

## MECHANISM OF COAGULATION OF DISPERSE ELEMENTS IN MEDIA ISOLATED FROM EXTERNAL ACTIONS

S. V. Stebnovskii

UDC 532.5-536.12

*A physical model of the experimentally observed coagulation (the mutual approach) of spherical liquid, solid, and gaseous disperse elements (of diameter of up to 1 cm) in polar liquid and viscoelastic thixotropic matrices when the system is completely isolated from the external forces and the gradient temperature and concentration fields is proposed. It is shown that a weak stress-field gradient is formed in a polar liquid or viscoelastic matrix in the presence of interphase tension at the matrix-spherical disperse element interface, i.e., when the capillary pressure is negative at the convex boundary of the matrix. If the second disperse particle enters into this field, the resulting force acts on it in the direction of the first particle, thus ensuring their coagulation over large time lapses.*

The author performed experimental studies dealing with the behavior of two spherical disperse elements (drops in a low-viscous liquid matrix, solid particles in a high-viscous liquid matrix, and air pores in an elastic gel) in the case where the system is completely isolated from external actions [1, 2]. In addition, under similar conditions, the stability of the structure of coarse-disperse emulsions was considered at a volume concentration of drops not smaller than 0.2 and a drop diameter of 1 cm. It was shown that within the framework of those studies, in the case of complete isolation of two or more disperse elements from the external force and the gradient temperature and concentration fields, these elements are attracted together to a complete contact (coagulation) if the initial distance between them is of the order of their dimensions or smaller. The coagulation period is  $\tau_1 \approx 1$  h if the drops interact in a fresh alcohol-water solution,  $\tau_2 \approx 100$  h for solid spheres in glycerin, and  $\tau_3$  is almost one order of magnitude greater than  $\tau_2$  for pores in the gel. The question of the mechanism of mutual approach of disperse elements (DE) remains open. In the present study, an approach is proposed to construct a spherical model of this process.

1. The coagulation processes studied in [1, 2] occur in the media isolated from external actions; nevertheless, the DE are attracted together, i.e., a thermodynamic flow occurs and, hence, according to the Onsager principle, there exist thermodynamic forces inducing this flow. As follows from the data of [1, 2], the velocity of DE approach in a viscous medium does not decrease during coagulation (only at the last stage does the particle velocity decrease slightly because of increase in the forces of their mutual electrostatic repulsion). Therefore, the particle is influenced on the entire path of its displacement, i.e., it moves in a certain gradient physical field. We shall analyze the nature of this field. It follows from the general condition of thermodynamic equilibrium of an isolated system [3] that a system that is isolated from external actions can be in a state of thermodynamic equilibrium if the following two conditions are fulfilled, namely: macroscopic motions cannot occur in the system, i.e., the pressure is the same at all points in the medium; the temperature is the same in all the elements of the system. In other words, the temperature and pressure fields should be gradientless in an isolated, thermodynamically equilibrium system. In the experiments of [1, 2], the DE are attracted together. Hence, by definition, the isolated system is in a thermodynamically nonequilibrium state and at least one of the above conditions is not satisfied in this case. Since the temperature field is supported

by a uniform (gradientless) field during the experiment, the DE can be attracted together due to only the pressure-field gradient in the medium.

We shall consider the mechanism of formation of a gradient pressure field in a condensed matrix-spherical disperse element system isolated from external actions. In real conditions, owing to atmospheric pressure, a hydrostatic background  $P_0$  is always present in the matrix (if the gravity is omitted). In addition, if the interphase-tension coefficient  $\gamma_{ij}$  is not zero at the matrix-spherical DE interface, a jump in pressure occurs at this interface, so that the pressure is equal to

$$P_* = P_0 - P_c = P_0 - 2\gamma_{ij}/R_0 \quad (1)$$

at the convex surface of the matrix [4]. Here  $P_c = 2\gamma_{ij}/R_0$  is the capillary pressure and  $R_0$  is the DE radius. The question arises how this jump affects the pressure field in the matrix in the vicinity of the DE.

