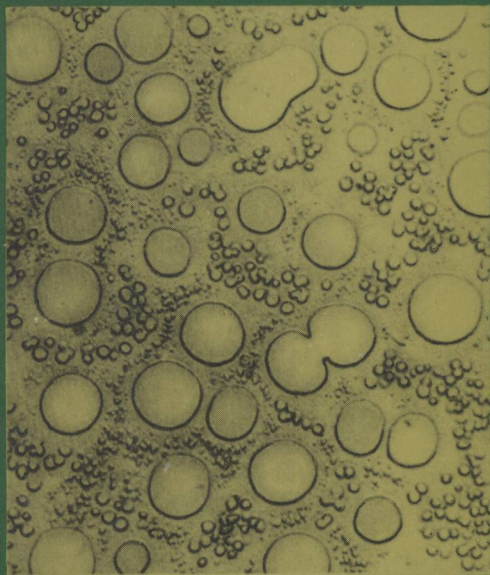


# Glass-Ceramic Materials

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Glass Science  
and Technology  
8



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Glass Science and Technology 8

# Glass-Ceramic Materials

**Liquid Phase Separation, Nucleation and Crystallization  
in Glasses**

**ZDENĚK STRNAD**

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## PREFACE

Glass-ceramic materials are new, solid substances that are especially useful because of their exceptional technical parameters, including a wide range of unusual combinations of properties. The characteristics of glass-ceramic materials basically depend on the properties of the finely separated crystalline phase and the residual glass phase which make up the glass-ceramic material. The kind of crystalline phase and thus also the final properties of the glass-ceramic material can be controlled by the initial glass composition and by its heat treatment. In this way, an almost unlimited number of types of glass-ceramic material can be prepared with various combinations of properties, many of which are useful in practice.

Glass-ceramic materials appear promising, not only because of their outstanding properties but also because the production process involves conversion of quite common silicate raw materials into substances with superior properties. This permits conservation of rarer traditional materials (e. g. nonferrous metals: chromium, cobalt, nickel), development and production of qualitatively new or functionally improved products, innovation in technology and also new, more efficient, engineering design; these materials are now often indispensable for improving the level of other production fields.

The production of glass-ceramic materials is becoming a more independent new field of material technology, based on special manufacturing processes, especially controlled crystallization of glasses based on theoretical knowledge, primarily in the field of phase transformation in condensed systems and the physics of solid substances.

The introductory chapters of this book therefore deal with selected theoretical considerations in order to increase knowledge of the procedures underlying the manufacture of glass-ceramic materials. Glass formation, discussed in Chapter 1, is considered from the point of view of the kinetic theory based on the classical model of homogenous nucleation. Chapter 1 thus forms a natural introduction to the actual problem of phase transformation in glass-forming systems as well as a review of theoretical aspects of the preparation of glass as a starting material in the manufacture of glass-ceramic materials.

In addition to the main topics of nucleation and crystal growth, Chapter 2 also considers phase separation in the liquid phase, which frequently has a marked effect on the actual process of controlled crystallization of glasses. Basic information on bulk crystallization of glasses in simple systems, yielding the compositions of the most important glass-ceramic materials, is given in Chapter 3.

Chapter 4 follows the theoretical section and gives the basis of the actual procedures for the preparation of glass-ceramic materials. Chapter 5 describes important methods suitable both for research and development of glass-ceramic materials as well as for control of production technology and of the final properties of the products.

A description of the most important physico-chemical properties of glass-ceramic materials is given in Chapter 6. The concluding Chapter 7 includes a set of tables listing the individual types of glass-ceramic materials (with their properties and applications) that are manufactured or have been tested on a large scale.

