

## Kinetics of sub-liquidus phase separation in silicate and borate glasses. A review

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**Abstract.** — Many silicate and borate glass systems exhibit sub-liquidus immiscibility. The fine-scale microstructure of phase separated systems has been studied mainly by electron microscopy and small angle X-ray scattering. The classical theories of homogeneous nucleation, spinodal decomposition and coarsening, and more recent statistical theories of segregation are outlined. These theories are compared with experimental data for the kinetics of amorphous phase separation. In the early stages of separation, for compositions and temperatures in the region between the binodal and spinodal and in particular close to the binodal, the results are consistent with a homogeneous nucleation process. The classical theory of spinodal decomposition only agrees qualitatively with experimental data for the central region of the miscibility gap. The kinetics of coarsening are in general agreement with theory. Recent predictions from computer simulation studies on model alloys appear to be valid for glass systems. Experimental studies of the influence of amorphous phase separation on crystallization of glasses are also reviewed. In certain circumstances there is clear evidence that amorphous phase separation enhances the rates of crystal nucleation and growth.

**Key words :** phase separation, silicates and borates, glasses, SAXS, TEM.

*Cinétique de la séparation de phases subliquides dans les silicates et borates vitreux.*

**Résumé.** — Beaucoup de silicates et borates vitreux ont une lacune métastable de miscibilité. La microstructure très fine des verres avec séparation de phases a été étudiée principalement par microscopie électronique et diffusion de rayons X aux petits angles. Les théories classiques de nucléation homogène, décomposition spinodale, "coarsening" et les plus récentes théories statistiques de la ségrégation sont exposées. Ces théories sont comparées avec les données expérimentales liées à la cinétique de la séparation de phases. Les résultats associés aux premiers stades, près de la binodale, sont en accord avec un modèle de nucléation homogène. La théorie classique de la décomposition spinodale montre un accord seulement qualitatif avec les résultats expérimentaux dans la région centrale de la lacune de miscibilité. La cinétique de "coarsening" après les stades initiaux, sont en accord général avec la théorie. Des prédictions récentes des études par simulation à l'ordinateur sur des alliages modèles paraissent être valides aussi pour les systèmes vitreux. Les études expérimentales de l'influence de la séparation de phases amorphes sur la cristallisation des verres sont aussi présentées. Ces études montrent des évidences claires permettant de conclure que la séparation de phases favorise la nucléation cristalline.

**Mots-clés :** séparation de phases, silicates et borates, verres, diffusion aux petits angles, microscopie électronique.

### I. - INTRODUCTION

Phase separation occurs in many organic and inorganic materials including polymers, metallic alloys and ceramics. It is observed in certain systems containing two or more components, for a limited composition and temperature domain of the equilibrium diagram which is called a miscibility gap. Many silicate systems which show immiscibility in the liquid state (*i.e.* stable liquid-liquid immiscibility) form opalescent glass on cooling (*e.g.* CaO-SiO<sub>2</sub>, MgO-SiO<sub>2</sub>). This opalescence is due to light scattering caused by a heterogeneous microstructure composed of phases with different compositions. The microstructure (frequently droplets of one phase in another) is often sufficiently "coarse" to be revealed by optical microscopy.

Glasses which are obtained by cooling *homogeneous* (single phase) liquids are generally transparent but many of them have a heterogeneous structure on a submicroscopic scale. This "microphase separation" is found in numerous binary, ternary (and more complex) silicate and borate systems (*e.g.* Na<sub>2</sub>O-SiO<sub>2</sub>, Li<sub>2</sub>O-SiO<sub>2</sub>, BaO-SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>, Na<sub>2</sub>O-CaO-SiO<sub>2</sub>, Li<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>), and is due to the existence of a metastable gap below the liquidus.

Heat-treatment of quenched glasses inside metastable miscibility gaps, leads to a very fine microstructure. The morphological aspects and the kinetics of phase separation of these systems are studied mainly by electron microscopy and small angle X-ray scattering.

