Journal of Applied Mechanics and Technical Physics, Vol. 40, No. 3, 1999

THERMODYNAMIC INSTABILITY OF DISPERSE MEDIA ISOLATED FROM EXTERNAL ACTIONS

S. V. Stebnovskii

UDC 532.5 + 536.12

The evolution of the structure of a medium containing disperse elements (the drops in a weakly viscous fluid, rigid spheres in glycerin, and air pores in a gel) is studied experimentally in the case where the gradient temperature and the concentration fields are absent in the system, and the medium is isolated from the influence of an external force field (including gravity forces). It is shown that these systems are nonequilibrium: if the initial distance between disperse particles is of the order of their sizes, the particles approach until they come in contact (coagulation) irrespective of the scale of the system.

It is known [1, 2] that heterogeneous systems such as emulsions and suspensions (including sols) have a tendency to change their structure in time, i.e., the disperse elements consolidate into aggregates (and the drops merge). Since a disperse medium has an excess free energy (the surface energy at the disperse phase–matrix interface), this state of the system is thermodynamically unstable.

It is commonly accepted that, in the case of a liquid matrix, the basic reasons for the instability of the structure of a medium, which show up as the approach of the particles and the formation of aggregates, are the Brownian motion, the effect of van der Waals forces (when the distance between particles is very small), the action of a gravity field, the convection, and the thermocapillary effect. But the Brownian motion can manifest itself only in the case where the particle sizes are smaller than 10^{-5} cm. However, according to the results obtained from observations under zero-gravity conditions [3], the bubbles in the water filling a spherical vessel coagulated with time (approached) and coalesced (merged) into one bubble at the center of the vessel. Geguzin et al. [4] explained these effects by the drift of bubbles, which is accompanied by their collisions, subsequent coalescence, and gas transport ("transfer") from one bubble to another through a liquid medium.

However, it was established experimentally in [5] that liquid drops, including very large (up to 1 cm) drops suspended in a liquid matrix at an initial distance between them not exceeding their sizes, also coagulate slowly before the mutual contact with subsequent coalescence. Hence, the disperse elements interact if the process of "transportation" of the material from one element to another through the liquid matrix does not occur.

This work is a continuation of the studies in [5], but here a special precision experimental technique is applied. This technique is used to consider the interaction between large-scale disperse elements with various physical properties, and liquid and gel-like media with various rheological parameters are used as the matrix.

Experimental Study of the Interaction between Disperse Elements in Liquid and Thixotropic Matrices. (1) The experiments were carried out on an experimental stand which allows one to investigate the behavior of drops or solid particles suspended in an equidense thermostatic liquid matrix isolated from the influence of vibrational and electromagnetic fields (Fig. 1). Here A is the thermostatic chamber consisting of a $20 \times 20 \times 20$ cm vessel 1 containing a medium 10 with suspended disperse elements 9; the walls of the vessel are equipped with a thermostatic water jacket 6 and a heat-insulated facing 7; the cover

Lavrent'ev Institute of Hydrodynamics, Siberian Division, Russian Academy of Sciences, Novosibirsk 630090. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 40, No. 3, pp. 53–58, May–June, 1999. Original article submitted June 25, 1997.