The text of the book is complemented by figures supplied by foreign manufactures, research institutes and laboratories: Corning Glass Works, Owens-Illinois Inc., USA; GEC Power Engineering Ltd., Stafford Laboratory, Great Britain; Schott Glaswerke, FRG; Mendelejev Institute for Chemistry and Technology, The Department of Technology of Glass and Sitalls, USSR; NGK Insulators Ltd., Nippon Electric Glass Co., Ltd., Fuji Photo Film Co., Ltd., Japan; Sklo-Union-Research and Development Institute for Industrial Glass, State Glass Research Institute, Czechoslovakia. I wish to thank all these institutions and especially some of their employees, as well as a number of other people who kindly gave their permission to publish data and figures and who helped by providing material for this book. I especially wish to thank the following people: Dr. G. H. Beall, Dr. D. G. Burnett, Dr. J. Broukal, Dr. M. Cable, Prof. R. W. Douglas, Dr. P. F. James, Prof. P. W. McMillan, T. Murakawa, Dr. G. Partridge, Prof. N. M. Pavlushkin, Prof. S. Sakka, Dr. G. P. Smith, Prof. J. Staněk, Dr. M. Wada and Dr. J. Voldán.

I would also like to thank Dr. Zdeňka Vejšická for coauthoring the sixth and seventh chapters and especially for drawing up the tables on the properties of glass-ceramic materials.

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Zdeněk Strnad

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Glass-ceramic materials are polycrystalline solids containing residual glass phase, prepared by melting glass and forming it into products that are subjected to controlled crystallization. The concept of controlled crystallization of glass designates the separation of a crystalline phase from the glassy parent phase in the form of tiny crystals, where the number of crystals, their growth rate and thus also their final size are controlled by suitable heat treatment.

Successful preparation of glass-ceramic materials depends especially on ensuring the formation of a sufficiently large number of crystal nuclei that are uniformly distributed throughout the bulk of the glass and that continue to grow (usually to a size of 0.1 to 1.0  $\mu\text{m}$ ) at increased temperature until the crystalline phase occupies a volume that mostly lies between fifty and one hundred percent of that of the original glass volume. The initial glasses for the preparation of glass-ceramic materials, i. e. usually inorganic oxide glasses, are prepared in the usual manner, i. e. by cooling a glass-forming melt after previous shaping as required. It is thus characteristic for the preparation of glass-ceramic materials that the starting substance is a glass that changes into a fine-grained polycrystalline material with required properties as the result of controlled heat treatment. Controlled crystallization not only permits control of the actual phase conversion (i. e. the kind and morphology of the crystalline phase) but also allows treatment with maintenance of the apparent viscosity of the polycrystalline material during the conversion, containing residual glass, within limits that ensure that the original glass shape is not deformed.

Before considering the individual processes occurring during conversion of glass into a glass-ceramic material, a description will be given of crystallization of glasses from the point of view of phase equilibria and especially of the glassy state and conditions for its formation.

## 1.1 PHASE EQUILIBRIA IN GLASS-FORMING SYSTEMS

In order to improve our understanding of the relationship between the glassy state and the equilibrium states of solid crystalline and liquid substances, it is useful to follow the dependence of the free energy of the system on the temperature during cooling of a melt.

If a melt is to be cooled below the melting point  $T_1$  (or below the liquidus tempe-

perature  $T_1$  in multi-component systems) so that a crystalline phase is not separated, a supercooled state of the liquid can be attained under certain conditions i. e. in internal (metastable) equilibrium, whose free energy changes along curve 2 obtained by extrapolation of the curve of stable liquid 1 below the melting point (Fig. 1-1). On further cooling, the metastable equilibrium in the supercooled liquid

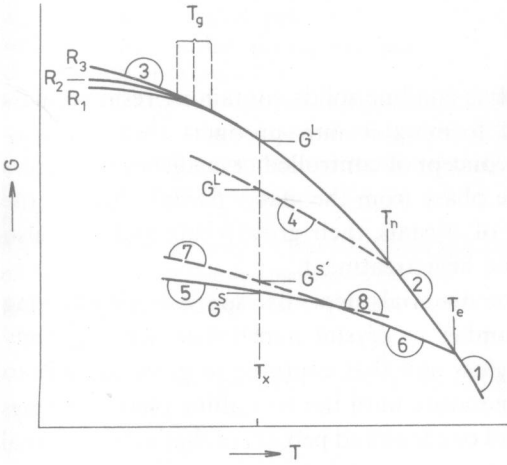


Fig. 1-1 Schematic diagram of dependence of the free energies of systems on the temperature, depicting the relationship between the glass state and the equilibrium state of the liquid and crystalline phase;