In many studies [5, 6], there are indirect data showing that water should possess not only volume but also weak shear elasticity. The point is that molecules of polar liquids (water, alcohols, etc.) have a high degree of association [7] owing to the hydrogen bonds (H-bonds) and form skeleton structures in a quiescent state. The fact that the H-bond energy is 5–9 kcal/mole, i.e., one order of magnitude greater than the energy of the van der Waals interaction and a factor of 5–6 smaller than the energy of the chemical bonds, allows one to judge the strength of these structures. This made it possible to assume that the structural character of polar liquids, which is due to the H-bonds in a quiescent state, should ensure a certain shear elasticity during a very weak and slow deformation. Apakashev and Pavlov [8] showed experimentally that water behaves like a medium with a very low strength limit and a shear modulus  $G$  of the order of  $10^{-6}$  Pa at very slow deformation rates (of the order of  $10^{-3}$  sec $^{-1}$ ); we note that  $G = 1$  Pa for glycerin.

Thus, since polar liquids such as water, glycerin, and a gel, which is an elastic thixotropic medium, were used in the experiments of [1, 2] as the matrices, with allowance for the fact that the characteristic rates of DE coagulation are smaller than  $10^{-4}$  cm/sec, the matrices can be regarded in these conditions as elastic media which possess weak shear strength. Consequently, the problem of the effect of the jump in pressure at the DE boundary (1) on the pressure field in a matrix can be treated within the framework of the theory of elasticity.

2. Using the known principle of hardening, we remove a spherical volume of radius  $R_0$  from an infinite condensed elastic medium and fill the cavity with a certain material  $i$  having interface tension  $\gamma_{ij}$  with the ambient medium  $j$ . We consider a model problem of generation of a stress field in an infinite isotropic elastic medium subjected to a constant hydrostatic pressure  $P_0$  and containing a spherical macroinclusion (sphere) of radius  $R_0$  with interphase-tension coefficient  $\gamma_{ij}$ .

Since bubble cavitation begins to develop in a real liquid when  $P_0$  falls off to the level of pressure of the saturation vapor  $P_V$ , we assume that  $P_0 > P_V$  in the liquid phase and  $P_0 \geq 0$  in a solid matrix. If the medium were homogeneous, a uniform stress field  $\sigma = -P_0$  would form in its entire volume. However, since the medium contains a sphere of radius  $R_0$ , the pressure  $P_*$ , which is due to the hydrostatic pressure  $P_0$  and the capillary pressure  $P_c$  at the interphase matrix-sphere interface, act on the spherical boundary of the matrix in the general case. Locating the origin of the spherical coordinate system  $(r, \theta, \varphi)$  at the center of the sphere, one can write the value of the radial stress component at the spherical boundary of the matrix in the form

$$\sigma_{rr}\Big|_{r=R_0} = -P_*(P_0, P_c) \quad (2)$$

according to the equilibrium condition.

We shall consider the classical elasticity problem with the use of the definition of the stress field in a medium containing a spherical inclusion of radius  $R_0$ . Condition (2) is satisfied at the boundary  $r = R_0$  and, hence, the system is in equilibrium and its deformation  $u(u_r, u_\theta, u_\varphi)$  is directed along the radius and depends only on  $r$ . It follows from the equilibrium condition, which is of the form [9]  $\nabla \text{div } u = 0$  in this case, that  $u = ar + b/r^2$ ; as a result, with allowance for spherical symmetry, one can write the strain-tensor components

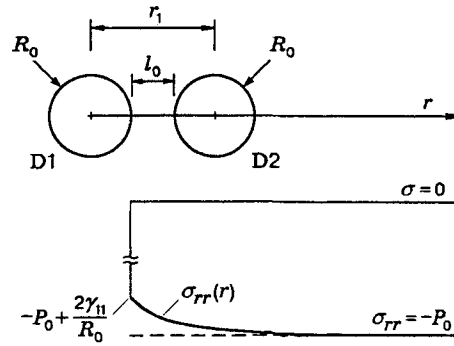


Fig. 1

in the form

$$u_{rr} = a - 2b/r^3, \quad u_{\theta\theta} = u_{\varphi\varphi} = a + b/r^3. \quad (3)$$