The heterogeneous microstructure of phase separated glasses can have a very significant influence on all their properties. Experimental studies of density, elas-

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tic modulus, viscosity, electrical conductivity, etc., as a function of composition in these glasses, often show unexpected behaviour due to their heterogeneous microstructure. Moreover, the influence of amorphous phase separation on crystal nucleation and growth behaviour has received particular attention by many authors.

The origin of immiscibility in glasses in terms of atomic coordination and bond strength, its thermodynamical aspects and its influence on physical properties have been discussed in several review papers (James, 1975; Uhlmann and Kolbeck, 1976; Tomozawa, 1979).

Many theoretical and experimental studies of metastable phase separation have been concerned with the kinetics during isothermal heat treatment of simple binary glasses. Experimentally, the specimens are first rapidly cooled (quenched) from the one phase region into the miscibility gap (see figure 1). The structural variations of the phase separated glasses are studied from the early stages to advanced stages, when the phases have their equilibrium composition. The heat treatment temperatures of the studied glasses are higher or lower than the glass transition temperatures. No distinction between "glass" and "supercooled liquid" states is made in phase separation studies.

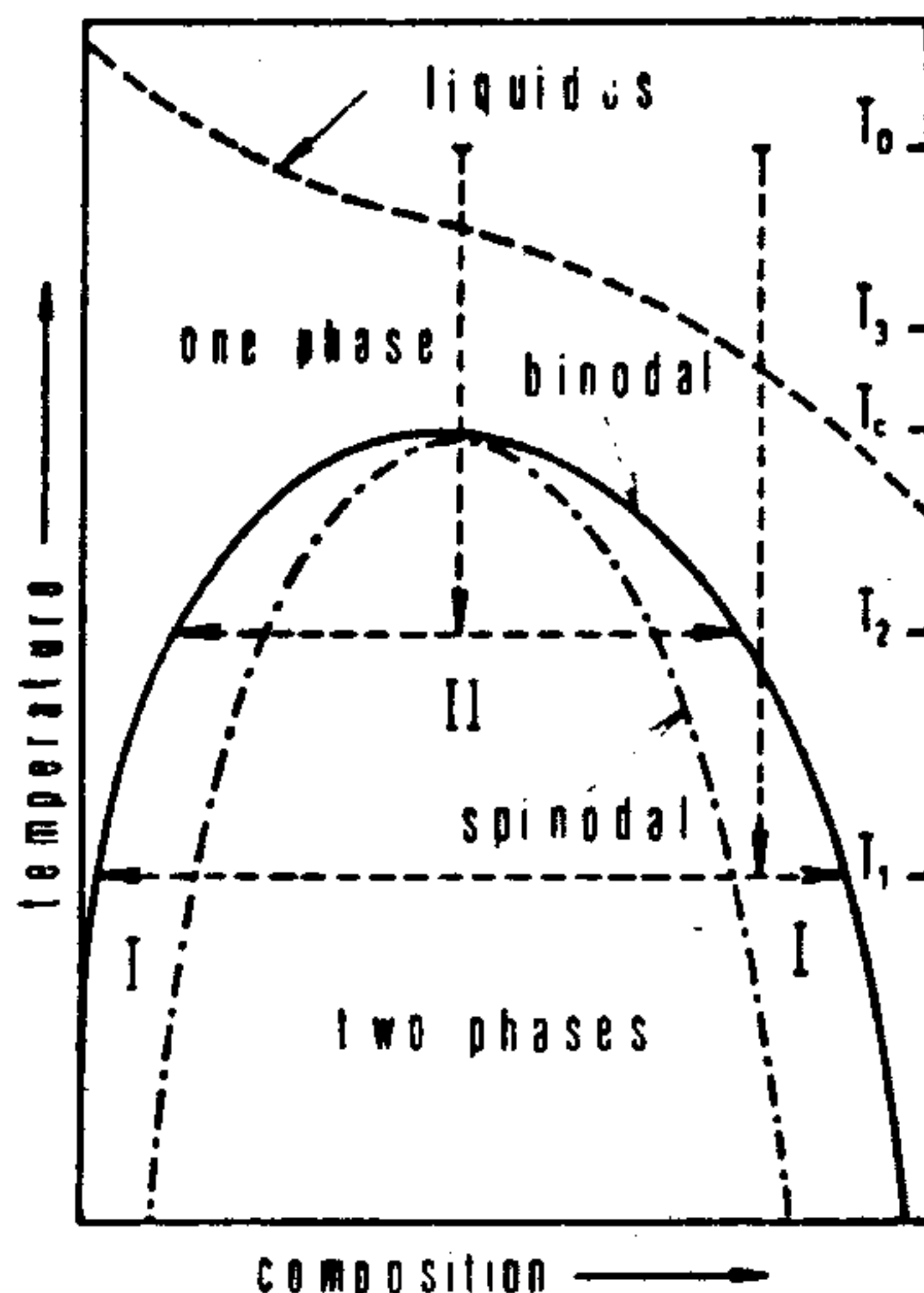


FIG. 1. — Schematic sub-liquidus miscibility gap. The arrows indicate quenches and later isothermal heat treatments within the "nucleation and growth" region (I) and "spinodal" region (II).

The classical theories of nucleation, growth and coarsening involve structural parameters defined in "real space" (time variation of the diameter and number of segregated zones). These parameters and their time evolution can be determined directly by electron microscopy. Other theoretical approaches express their predictions in terms of the Fourier transform of the composition function as, for example, the theory of Cahn (1961) for spinodal decomposition. In this case the theory is more easily checked by small angle X-ray (or neutron) scattering.