$R$  = cooling rate,  $R_1 < R_2 < R_3$ ;

1 - stable liquid, 2 - supercooled liquid, 3 - glass state, 4 - metastable, separated liquid, 5, 6 - stable crystalline phase, 7, 8 - metastable crystalline phase,  $T_e$  - equilibrium temperature of the phase transformation (S-L),  $T_n$  - immiscibility temperature,  $T_g$  - glass-transformation temperature

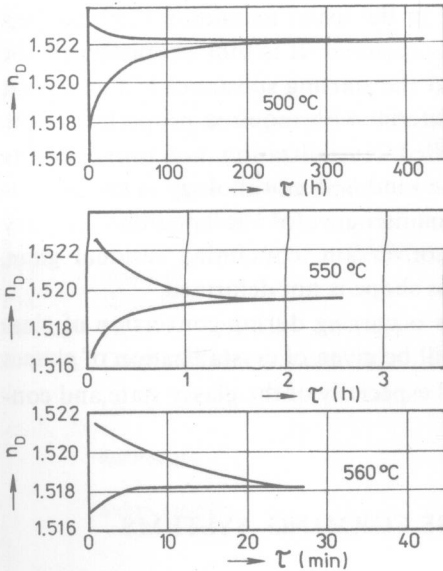


Fig. 1-2 Dependence of the change in the refractive index  $n_D$  on time for glasses with different thermal histories at heating temperatures of 560, 550 and 500 °C [275]

phase is increasingly difficult to maintain because of the increasing viscosity; this can be observed on the basis of some of the properties of the supercooled melt (molten glass) e. g. the refractive index, density and viscosity in dependence on time at a constant temperature (Fig. 1-2).

Fig. 1-2 depicts establishment of metastable equilibrium, studied in terms of changes in the refractive index with time. The upper curves correspond to changes in the refractive index in samples that were preliminarily heated for a long time below the experimental temperature; the lower curves correspond to very rapid cooling of melt samples. It is apparent from Fig. 1-2 that, in both cases, the refractive index changes towards the same final equilibrium value. The higher the temperature at which the molten glass is maintained, the lower is its viscosity and the faster is the establishment of an equilibrium state, and vice versa. The process during which the molten glass attains a more stable state is termed stabilization. If the sample is cooled at a constant rate that is greater than the rate of establishment of metastable equilibrium, then this equilibrium can no longer be established at a certain temperature; this temperature is termed the *transformation temperature*,  $T_g$ . At this temperature, the supercooled melt is converted into a glass and the viscosity usually attains a value of about  $10^{13}$  dPa s. Thus the properties of the glass in a certain temperature range will depend on its thermal history; this region is termed the *transformation temperature interval*.

A second limiting pathway of melt cooling is crystallization of the melt with formation of a stable, equilibrium crystalline phase, so that the free energy of the system will exhibit a minimum and will change in dependence on the temperature according to curves 5 and 6 (Fig. 1-1).