0021-8944/99/4003-0407 $22.00

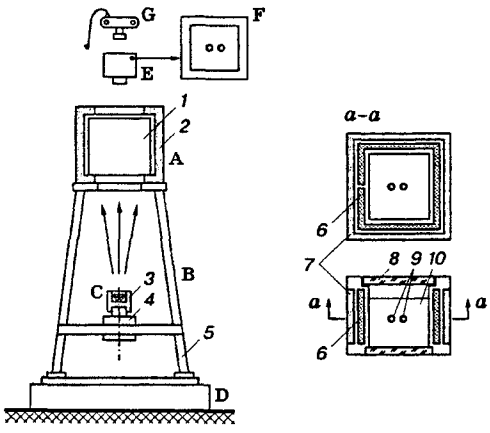

Fig. 1

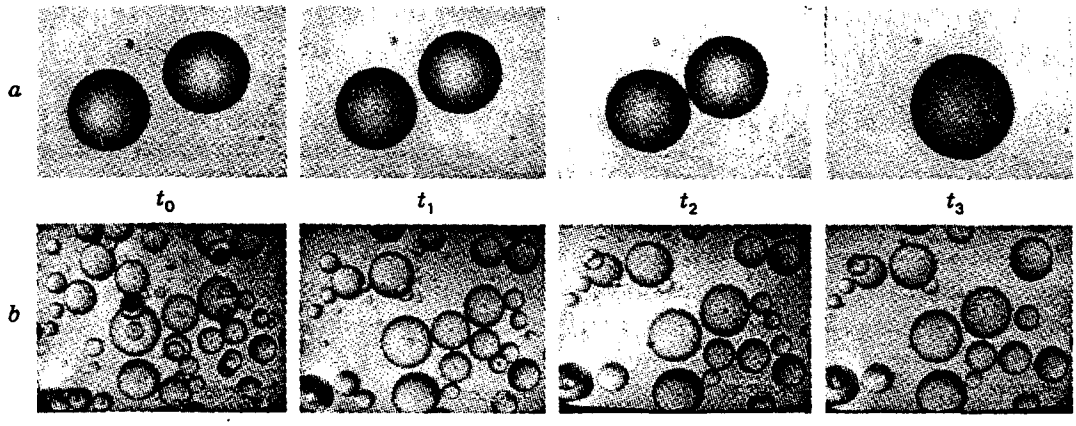

Fig. 2

of a vessel 8 and the bottom are transparent; from outside, the vessel is covered with grounded aluminum foil reflecting heat radiation. The vessel is in a heat-shielding casing 2 and is installed on a mount B, to which a system of illumination C, which consists of a thermal filter 3 and a capacitor with a source of light 4, is fixed. A mount 5 is on a steel plate located on a vibration-insulated foundation D of layered (felt–sand with foam plastic granules–felt) structure.

The process in the examined medium was visualized and recorded with a video camera E, from which the data were displayed on a TV screen F. Here, one can use a light-reflecting screen instead of the system of illumination C. The process was also recorded by a camera G with illumination. The vessel was equipped with a system to monitor the temperature field in the medium.

(2) The interactions between two liquid drops and the stability of the structure of a drop cluster in the liquid matrix were studied for various radii of the drops R and various initial distances between them l_0. As the matrix, an alcohol–water solution (AWS) with a density equal to the density of the fluid in the drops was used. The experiments were performed with drops from Vaseline, sunflower, and industrial oils.

As a result, it was revealed that the mutual approach of two drops and their subsequent coalescence occur in a fresh AWS for all materials of drops and for all their sizes used in the experiments if l_0 satisfies the condition $\bar{l}_0 = l_0/R \leqslant 2$. Figure 2a shows the typical video frame of this process for the case of the interaction between Vaseline drops for $R = 0.17$ cm, $\bar{l}_0 = 0.54$, $t_0 = 0$, $t_1 = 35$ min, $t_2 = 48$ min, and $t_3 = 54$ min.

Figure 3 shows the experimental data on the dependence of the time of complete approach of two identical drops (the period of coagulation) T_* on $\bar{l}_0$ in the case of interactions between the sunflower-oil drops.

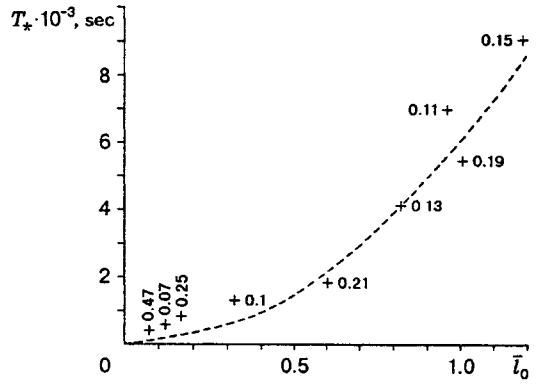

Fig. 3

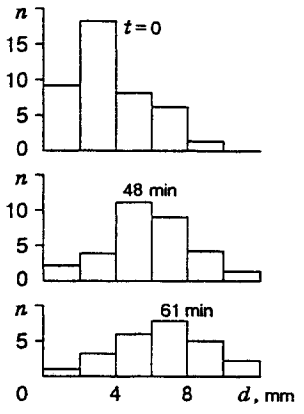

Fig. 4

The value of the radius of the interacting drops is indicated in centimeters at each experimental point. In the entire range $0 < \bar{l}_0 \leqslant 1.2$, the parameter T_* increases monotonically with $\bar{l}_0$ irrespective of the radius of the drops, i.e., the process of coagulation does not depend on the scale of the system. On the site $0.5 < \bar{l}_0 < 1.2$, we have $T_* \sim \bar{l}_0^2$ (dashed curve). For $\bar{l}_0 < 0.5$, the process of coagulation slows down, which is, apparently, due to the mutual repulsion of the electric fields of diffuse layers generated on the drop surfaces by the free ions adsorbed from the liquid matrix. For $\bar{l}_0 > 0.5$, the effect of deceleration is observed at the last stages of coagulation, when $\bar{l}(t) < 0.5$. For $1.2 < \bar{l}_0 \leqslant 1.3$, the interaction between the drops weakens to an extent that the effect of various random processes (the fluctuations of the temperature field, the concentration of impurity in the matrix, etc.) becomes significant. For $\bar{l}_0 > 1.3$, the drops make a very slow random drift until they approach randomly at the distance $\bar{l}_0 \leqslant 1.2$, and coagulation begins.