Here we present the relevant theories and the main experimental studies of the kinetics of amorphous phase separation and its influence on the crystallization of glasses. Classically two mechanisms for the early stages of phase separation were proposed: nucleation and growth of amorphous droplets (near the binodal curve) and spinodal decomposition (in the central region of the miscibility gap). In the later stages it has been found that structural coarsening predominates.

## II. - SUMMARY OF RELEVANT THEORIES

### II.1. - Nucleation

According to the classical theory of homogeneous nucleation (see, for example, Zettlemoyer (1969)) the rate of nucleation,  $J$ , is given by:

$$J = A \exp[-(\Delta G_D + W^*) / k_B T] \quad (1)$$

where  $W^*$  is the free energy of formation of a critical nucleus,  $\Delta G_D$  is the activation energy for atomic transport across the interface,  $k_B$  is the Boltzmann constant,  $T$  is the temperature and  $A$  is essentially a constant.  $W^*$  is given by  $16 \sigma^3 / 3 \Delta G_V^2$  for a spherical nucleus, where  $\sigma$  is the interfacial free energy between phases and  $\Delta G_V$  is the bulk free energy change per unit volume of phase transformed.

In the classical theory it is assumed that the boundary between nucleus and matrix is sharp. If we consider the nucleation rate of droplets below the immiscibility temperature  $T_m$ , classical theory predicts a range of undetectable nucleation just below  $T_m$  followed by a rapid rise in  $J$  at some critical undercooling. It reaches a maximum as the temperature is further decreased and finally decreases rapidly at high undercoolings due to a decrease in diffusion rates.

It should be emphasized that, *in principle*, nucleation (classical or otherwise) could occur even within the spinodal region of the miscibility gap (see figure 1), although it is generally considered that nucleation is more likely to take place outside the spinodal and close to the binodal.