Between these two extreme cases of a supercooled melt and a stable crystalline phase will lie the original glass on reheating between the transformation  $T_g$  and liquidus temperatures  $T_l$ , where a number of further metastable equilibrium states can exist, whose participation in isothermal heat treatment depends on kinetic factors of the individual phase changes. For example, in isothermal treatment of the supercooled melt at temperature  $T_x$  (Fig. 1-1), a decrease in the free energy of the system,  $G^L \rightarrow G^{L'}$ , i. e. a more stable state can be attained by separation into two liquid phases ( $G^{L'} = nG_1^{L'} + (1 - n)G_2^{L'}$ ) or by coming out of a metastable crystalline phase  $G^{S'}$ , or a stable equilibrium state  $G^S$  may be attained. Metastable phases appear very frequently in glass-ceramic materials, not only as transition phases that can have a considerable effect on the course of the crystallization (e. g. metastable phase separation in the liquid phase), but also as the final crystalline phase responsible for the exceptional properties of a number of industrially manufactured glass-ceramic materials.

## 1.2 GLASS FORMATION

Glass formation can be defined as the ability of a melt to form a glass on cooling, i. e. a solid, noncrystalline substance whose upper temperature of existence is given by the transformation temperature  $T_g$ ; on exceeding this temperature, the glass is converted into a supercooled melt (molten glass).

As has already been mentioned in discussion of the usual method of preparing glass-ceramic materials, the glass product is first shaped and then is subjected to controlled crystallization. Thus the requirements on the glass-forming ability of the melt during cooling and shaping must be the same as for ordinary glass. The glass-forming material must be sufficiently stable during cooling so that it can be worked using ordinary glass-shaping techniques, such as pressing, blowing, casting, drawing, rolling, etc., without separation of a crystalline phase. When the glass is reheated to a suitable temperature, the stability of the molten glass is, however, very different from that of ordinary glass, as it can be quite readily converted into a fine-grained, crystalline material. It is thus apparent that the factors determining the ability of the melt to form a glass during cooling as well as the stability of the molten glass after reheating between temperatures  $T_g$  and  $T_1$  are decisive in the choice and design of the initial composition for the production of glass-ceramic materials.

The validity of general models and theories of glass formation from a structural and thermodynamic point of view is basically limited by incomplete information on the actual nature of the glass state. The kinetic theory of glass formation avoids this problem by not considering the conditions for formation of the glass state but rather the kinetics of formation of the crystalline phase. It is not basically important which substances can form glasses, but rather under which conditions the liquid must be cooled to prevent detectable crystallization.

As G. Tammann [1] found more than half a century ago, crystallization of a supercooled liquid is controlled by two basic factors. The first of these is the nucleation rate, i. e. the number of nuclei formed in a unit volume per unit time; the second is the rate of crystal growth, i. e. the rate of shift of the phase boundary of the crystalline phase in the liquid. Tammann also recognized that the dependence of these kinetic factors on temperature passes through maxima; the quicker the melt is cooled across the temperature of maximal nucleation and growth rates, the smaller is the probability that a crystalline phase will be formed during cooling of the melt and the greater is the possibility of glass formation. It is interesting that, although Tammann clearly defined the main kinetic factors in glass formation, these factors have been treated separately in the beginning of the development of the kinetic theory. An example is the work of Dietzel and Wickert [2], who evaluated glass formation using the reciprocal value of the maximal growth rate and connected glass-forming ability primarily with high viscosity of the supercooled melt, with low liquidus temperature and with a large difference between the chemical compositions of the crystalline and parent phases (the Dietzel [3] concept of eutetic composition). This approach would be justified to a certain extent assuming that the supercooled liquid always contains a sufficient number of nuclei.

It is apparent from Tab. 1-1 that substances that readily form glasses may have maximal growth values of up to  $10 \mu\text{m s}^{-1}$ . Even if the substance with the lowest growth rate in Tab. 1-1,  $\text{SiO}_2$ , is considered, with a mean growth rate (of cristoballite) estimated from Fig. 1-3 of  $7 \cdot 10^{-2} \mu\text{m min}^{-1}$  ( $1.1 \cdot 10^{-3} \mu\text{m s}^{-1}$ ) in the

