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ON THE CONSTRUCTION OF A KINETIC THEORY OF GELATINATION PROCESSES

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The problem of the formation of gels, pastes, and various tactoid structures has for a comparatively long time attracted the attention of researchers, whose opinions concerning the nature of these systems differ considerably. The study of gelatination processes in dilute sols and suspensions shows that the formation of gels in a number of such systems can be explained by the fixation of colloidal particles at comparatively large distances due to long-range forces of molecular and ionic-electrostatic origin (1).

When the behavior of colloidal particles is considered under conditions determining the formation of such gels, it becomes possible to draw an analogy between the transition of bodies of molecular structure from the liquid to the solid state and the gelatination of dilute sols. In the latter case, instead of the forces of attraction and repulsion between individual molecules, there act forces of molecular attraction and ionic-electrostatic repulsion between colloidal particles. The analogy becomes obvious if one compares the potential curve of molecular interaction (Fig. 1a) with a portion of the potential curve of interaction between colloidal particles situated to the right of point A (Fig. 1b). The presence of a potential barrier and of a lower energy level beyond it, for the case of interaction of colloidal particles, indicates the possible relaxation character of their fixation.

Proceeding from these ideas, one can establish the nature of the shear elasticity, which is the principal characteristic of a gelatinated system, and also consider the behavior of colloidal particles inside the gel. For this purpose it is necessary to take into account the interaction not of a single pair of particles, but of their aggregate, which constitutes a quasicrystalline lattice of the gel.

The mutual fixation of particles at distances corresponding to the positions of potential wells must at the same time determine the minimum value of the potential energy of the system as a whole, satisfying the condition $dU_{\text{syst}}/dh = 0$*.

In the case of a reversible elementary displacement (shear) of the system, this condition will be violated and the energy level of the system will rise, which, in accordance with the known relation $dF = dR$, where R is the work of external forces and F is the free energy, requires the application of external shear forces. At small angles of displacement φ, $dR = \tau\, d\varphi$, where τ is the shear stress. Consequently,

$$\tau = \frac{dE}{d\varphi} \tag{1}$$

and the shear elasticity

$$G = \frac{d\tau}{d\varphi} = \frac{d^2F}{d\varphi^2}. \tag{2}$$

In this case the system will behave as a gel if the relaxation time of the colloidal particles, both in the processes of their adhesion and in their transition to a vacant site of the quasicrystalline lattice, substantially exceeds the duration of the external actions. If one of the indicated conditions is not satisfied, the system will either age rapidly or its elastic properties will be masked by flow.

As a first approximation, taking into account the collective interaction of the colloidal particles forming the gel lattice, let us consider the character of the potential curve for a "test" particle B having two rigidly fixed symmetric neighbors A and C (Fig. 2). In this case the depth of the potential well ∇U, which determines the fixation of particles at the lattice sites, proves to be considerably greater than in the interaction of two separate particles (Fig. 1b). In the latter case, for the appearance of a well fixing, however, only their relative distance, it was necessary that at some distance the attractive forces exceed the repulsive forces. In collective interaction, however, potential wells for intermediate particles will exist even under the condition that at all distances the repulsive forces exceed the attractive forces. Naturally, such wells can lead to mutual fixation of the particles of a colloidal system at definite distances only provided that the volume of the medium is limited, fixing the maximum separation of the outer particles of the disperse phase.* In addition, a certain minimum concentration of the disperse phase is necessary, since otherwise the depths of the corresponding potential wells will be small in comparison with the energy of Brownian motion and fixation of the particles will not occur. If the volume of the medium is not limited or the concentration in the limited volume is below the minimum, then gelatinization is possible only in the presence of potential wells with a negative

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* Such a state of the system obviously does not signify true thermodynamic equilibrium corresponding to the possible lowest energy level. In our case, however, the potential barrier prevents the attainment of this lowest level. The latter circumstance determines the relaxation character of the subsequent processes that define the aging of the gelatinated system.

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

value of the energy (see Fig. 1) and will have a local character (flocculation and the formation of tactoid structures).

Fig. 1. Potential curves. (*a*)—for two molecules, (*b*)—for two colloidal particles in the presence of a well at a large distance

Fig. 2. Total potential curve of the interaction of a "test" particle with particles A and C

The conditions for fixation of particles are substantially influenced by their shape and size. It is known that the resultant of the intermolecular attractive forces depends on the shape of the surfaces being brought together. It is easy to show that it depends on the thickness of the interacting particles, whereas the resultant of the ionic-electrostatic repulsive forces is practically independent of the thickness.