Substituting the first relation from (3) into the expression which describes the generalized Hooke's law

$$\sigma_{lm} = \frac{E}{1+\nu} \left( u_{lm} + \frac{\nu}{1-2\nu} u_{kk} \delta_{lm} \right),$$

where  $E$  is Young's modulus and  $\nu$  is the Poisson ratio, and taking into account the boundary condition (2), expression (1), and the condition at infinity  $\sigma_{rr}|_{r \rightarrow \infty} = -P_0$ , we obtain the following relation which determines the gradient field of radial stresses in the matrix in the vicinity of the sphere:

$$\sigma_{rr} = -P_0 - (P_* - P_0)/\bar{r}^3 \quad (\bar{r} = r/R_0). \quad (4)$$

It follows from (4) that the inequality  $P_* \neq P_0$  is the condition for the formation of a gradient stress field in the medium, i.e., the field that is necessary to create the thermodynamic forces in the medium which are responsible for thermodynamic flows (the motion of the inclusions in this case).

We shall analyze the solution (4) for all the possible relations between the physical parameters of the matrix and the sphere, assuming that the subscripts 0, 1, and 2, which determine the aggregate states of the matrix  $i$  and the sphere  $j$ , refer to the gas, the liquid, and the solid elastic material, respectively. Since a certain store of free (surface) energy always exists at the interface of two immiscible media, we have  $\gamma_{ij} > 0$ .

Within the framework of the problem considered, the following cases are of interest:  $i = 1$  and  $j = 0$  (a bubble in a liquid),  $i = 1$  and  $j = 1$  (a drop in a liquid),  $i = 1$  and  $j = 2$  (a solid particle in a liquid), and  $i = 2$  and  $j = 0$  (a gas pore in a solid elastic medium). In these cases, the conditions at the matrix-sphere interface form the gradient stress field (4) in the matrix. It is clear that the stress gradient will be insignificant in hydromechanic problems too and, generally, these weak inhomogeneities of the stress field are not taken into account in the theory of elasticity. [For example, in the case of a drop in a liquid, even if  $R_0 \leq 10^{-2}$  cm, with allowance for the fact that  $\gamma_{10} < 10^{-2}$  N/cm and  $\gamma_{11} < \gamma_{10}$  for any liquid, we have  $|(2\gamma_{11}/R_0)/P_0| \ll 1$  for  $P_0 = 10^5$  Pa.] Correspondingly, a weak stress-field gradient entails a weak mass transfer; however, these fluxes becomes significant over large time lapses [1, 2].

3. As an example, we estimate the force by which the gradient stress field  $\sigma_{rr}(r)$  formed around the sphere D1 (Fig. 1) acts on the sphere D2 located in this field. For simplification, we assume that both spheres located in a liquid matrix have the same radius  $R_0$ . There is no gravity field, but the pressure  $P_0$  is applied in the liquid medium at infinity. The initial distance between the spheres for definiteness is  $l_0 = r_1 - 2R_0$ , where  $r_1$  is the initial distance between the centers of these spheres (Fig. 1).

In the first approximation, we assume that  $\gamma_{11} > 0$  at the boundary of the first drop, and the interphase tension on the surface of the second drop (D2) from the side of the liquid matrix is completely blocked by a layer of a surfactant, so that  $\gamma_{11} = 0$ . The diagram of the radial stresses in the system is determined only by