Table 1-1 Crystallization data and viscosity values for some supercooled melts

Substance	Max. growth rate of prim. cryst. phase ( $\mu\text{m s}^{-1}$ )	Temp. of max. growth rate of prim. cryst. phase ( $^{\circ}\text{C}$ )	Melting point $T_f$ of prim. cryst. phase ( $^{\circ}\text{C}$ )	Log of melt viscosity at $T_f$ (dPa s)
$\text{SiO}_2$	$2.2 \cdot 10^{-3}$	1674	1734	7.36
$\text{P}_2\text{O}_5$	$1.5 \cdot 10^{-3}$	561	580	6.7
$\text{GeO}_2$	$4.2 \cdot 10^{-2}$	1020	1116	5.5
$\text{Na}_2\text{O} \cdot 2\text{SiO}_2$	1.5	762	878	3.8
Salol	$6.4 \cdot 10$	20	43	
Sn	$> 10^6$		232	

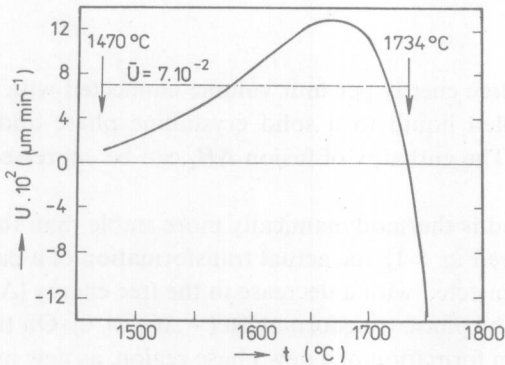


Fig. 1-3 Dependence at the rate of crystal growth of cristobalite  $U$  from quartz glass on the temperature [4]

temperature range 1470–1734  $^{\circ}\text{C}$ , where cristobalite is a stable phase, the common cooling rate of 1 to 10  $\text{K s}^{-1}$  in this temperature interval cannot prevent formation of crystals with a size from 0.58 to 0.058  $\mu\text{m}$ . However, experience has shown that far slower cooling permits formation of quartz glass without apparent crystallization (see also Tab. 1-2).

The rate of crystal growth thus cannot be the only factor determining the ability of a melt to form a glass, as the crystals grow from a certain number of crystal nuclei; these nuclei thus determine the actual phase transformation.

A model based on quantitative determination of the nucleation rate as a criterion of the glass formation was developed by Turnbull [5]. A situation where no nuclei are formed during cooling of the melt was found as a condition for the glass formation; this condition was defined by the relationship

$$n^* = V \int_0^{\tau} I_0 d\tau \quad n^* < 1 \quad (1-1)$$

where  $n^*$  is the number of nuclei formed in a sample of volume  $V$  during cooling time  $\tau$ .

Turnbull expressed the nucleation rate  $I_0$  using an expression for the steady-state nucleation rate in terms of the *classical theory of homogeneous nucleation* [6]. On supercooling a single-component liquid below the melting point  $T_t$  to temperature  $T$ , the driving force for nucleation of the crystallizing phase ( $-\Delta G_v$ ) can be expressed as the difference between the free energies of the liquid ( $G^L$ ) and solid ( $G^S$ ) phases per unit volume,

$$G^L - G^S = -\Delta G_v = (H^L - H^S) - T(S^L - S^S) \quad (1-2)$$

where  $H^L$  and  $S^L$  are the enthalpy and entropy of the liquid phase and  $H^S$  and  $S^S$  are the enthalpy and entropy of the solid phase per unit volume. As the enthalpy of fusion  $\Delta H_t \approx H^L - H^S$  and the entropy of fusion  $\Delta S_t \approx S^L - S^S \approx \Delta H_t/T_t$ , Eq. (1-2) can be expressed by the equation

$$\Delta G_v = -\Delta H_t \frac{\Delta T}{T_t} \quad (1-3)$$

where  $\Delta G_v$  is the change in the free energy per unit volume connected with a phase transformation of the supercooled liquid to a solid crystalline phase and  $\Delta T = T_t - T$  is the supercooling. The enthalpy of fusion  $\Delta H_t$  can be expressed as the heat of fusion  $L_t = -\Delta H_t$ .