Proceeding from the macroscopic theory of molecular interaction of condensed bodies (3), but admitting, as an approximation, the additivity of the interaction of individual microvolumes possessing the properties of condensed—of an adsorbed medium, we find, by summing the energy of the individual microvolumes, the general expression for the interaction energy between two plates, referred to unit area:

$$U = -\frac{A}{2h}\left[1 - \frac{2}{(1+b/h)^2} + \frac{1}{(1+2b/h)^2}\right], \tag{3}$$

where A is a constant quantity and b is the thickness of the plate.

For $b = \infty$, instead of (3) we obtain the expression known from the rigorous macroscopic theory (3), and corresponding to the case of interaction of two half-spaces separated by a gap h:

$$U_\infty = -\frac{A}{2h^2}.$$

Consequently,

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* Apparently, the hexagonal lattices of particles of synthetic latex studied by Hamilton and Hamm (2) should be assigned to this type of quasicrystalline lattices.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

$$\frac{U}{U_\infty} = 1 - \frac{2}{(1+b/h)^2} + \frac{1}{(1+2b/h)^2}.$$

In Fig. 3 this dependence is represented by the curve $\frac{U}{U_\infty}(\frac{b}{h})$, which shows that the influence of the particle thickness on the energy of their interaction is insignificant only in the case of very small distances between the particles (of the order of 10^{-1} of their thickness). At distances of the same order as the particle sizes, however, the molecular component of the interaction energy is approximately half the limiting value.

Fig. 3. Curve of the interaction energy of colloidal particles as a function of the ratio of the particle thickness b to the gap between them h

On the basis of (^{4,5}) and taking equation (3) into account, an expression may be obtained for the interaction of two plates. For example, for the case when the distance between the particles is significantly smaller than the thickness of the ionic atmosphere, it will have the form

$$U = \frac{\pi}{2} D \left(\frac{kT}{Ze}\right)^2 \frac{1}{h} - \frac{\zeta\delta\sigma}{h^2}\left[1 - \frac{2}{(1+b/h)^2} + \frac{1}{(1+2b/h)^2}\right], \tag{4}$$

where D is the dielectric permittivity of the medium; Z is the electrovalence of the counterion; e is the electron charge; ζ is a constant quantity, close in order of magnitude to unity; b is the thickness of the particle; δ is the size of the particle molecules; σ is the surface tension at the particle-solution boundary; h is the distance between the particles; kT has its usual meaning.

Fig. 4. Potential curves for the case of interaction of colloidal particles of different thickness: 1 $-b = 5$ μ; 2 -10 μ; 3 -20 μ

The different curves $U(h)$ in Fig. 4 correspond to different thicknesses of the three interacting particles. Comparison of the curves shows that, when the particle thickness is decreased from 20 to 5 μ, the depth of the potential well increases by more than a factor of 4. The presence of higher energy barriers and deeper potential wells in the case of plate-shaped particles must evidently determine the greater rigidity of fixation of these particles and their greater stability against sticking together in comparison with spherical particles. To describe real quasicrystalline lattices, the polydispersity of colloidal particles should be taken into account. However, in principle, the behavior of particles in re-

in the gel network must be the same as in the cases considered above. An analogy to this is the manifestation of elastic properties both in crystalline and in amorphous bodies.

The considerations set forth at the beginning of the communication and concerning the nature of gelation processes can be extended to such systems as highly concentrated emulsions and foams. In the latter case, the equilibrium state of the layer separating gas bubbles is determined by the algebraic sum of the molecular component of the disjoining pressure, which in this case has a negative value (corresponding to the tendency of the bubbles to approach one another), and the ionic-electrostatic component of this pressure, which has a positive sign.

A distinguishing feature of foam-like systems is that their shear is accompanied not only by deformation of the layers separating the particles, but also by a change in the specific surface area (^{6}). In the simplest case, when under shear of the system the potential energy of interaction between molecules in the volume of the layers separating the droplets remains practically unchanged, for the differential of that part of the free energy which depends on the surface tension one may write the expression $dF = d(\sigma\omega)$, where σ is the surface tension, depending on the concentration of stabilizer molecules at the interphase surface, and ω is the specific surface area of the system.

Using the last expression, on the basis of (1) and (2), after the corresponding transformations we obtain

$$\tau = \frac{2\varphi}{d}\left(\sigma + \omega\frac{d\sigma}{d\omega}\right), \tag{5}$$

$$G = \frac{d\tau}{d\varphi} = \frac{2}{d}\left(\sigma + \omega\frac{d\sigma}{d\omega}\right), \tag{6}$$

where d is the size of a droplet.

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