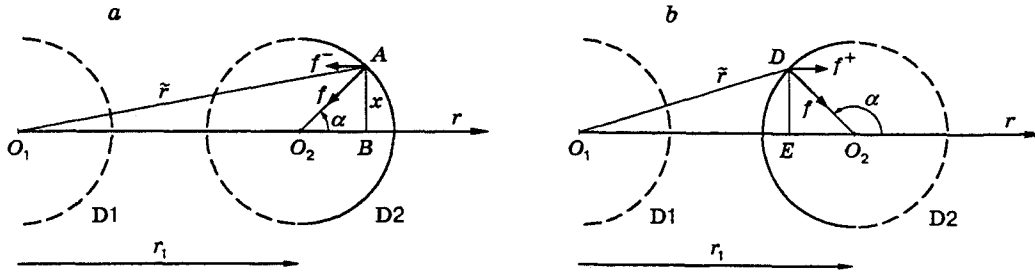


Fig. 2

the condition at the boundary of D1:

$$\sigma_{rr} = -\left(P_0 - \frac{2\gamma_{11}}{R_0} \frac{1}{\bar{r}^3}\right). \quad (5)$$

We calculate the resulting force applied to D2 at the initial moment of time in the gradient stress field of the drop D1. To do this, we first determine the radial stresses  $\sigma_{rr}(\bar{r})$  on the surface of D2, where  $\bar{r}$  is the coordinate of the surface point in the  $(r, \theta, \varphi)$  coordinate system whose center is aligned with the center of D1 (Fig. 2). From the above geometrical constructions [ $\triangle O_1AB$  and  $\triangle O_2AB$  for the right hemisphere of the sphere D2 (Fig. 2a) and  $\triangle O_1DE$  and  $\triangle O_2DE$  for the left hemisphere (Fig. 2b)], the coordinate  $\bar{r}$  of the point on the surface of the sphere D2 is determined in the form

$$\bar{r} = R_0(1 + \bar{r}_1^2 + 2\bar{r}_1 \cos \alpha)^{1/2} \quad (0 \leq \alpha \leq \pi, \quad \bar{r}_1 = r_1/R_0 \geq 2). \quad (6)$$

Substituting (6) into (5), for the radial stress on the sphere surface, we obtain

$$\sigma_{rr} = -\left[P_0 - \frac{2(1 + \bar{r}_1^2 + 2\bar{r}_1 \cos \alpha)^{-3/2} \gamma_{11}}{R_0}\right] \quad (0 \leq \alpha \leq \pi, \quad \bar{r}_1 \geq 2).$$

The resulting force which acts on the drop D2 in the gradient field (5) can be presented in the form

$$F = F_R + F_L, \quad F_R = \int_0^{\pi/2} f^-(\alpha) d\alpha = \int_0^{\pi/2} f(\alpha) \cos \alpha d\alpha, \\ F_L = \int_{\pi}^{\pi/2} f^+(\alpha) d\alpha = - \int_{\pi}^{\pi/2} f(\alpha) \cos \alpha d\alpha,$$

where  $F_R$  and  $F_L$  are the forces exerted by the right and left hemispheres of the sphere D2 (Fig. 2), respectively. Substituting

$$f(\alpha) = \sigma_{rr} ds = \sigma_{rr} 2\pi x R_0 d\alpha = 2\pi R_0^2 \left[ -P_0 + \frac{2(1 + \bar{r}_1^2 + 2\bar{r}_1 \cos \alpha)^{-3/2} \gamma_{11}}{R_0} \right] \sin \alpha d\alpha,$$

where  $x = R_0 \sin \alpha$  (Fig. 2), into these expressions, we obtain the relation

$$F = -\frac{8\pi R_0 \gamma_{11}}{\bar{r}_1^2 (\bar{r}_1^2 - 1)} \quad (\bar{r}_1 = r_1/R_0 \geq 2). \quad (7)$$

It follows from the above relation that in the gradient stress field of the sphere D1, a force is applied to the sphere D2 ( $\gamma_{11} = 0$  on its surface) in the direction of D1, which is proportional to the radius of the spheres and the interphase-tension coefficient on the surface of D1 and inversely proportional to the fourth power of the distance between the centers of the spheres which is nondimensionalized over the radius of these spheres. Here the constant constituent of the stress field, i.e., the hydrostatic pressure  $P_0$ , does not affect the interaction between the spheres. For example, if the sphere D2 is in the gradient stress field of an olive-oil drop in water, substituting  $\gamma_{11} = 2 \cdot 10^{-4}$  N/cm,  $P_0 = 10^5$  Pa,  $R_0 = 0.2$  cm into (7), for  $\bar{r}_1 = 3$  ( $l_0 = R_0$ ), we have  $F = 1.4 \cdot 10^{-5}$  H, and  $F$  decreases in absolute magnitude to  $-1.6 \cdot 10^{-6}$  N for  $\bar{r}_1 = 5$  ( $l_0 = 3R_0$ ). It is

noteworthy that, according to the experimental data of [1, 2], the interaction between the drops attenuates rapidly for  $l_0 > 1.2R_0$ .