Analysis of the experimental results showed that T_* also depends on the material of the drops. Thus, the rate of coagulation of Vaseline-oil drops is greater than that of sunflower-oil drops.

(3) The evolution of the structure of a diluted coarse-disperse emulsion (industrial-oil drops suspended in an AWS) in time was investigated. It was established that, in the emulsion medium, after two drops have approached and coalesced, the formed drop is displaced rapidly relative to the center of mass of the coalescing drops, spending the released excess free energy and thus perturbing the surrounding drop ensemble. After a series of coalescence acts, the disperse composition of the emulsion become coarser, as shown on the video frame (Fig. 2b) ($t_0 = 0$, $t_1 = 38$ min and 29 sec, $t_2 = 47$ min and 46 sec, and $t_3 = 51$ min and 25 sec) and histograms (Fig. 4); therefore, the free energy of the system decreases spontaneously (in Fig. 4, d is the diameter of industrial-oil drops and n is the number of drops of the corresponding diameter).

It follows from the experimental results that not only highly concentrated finely disperse emulsions [1], but also diluted coarse emulsions exhibit the tendency of drops toward coarsing, i.e., the effect of the thermodynamic instability does not depend on the scale of the process.

(4) Alongside with the problem of the stability of the structure of emulsions, there is a similar problem for suspensions in which finely disperse solid particles also coagulate with time, thus forming coarse aggregates. In this connection, the behavior of two large rigid spheres suspended in a very viscous homogeneous fluid, namely, glycerin, was studied. This excluded the influence of spontaneously arising weak mass fluxes on their interaction. The spheres had a two-layer structure: a spherical polymer skeleton covered with a layer of modeling clay. The relation between the volumes of the polymer (its density is smaller than that of glycerin) and modeling clay (its density is greater than that of glycerin) was chosen in a way such that the average-mean density of the two-layer sphere coincided with the density of glycerin.

The stand experiments showed (see Fig. 1) that the rigid spheres suspended in a very viscous matrix are attracted with time to each other. Figure 5a shows the video frames of the mutual approach of two spheres ($t_0 = 0$, $t_1 = 6.5$ h, $t_2 = 21.5$ h, $t_3 = 40.5$ h), and Fig. 5b shows the diagrams of the variation,

