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Abstract

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ON SPONTANEOUS DISPERSION UNDER CONDITIONS OF A STRONG DECREASE IN THE FREE INTERFACIAL ENERGY

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It is known that in certain cases, with limited or even very small mutual solubility of two phases (liquid—liquid, or solid—liquid), the spontaneous formation of a finely dispersed colloidal system—an emulsion or suspension with particle sizes of the order of 10^{-5}—10^{-6} cm—is possible (we have in mind here low-molecular substances, in particular metals, for which such particles are "phase" particles). Since the formation of such a colloid is associated with a sharp increase in the phase-separation surface and the corresponding increase in the free surface energy of the system, it is obvious that this process is possible only under conditions of very small values of the free energy of the interfacial surface.

The first approach to an analysis of the thermodynamic stability of lyophilic colloidal emulsions was outlined by M. Volmer ([1–4]). Taking into account the interaction of colloidal particles with molecules in the state of a true solution, Volmer showed that the distribution of particles by size, or by number of molecules, in such emulsions can be described by a function of the type $\mathrm{const} \cdot r^m \cdot \exp(-4\pi r^2\sigma/kT)$, where r is the particle radius, σ is the free interfacial energy; the exponent m depends on the choice of one or another model. For certain values of σ (considerably below 1 erg/cm^2) the maximum of the distribution may lie in the region of the colloidal phase.

Another approach to an analogous problem—the elucidation of the thermodynamic conditions for the spontaneous dispersion of a solid in a liquid into colloidal particles—was proposed by Rehbinder and Shchukin ([2,3]), who showed that the increase in free energy associated with the development of the interfacial surface in the formation of a finely dispersed colloidal system can be compensated by the growth of the entropy (entropy of mixing) of the system. For a monodisperse system such compensation is expressed by the equality:

$$\Delta F = 4\pi r^2 \sigma n_1 + kT \left\{ n_1 \ln \frac{n_1}{n_1 + n_2} + n_2 \ln \frac{n_2}{n_1 + n_2} \right\} \simeq$$

$$\simeq 4\pi r^2 \sigma n_1 - kTn_1 \left\{ \ln \frac{n_2}{n_1} + 1 \right\} = 0, \tag{1}$$

where $n_1 = n_1(r)$ is the number of colloidal particles with radius r, n_2 is the number of solvent molecules ($n_1 \ll n_2$); at room temperature, spontaneous dispersion into particles of colloidal size, according to this equality, is possible when σ is lowered to tenths and hundredths of an erg per 1 cm^2. It can be shown that application of this scheme to polydisperse systems gives a size distribution analogous to that proposed by Volmer.

Thus, for the spontaneous emergence of a thermodynamically stable colloidal emulsion or suspension, it is necessary that σ be lowered to very small values, which is observed, for example, in the case of critical emulsions formed in a two-phase liquid system in a certain region of temperatures and concentrations near the mixing point. Similar conditions apparently also occur in those cases where the disperse phase, along with high lyophilicity, possesses a sharply pronounced finely dispersed layered structure (such are, in particular, bentonite clays,

spontaneously dispersing in water in the absence of any appreciable true solubility); let us note that in this case the presence of a minimum on the curve $\Delta F = \Delta F(r)$, which does not follow directly from relation (1) and requires additional assumptions about the limitation of true solubility, is readily explained (for example, in connection with the increase of σ for very small particles).

However, spontaneous dispersion (in the absence of external mechanical actions) of a solid in a liquid medium can also be observed at not very small values of the interfacial energy σ (of the order of units or even tens of erg/cm^2). Thus, we previously established that tin single crystals, in the presence of a thin film of liquid gallium, gradually, as a result of a specific recrystallization, acquire the structure of fine-grained polycrystals ([4,5]). Since the value of σ here is certainly not less than units of erg/cm^2, the driving forces of dispersion have a different ("non-entropic") nature, which must be reflected both in the kinetics of the process, and in the degree of dispersity of the structure formed, and in the stability of this structure. Such driving forces (ensuring a decrease in the free energy of the system as a whole and the appearance of a minimum on the curve $\Delta F = \Delta F(r)$) may be: 1) release of the elastic energy present in the crystal (the energy of dislocations) in the course of recrystallization, with the supersaturations necessary for the formation of nuclei of new particles being created precisely at the mouths where dislocations emerge on the crystal surface; 2) formation of a solid solution,–if, in the process of recrystallization of a body accompanied by refinement of the structure, solution formation proves kinetically more favorable (proceeds faster) than during ordinary diffusion of the given liquid into the given solid.

