

the embryo which minimizes the energy of the system for the formation of a nucleus. For simplicity, assume that n atoms in an embryo form a sphere. When the spherical embryo is formed, energy of the entire assembly increases by the amount ΔW defined by the expression⁵¹

$$\Delta W = n G_{21} + (36\pi V_2^2)^{1/3} \sigma n^{2/3} \quad (5.4)$$

where V_2 is volume per atom of the second phase and σ is surface energy per unit area of the interface between the two phases. The surface energy term in Eq. (5.4) makes it necessary for G_{21} to attain a certain negative value before transformation can begin.

Consider now the stability of embryos according to their size. Embryos containing n^* atoms maximize ΔW , where

$$n^* = \frac{-32\pi\sigma^3 V_2^2}{3G_{21}^3} \quad (5.5)$$

Having reached this size, they continue to grow.

In macroscopic assemblies, fluctuations will lead to local transitory phase transformations. These fluctuations are also responsible for establishing a distribution of embryos of different sizes within a stable phase which has the same atomic arrangement as the new phase. Frenkel⁵³ treated each embryo as a molecule of a particular kind, independent of the others, and randomly present as a dilute solution in phase 1. The thermodynamic Gibbs potential of such a solution is given by the expression

$$G = N_1 G_1 + \sum_n N_n \left[G_2^n + (36\pi V_2^2)^{1/3} \sigma n^{2/3} \right] + kT \left[N_1 \log \left(\frac{N_1}{N'} \right) + \sum_n N_n \log \left(\frac{N_n}{N'} \right) \right], \quad (5.6)$$

where N_n is the number of embryos containing n atoms and $N' = N_1 + \sum_n N_n$ denotes the total number of species, those of different size being treated as molecules of different kinds.

Size distribution of clusters was determined by maximizing Eq. (5.6) to obtain the expression,

$$N_n = N \exp \left(- \frac{\Delta W(n)}{kT} \right), \quad (5.7)$$

where $N = \sum_n n N_n$ is total number of atoms per cm^3 , k is the gas constant, and T is temperature.

According to Frenkel,⁵³ the kinetics of transformation in solids does not differ, in principle, from kinetics of the condensation process considered above, except for certain special features connected with the shapes of crystals. Therefore, we assume that Eq. (5.7) is valid for solid systems.

If the distribution of embryos has insufficient time to change from its initial form when a large stress is rapidly applied, a certain number of embryos are suddenly found to exceed the critical or stable size for the new, thermodynamic state, becoming "trapped" on the side of the energy curve favoring growth. The number of embryos that begin to grow under these conditions can be calculated from the distribution function of stable embryos for old and new states. The number of embryos N_{12} in the interval (n_1, n_2) is given by the expression,