Evidently, this estimates does not include the circumstance that the interphase tension at the boundary of the sphere D2 changes the structure of the gradient stress field; therefore, it is necessary to take into account the interaction between the stress fields of both spheres in the next approximation, i.e., to consider the case where  $\gamma_{11} \neq 0$  on the surface of D2 as well, which leads to the formation of a resulting self-consistent stress field. Here we do not consider the solution of this problem. We simply note that it is convenient to pass to an orthogonal bispherical coordinate system  $(\alpha, \beta, \varphi)$  [10] in which the equations of the surfaces of D1 and D2 become the simple relations  $\beta = \beta_0$  and  $\beta = -\beta_0$ , and the problem can be solved using the Boussinesq approximation [11].

4. It is necessary to note that, if the motion of the approaching spheres in a liquid matrix occurs according to known laws of hydromechanics (the motion of a spherical body in a liquid possessing a certain structural viscosity), the mechanism of motion of disperse macroparticles is not evident in the gel (viscous thixotropic material). The point is that at a level of shear stresses  $\tau$  not exceeding a certain threshold shear stress  $\tau_*$ , the thixotropic material behaves like an elastic solid, i.e., its elastic properties are due to its morphology. For example, for  $\tau < \tau_*$ , the gel is a low-viscosity liquid matrix in which while aggregated, the macromolecules of the filler (the chemical composition of which was given in [2]) form a complex skeleton which imparts elastic properties to the medium. For  $\tau > \tau_*$ , the skeleton fails, and the medium becomes a sol, i.e., a low-viscosity diluted ultradisperse suspension, and the sphere is able to move in it.

5. In the physical model of the formation of a gradient stress field in a matrix that has been analyzed above, the effect of other factors, except the interphase tension  $\gamma_{ij}$  at the matrix-sphere interface, is not allowed for. As is known, real condensed media contain various admixtures which can affect  $\gamma_{ij}$  (in particular, cause a change in  $\gamma_{ij}$  in time) or form electric fields in the vicinity of the spheres. (In addition, the electric field in the vicinity of the drop generates owing to its motion relative to the ambient medium [12].) For example, if a liquid matrix contains a sufficiently high concentration of free ions of both signs, absorbing on the DE surface, they form double diffuse (Helmholtz) layers; first, these layers reduce the level of  $\gamma_{1j}$  and, second, form similar electric fields around the spheres. Owing to this, the electrostatic repulsion between the DE can attenuate, compensate, or even be greater in intensity than the forces of their mutual attraction, which are due to a gradient stress field. As a result, the DE can be attracted together (the fresh drops in a fresh solution [1, 2]), can behave neutrally relative to each other (the old drops in an old alcohol-water solution [1]), or be repelled from each other (the fresh drops in an old alcohol-water solution [1]). If one increases the ionic strength of the solution, the thickness of the double diffuse layer on the DE surface increases and, hence, the value of  $\gamma_{1j}$  increases; consequently, the rate of their mutual attraction will increase [1].

Thus, if the system is completely isolated from the action of external forces, gradient temperature fields, and the concentration of the admixtures, the disperse elements in polar liquids or in a thixotropic material, in which the DE have interphase-tension coefficient  $\gamma_{ij} > 0$ , are influenced by the resulting gradient pressure field. The gradient of this field is very weak and, hence, the interaction between the DE is very weak; however, this interaction forces the system of DE to coagulate over large time lapses (from one hour to several weeks [1, 2]).

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