mechanism of this course of the change in strength should be regarded approximately as was done in work ([13]). As the solid phase is modified, the appearance of lyophilic regions on the particle surface increasingly facilitates the packing of particles, which leads to a decrease in volume and an increase in the number of contacts destroyed upon deformation. At the same time, despite the lyophilization of the surface, owing to the macromosaic character of the adsorption layer ([12]), a sufficient number of lyophobic–lyophobic contacts is preserved, and thus the strength of the system increases. With further modification, when $\alpha \to 1$, strong contacts disappear owing to complete lyophilization, and the strength falls.

All that has been set forth indicates a way toward a quantitative evaluation of the magnitudes of the interaction forces between particles of the solid phase in various media.

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