As the crystalline phase formed is thermodynamically more stable than the initial phase ( $G^S < G^L$  for  $\Delta T > 0$ ) (see Fig. 1-1), the actual transformation of a particular volume of the initial phase is connected with a decrease in the free energy ( $\Delta G_v < 0$ ) and a positive driving force for the phase transformation ( $-\Delta G_v > 0$ ). On the other hand, the free energy increases on formation of a new phase region, as new interfaces are formed. Assuming that the new phase regions formed are homogeneous, that they have equilibrium composition with sharply defined phase boundaries with no formation of stresses and that the value of the interfacial energy does not depend on the curvature of the boundary, the change in the free energy accompanying the formation of such a region ( $\Delta G_r, G_i$ ) can be expressed as the sum of two expressions, one proportional to the volume ( $\sim r^3$ ) and the second to the surface area ( $\sim r^2$ ). If the new regions are spherical in shape with radius  $r$ , then

$$\Delta G_r = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad (1-4)$$

or

$$\Delta G_i = iv \Delta G_v + (36\pi)^{1/3} (iv)^{2/3} \gamma, \quad (1-5)$$

where  $\gamma$  is the interfacial energy per surface area unit,  $i$  is the number of structural units (molecules, atoms) in the region formed, and  $v$  is the volume of a single structural unit in the new phase.

It is assumed in the theory of homogeneous nucleation that the formation of the

smallest regions of the new phase is a result of thermal agitation that can lead to temporary local changes in the density on a molecular scale.

If the initial phase is thermodynamically stable, then the fluctuating heterogeneities are temporary and rapidly disappear, because they do not attain a certain critical size. This quasi-equilibrium state can be characterized by the equilibrium constant

$$K = \frac{n_r}{n} \quad (1-6)$$

where  $n_r$  is the equilibrium number of regions formed with a radius of  $r$  and  $n$  is the number of molecules per unit volume in the initial phase.

Assuming ideal behaviour of the system and that  $n_r \ll n$ , constant  $K$  is related to  $\Delta G_r$  in Eq. (1-4) by the standard thermodynamic relationship

$$K = \frac{n_r}{n} = \exp - \frac{\Delta G_r}{kT} \quad (1-7)$$

Equilibrium number  $n_r$  can then be expressed as

$$n_r = n \exp - \frac{\Delta G_r}{kT} \quad (1-8)$$

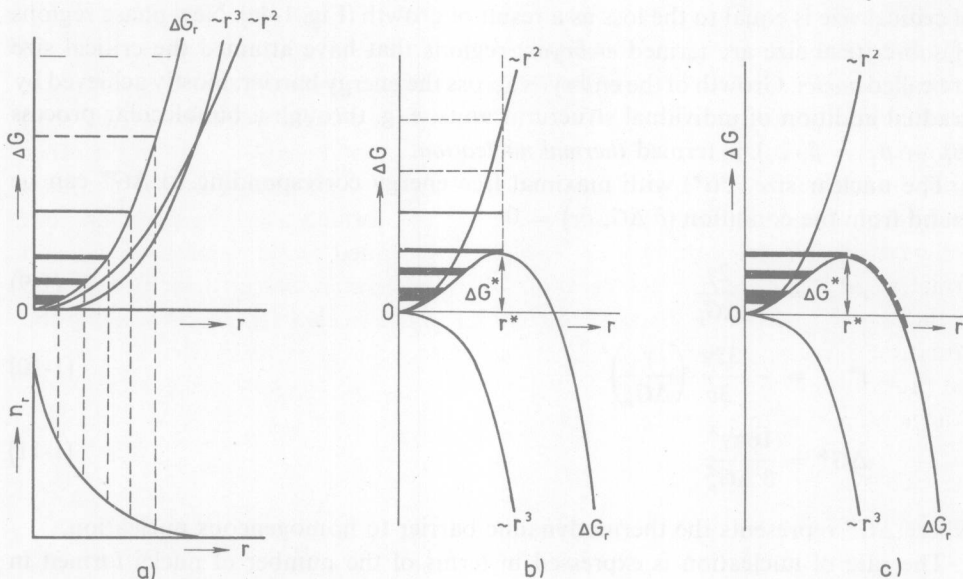


Fig. 1-4 Dependence of  $\Delta G_r$  as a function of  $r$ , depicted as the sum of the surface ( $\sim r^2$ ) and volume ( $\sim r^3$ ) free energies