Cahn and Hilliard (1958, 1959) have developed an alternative "diffuse nucleus" theory which avoids the classical assumptions that the nucleus is uniform and has the equilibrium composition of the separating phase. They considered the free energy of a system having a spatial variation in composition and expressed the local free energy per unit volume as a sum of two parts: the free energy per unit volume of a solution of uniform composition (Figure 2) and a term representing the increase in free energy due to the composition gradient (analogous to the interface term in classical theory). Using this approach the properties of the critical nucleus in the metastable region were derived. At low supersaturations, the properties of the nucleus were close to those assumed in the classical theory. However, as the supersaturation increased, the free energy needed to form a critical nucleus,  $W^*$ , became progressively less than the corresponding classical value and approached zero at the spinodal. Furthermore, the nucleus interface became more diffuse and the composition at the centre of the nucleus approached that of the matrix.

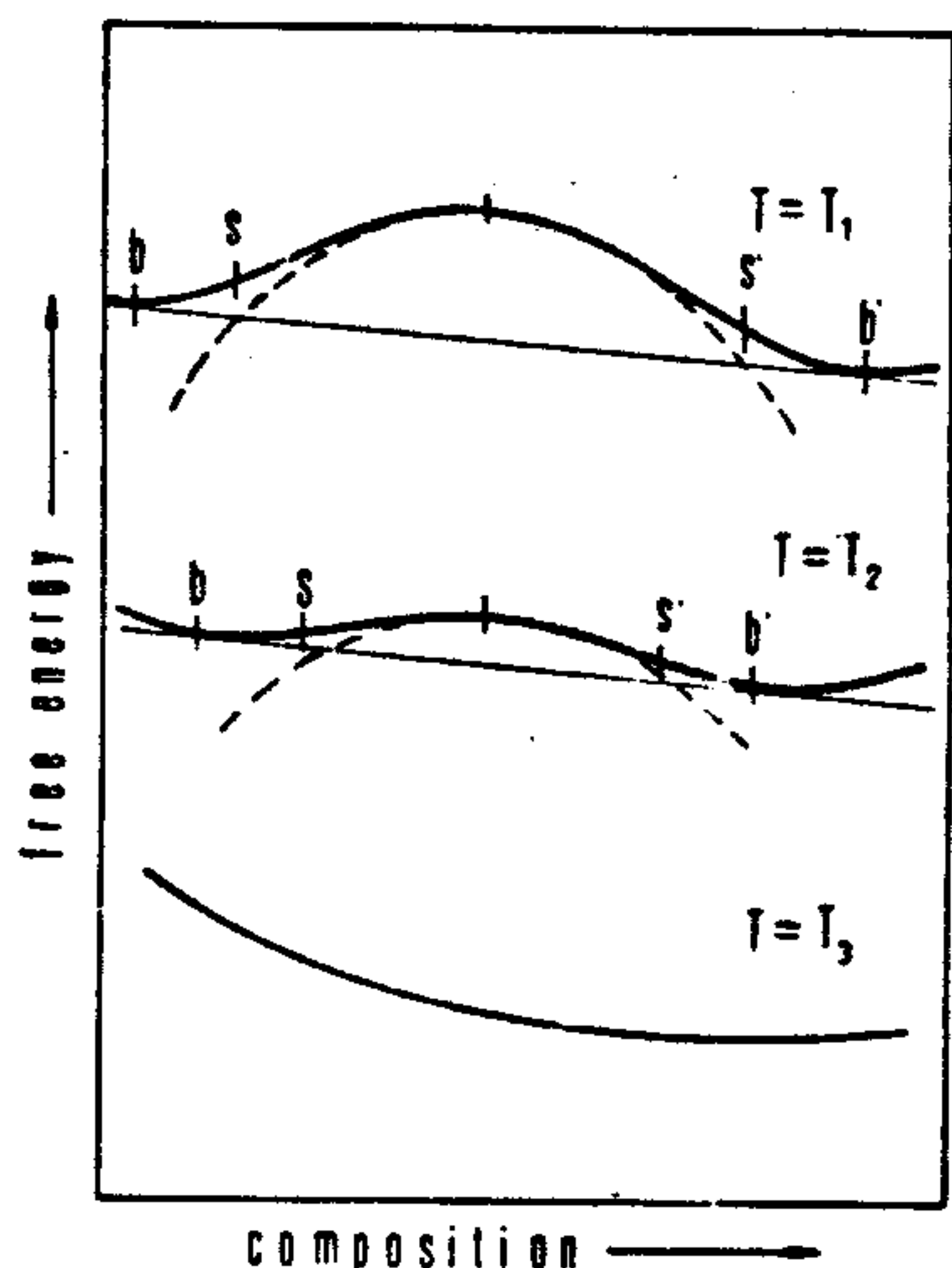


FIG. 2. — Schematic free-energy per unit volume of a homogeneous binary solution as a function of the composition.  $b$  and  $b'$  define the binodal (Fig. 1). The spinodal line is determined from the compositions  $s$  and  $s'$  associated with the inflexion points of  $f(c)$ .  $T_1 < T_2 < T_c$  and  $T_3 > T_c$  (Fig. 1).

## II.2. - Particle growth and coarsening

Consider a distribution of isolated droplets produced by homogeneous nucleation in the region of the

miscibility gap between the spinodal and binodal curves. In the very early stages, the matrix is highly supersaturated and the droplets are expected to grow by long range diffusion. Thus at constant temperature for a given time  $t$ :

$$\bar{r}^2 \propto t$$

where  $r$  is the average droplet radius. At a later stage when the matrix approaches its equilibrium composition a coarsening process begins to dominate in which the smaller droplets tend to dissolve and the larger ones grow at their expense. This process is driven by the overall decrease in interfacial free energy. For long range diffusion controlled growth (Wagner, 1961; Lifshitz and Slezov, 1959) the mean radius increases with time according to:

$$\bar{r}^3 - \bar{r}_0^3 = (8/9) (\sigma/k_B T) D C_\infty V^2 t \quad [2]$$