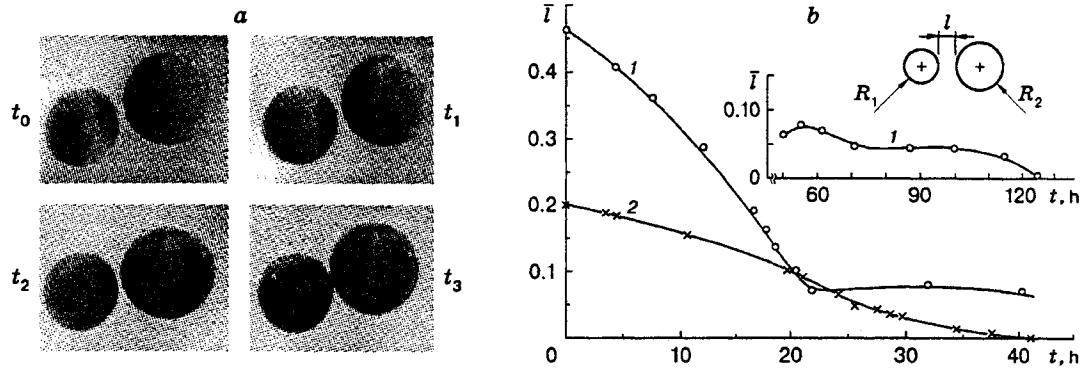

Fig. 5

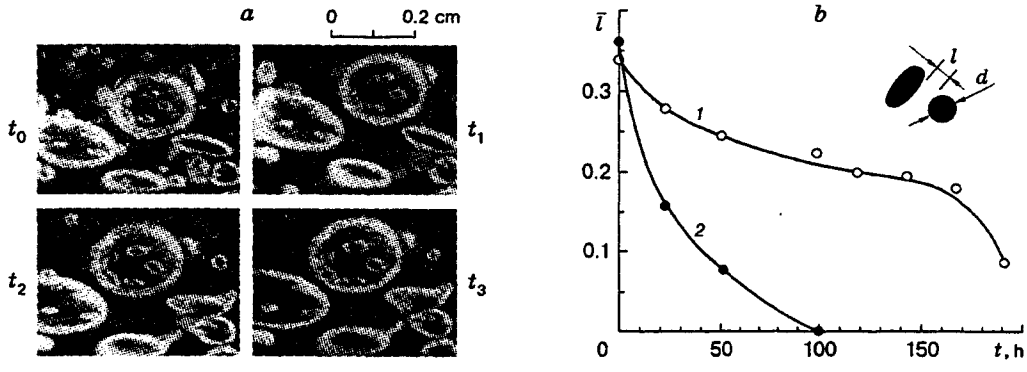

Fig. 6

in time, of the dimensionless gap between them, which is averaged over the sphere radius $\langle R \rangle$, $\bar{l} = l/\langle R \rangle$, where $\langle R \rangle = (R_1 + R_2)/2$. Curve 1 corresponds to the case $R_1 = 0.3$ cm and $R_2 = 0.21$ cm, and curve 2 to $R_1 = 0.35$ cm and $R_2 = 0.41$ cm. In contrast to the process of drop approach in a weakly viscous AWS, the rigid spheres in glycerin coagulate two orders slower; the deceleration of the approach at the last stage has an oscillatory character. This specific feature is, apparently, connected with the influence of the rheological properties of the very viscous Newtonian fluid of the matrix on the process of its displacement from the gap between the spheres.

(5) For better insight into the thermodynamic instability of heterogeneous media, we performed experiments in which the interaction between the air pores in a gel (the gel composition is as follows: water, polyvinylpirrolidone, propylene glycol, disodium salt of ethylene ditetraacetic acid) was considered. In this variant of the medium, first, the matrix and the disperse elements differ strongly in density; secondly, the third, gaseous variant of disperse elements is considered; finally, the matrix (gel) has shear elasticity: in its rheological properties, the matrix is attributed to the class of viscoelastic thixotropic media (a Bingham body). The use of the gel as the matrix allows one to exclude the possibility of occurrence of fluctuations of the mass rate and other spontaneous processes which affect the coagulation of disperse elements.

The experiments were carried out on a stand (see Fig. 1). To create an ensemble of pores above the free surface of the gel, the atmospheric pressure was decreased, and, as a result, the micropores contained in the medium were increased to 0.05–0.5 cm. Generally, the pores had a nonspherical shape owing to the significant structural viscosity of the gel hindering the process of spheroidization.

The experiments showed that the pores in an elastic thixotropic matrix mutually approach with a velocity considerably smaller than the velocity of the rigid spheres in glycerin. Figure 6a shows the video frames ($t_0 = 0$, $t_1 = 21$ h, $t_2 = 95$ h, and $t_3 = 190$ h), and Fig. 6b shows the diagrams of the mutual approach of two pores in the gel (curve 1 corresponds to the interaction between two pores, one of which is shaped like

an ellipsoid, and the second are the spheres of diameter 0.21 cm; curve 2 shows the interaction between two pores, one of which is of irregular form, and the second pore is shaped like a sphere of diameter 0.08 cm). Thus, in a rigid elastic matrix, the system of disperse elements is in a nonequilibrium state and goes to a state with a lower level of free energy owing to coagulation.

Analysis of Results. Three series of experimental studies of the behavior of the system of disperse elements in condensed matrices were performed under the condition that the system is isolated from external forces and temperature and concentration field gradients are absent in the medium. The aggregate state of the material of disperse elements varied from a gaseous to a solid state; as the matrix, condensed media from a weakly viscous fluid to a viscoelastic thixotropic material were used; the range of characteristic sizes of the disperse elements varied from 0.08 to 1 cm.

It was shown that, in all cases, the disperse media are not only thermodynamically unstable, which is explained by the excess free (surface) energy in the system, but also nonequilibrium: the disperse elements are attracted to each other even when external actions are lacking. Since the medium passes to a lower level of free energy after the mutual approach of the disperse elements and the system is isolated from external power sources according to the experimental condition, this process is irreversible. According to the Onsager principle, the reason for the occurrence of irreversible fluxes of the substance is the presence of thermodynamic forces in the medium, which are due to the inhomogeneous (gradient) spatial distribution of a certain physical parameter of the medium. Since the medium is isolated from external actions, there are no gradients of temperature or impurity concentration in it, and the formation of a physical field gradient in the medium can be caused by the conditions at the disperse element-matrix interface. The problem of the mechanism of interaction between disperse elements is omitted in this paper.

This work was supported by NASA (Grant No. NAS15-101010).

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