a) above the melting point  $T > T_i$ ; b) below the melting point  $T < T_i$  with retention of the equilibrium distribution of  $n_r$ ; c) below the melting point  $T < T_i$  at steady state. The lower graph (1-4a) depicts the dependence of the relative number for corresponding  $\Delta G_r$  and  $r$  according to Eq. (1-8)



Term  $\Delta G_r$ , as a function of  $r$  (or  $i$ ) for temperatures in the region around  $T_1$  is depicted schematically in Fig. 1-4. Above temperature  $T_v$ , the contribution of the second term ( $\sim r^2$ ) in Eq. (1-4) is, as usual, positive; the contribution of the first term ( $\sim r^3$ ) is also positive, because the driving force is negative ( $-\Delta G_v < 0$ ). The overall change in the free energy  $\Delta G_r$ , then increases indefinitely with increasing  $r$ , so that this process is not spontaneous. The equilibrium number of regions of the new phase rapidly decreases with increasing size according to Eq. (1-8) (Fig. 1-4a), and thus the formation of the new phase is suppressed. This thickness of the horizontal lines in Fig. 1-4a schematically designates the relative number  $n_r$ , for corresponding  $\Delta G_r$ , and  $r$  according to Eq. (1-8).

When the temperature decreases below  $T_v$ , the driving force becomes positive ( $-\Delta G_v > 0$ ) (Fig. 1-4b). The new phase regions formed with small  $r$  are again unstable until they attain a certain critical size  $r^*$ , at which further growth becomes spontaneous, as it is connected with an overall decrease in the free energy of the system (see Fig. 1-4b, where retention of an equilibrium number of formed regions of the new phase is simultaneously depicted, assuming a hypothetical vertical free-energy barrier at maximal  $\Delta G^*$ ). Equilibrium number  $n_r$  is not attained in practice, as the growth of the new phase regions with critical or larger size is connected with an overall decrease in the free energy of the system, so that a transformation occurs through establishment of *steady state*, where the number of newly formed regions of critical size is equal to the loss as a result of growth (Fig. 1-4c). New phase regions of sub-critical size are termed *embryos*; regions that have attained the critical size are called *nuclei*. Growth of the embryos across the energy barrier, mostly achieved by gradual addition of individual structural units, e. g. through a bimolecular process ( $\beta_{i^*} + \beta_1 = \beta_{i^*+1}$ ), is termed *thermal nucleation*.

The nuclear size  $r^*(i^*)$  with maximal free energy corresponding to  $\Delta G^*$  can be found from the condition ( $\partial \Delta G_r / \partial r$ ) = 0

$$r^* = - \frac{2\gamma}{\Delta G_v} \quad (1-9)$$

$$i^* = - \frac{32\pi}{3v} \left( \frac{\gamma}{\Delta G_v} \right)^3 \quad (1-10)$$

$$\Delta G^* = \frac{16\pi\gamma^3}{3 \Delta G_v^2} \quad (1-11)$$

where  $\Delta G^*$  represents the thermodynamic barrier to homogeneous nucleation.

The rate of nucleation is expressed in terms of the number of nuclei formed in unit volume per unit time. If it is assumed that the number of nuclei is equal to the equilibrium number, then, similar to Eq. (1-8), it holds that

$$n^* = n \exp \left( - \frac{\Delta G^*}{kT} \right). \quad (1-12)$$