where  $\bar{r}_0$  is the mean radius at the start of coarsening,  $\sigma$  the interfacial free energy,  $D$  the effective diffusion coefficient,  $C_\infty$  the equilibrium concentration of "solute" in the matrix and  $V$  the molecular volume of the droplet phase. The theory also predicts the number of droplets per unit volume  $N_V$  is proportional to  $t^{-1}$  and that the size distribution of particles is a certain universal function of  $r/\bar{r}$ . If the coarsening is not controlled by diffusion but by a surface reaction rate, process theory predicts  $\bar{r}^2 \propto t$  and  $N_V \propto t^{-3/2}$ .

The coarsening of a highly interconnected two phase system with constant volume fractions has been discussed by Haller (1965). Where mass transport across the interfaces is rapid and volume diffusion is the rate controlling process, the total interfacial area  $S_T$  is proportional to  $t^{-1/3}$ . The mechanism is similar to the coarsening of isolated droplets except that here the process involves mass transport from convex to concave interfaces. In the case of interface controlled coarsening, Haller found that  $S_T$  is proportional to  $t^{-1/2}$ .

## II.3. - Spinodal decomposition

The classical theory of spinodal decomposition describes the kinetics of phase separation of binary solutions in the central region of the miscibility gap. The theory starts from the definition of a free-energy function for the system in the two phase region. This function is assumed to be valid for the non-equilibrium solution obtained by quenching. Cahn (1961) derived a linear equation for spinodal decomposition which is subject to the following:

a) The free energy  $F$  of the non-equilibrium phase separating solution can be expressed by

$$F = \int \{ f(c, \bar{r}) + K [\nabla c(\bar{r})]^2 \} d\bar{r} \quad [3]$$

where  $f(c, \bar{r})$  is the free energy density of the homogeneous system (Figure 2) as a function of the composition  $c$  and of the position vector  $\bar{r}$ , and  $K [\nabla c(\bar{r})]^2$  is

the contribution to the free energy from the gradient of composition.

b) The "homogeneous" free energy density can be approximated by a parabolic function of composition (dashed lines in figure 2) which is a good approximation only for the *early stages* of phase segregation.

c) There is *no* contribution from statistical fluctuations in composition.

d) The atomic mobility is constant with time during segregation (absence of structural relaxation phenomena).