Fig. 1

In Fig. 1 the curves a schematically express the dependence $\Delta F(r)$, the change

Fig. 1

Figure 1: Fig. 1

in the free energy of the system, on the degree of dispersity for an ideal solid: a_1—in the case of true solubility, a_2—in the case of formation of a thermodynamically equilibrium system with particles of colloidal size; in the case a_3, dispersion into colloidal particles is impossible. Curve b corresponds to a real crystal with a sufficiently high dislocation density (at small r this curve coincides with a). Here the release of the elastic energy of dislocations upon dispersion may compensate for the increase in the free energy of the new interphase boundaries and lead to the appearance of a minimum of ΔF; upon formation of a solid solution, the curve as a whole (case c) and its minimum lie lower. The fundamental difference between a and b (and c) consists in the fact that in the second case the minimum of ΔF arises at a relatively coarse dispersity, when the role of the entropic factor is still insignificant, and this minimum corresponds to a thermodynamically nonequilibrium state possessing only greater or lesser temporal stability, since subsequently the system must, generally speaking, tend toward an increase in particle size (if they grow while retaining a low dislocation density). Indeed, all these features are observed in galliated single crystals of tin and zinc.

To confirm the nonequilibrium character of the structure arising during the dispersion of galliated tin single crystals, the numbers of reflections on Laue photographs taken during the dispersion process and after its completion were counted. It turned out that the initial sharp increase in the number of reflections is replaced after several days by a slow decrease in their number, apparently associated with aggregate recrystallization. More

it was possible to grow druses of tin single crystals from a solution of tin in gallium saturated at 100°; these crystals reach several millimeters and give mirror-like cleavages along the (100) planes, while the character of the X-ray reflections indicates a very perfect structure.

From the number of reflections arising during dispersion, one can also estimate the average size of the crystallites. Such an estimate gives a value of $(2 \div 8) \cdot 10^{-3}$ cm. In accordance with this, metallographic examination of the surface of gallium-treated tin single crystals (etched in a mixture of concentrated hydrochloric and nitric acids) showed that the grains reach several tenths of a millimeter, with an average size of about 0.02 mm.

To check whether, in the process of dispersion of a gallium-treated tin single crystal, along with the formation of a polycrystal structure there also occurs fragmentation of the blocks (down to a size of the order of $10^{-5} \div 10^{-6}$ cm), a study was carried out of gallium-treated single-crystalline and coarse-grained polycrystalline specimens on a URS-50-I X-ray diffractometer using iron radiation. Measurements of the width of the (011) lines with Bragg angle $\theta = 20^\circ 18'$ and (331)—(103) with $\theta = 68^\circ 54'$ showed nonsystematic changes in line width in the course of dispersion, lying within the accuracy of the measurements; consequently, during the dispersion process there are no changes in the block structure of tin (within the limits of individual newly appearing grains), and no measurable microdistortions of the lattice arise. At the same time, a shift of the lines was detected on the X-ray patterns, indicating the formation of a solid solution (with a decrease in the lattice parameter).

The formation of a solid solution is also indicated by measurements of the microhardness of tin, in particular near the boundary of the dispersion zone formed after a drop of liquid gallium was applied to the polished surface of a coarse-crystalline specimen (Fig. 2, see inset p. 1078): the microhardness (under a load of 10 g) in the gallium-treated zone is 42 ± 8 kg/mm^2, compared with 12 ± 2 kg/mm^2 for the initial tin.

The role of internal elastic stresses (the energy of dislocations) in the dispersion process is clearly manifested in the features of dispersion of gallium-treated zinc single crystals: well-annealed, undamaged specimens show no recrystallization; dispersion is observed only in deformed single crystals (at a sufficiently high dislocation density), mainly when there is significant damage to the surface of the specimens.

Thus, one should distinguish thermodynamically stable emulsions and suspensions, which in the full sense of the word form spontaneously at very small σ and have particles of colloidal dimensions, from the case in which, at not very small σ, the driving force of dispersion is the elastic energy of the dislocation structure (in combination with the formation of a solid solution or without it), giving rise to a relatively coarser and, in principle, unstable system; obviously, this second case is of special practical interest from the standpoint of facilitating external mechanical dispersion, for example, extremely fine vibratory grinding of solids.

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