The linear diffusion equation of Cahn was solved for isotropic systems by the Fourier method. The Fourier transform  $\eta(k,t)$ , as a function of the wavenumber  $k$  of the "composition wave" at a time  $t$ , of the composition fluctuation  $\delta_c(\vec{r},t) = c(\vec{r},t) - c_0$ , where  $c_0$  is the average composition, should satisfy the exponential relation

$$\eta(k,t) = \eta(k,0) e^{R(k)t} \quad [4]$$

where

$$R(k) = -Dk^2 \left( 1 - \frac{k^2}{k_c^2} \right) \quad [5]$$

is the amplification factor. In equation 5,  $k_c$  is a critical wave-number for which  $R(k) = 0$ . Equations 4 and 5 show that the amplitude of the composition wave has an exponential variation with time: for  $k < k_c$  the amplitude increases and for  $k > k_c$  the amplitude decays to zero.

A non linear equation for more advanced stages of the spinodal decomposition which includes a fourth order polynomial for the free energy density, was numerically solved by de Fontaine (1967). Cook (1970) added the contribution of statistical fluctuations in composition to the equation of Cahn and solved it for the linear approximation. Assuming a simple exponential time variation of the atomic mobility, Craievich (1975a) took into account the possibility of structural relaxations.

#### II.4. - Statistical theories

A new approach to the study of phase separation of non-equilibrium mixtures was put forward by Langer (1971). It starts from a statistical distribution function  $\rho([c(\vec{r})],t)$  over all the possible configurations  $[c(\vec{r})]$  of the system. The statistical description of Langer's theory is given as a function of the so called structure function,  $S(\vec{k},t)$ , which is the Fourier transform of the correlation function  $G(\vec{r},t)$  defined by

$$G(\vec{r},t) = \langle \delta_c(\vec{u},t) \delta_c(\vec{u} + \vec{r},t) \rangle \quad [6]$$

where the symbol  $\langle \rangle$  indicates the spatial mean value. The relationship between the structure function  $S(\vec{k},t)$  and the Fourier transform  $\eta(k,t)$  of the composi-

tion fluctuation  $\delta_c(\vec{r},t)$  is given by:

$$S(\vec{k},t) = |\eta(\vec{k},t)|^2 \quad [7]$$

Due to the statistical nature of the Langer theory, the contribution of thermal fluctuations is implicitly included. Its range of validity allows the description of more advanced stages of decomposition than the linear theory of Cahn. Qualitatively, Langer's theory predicts a non exponential growth of  $S(\vec{k},t)$  and a continuous displacement of its maximum to lower  $k$  for increasing time.

Recent numerical calculations by computer simulation were carried out using a dynamic three-dimensional Ising model (Sur *et al.*, 1977). These calculations for a model alloy start from a perfect disordered assembly of atoms, the configuration changes occurring by atomic permutations. The time evolution, after an initial transient stage, of the isotropic structure function,  $S(k,t)$ , has the following features (Marro *et al.*, 1979):

a) A dynamical scaling property expressed by:

$$F(x) = [k_1(t)]^3 \tilde{S}(k,t) \quad [8]$$

where  $\tilde{S}$  is a normalised structure function:

$$\tilde{S}(k,t) = \frac{S(k,t)}{\int S(k,t) k^2 dk}$$

$k_1$  is the normalised first moment of  $S(k,t)$ ,

$$k_1(t) = \frac{\int k S(k,t) dk}{\int S(k,t) dk}$$

and  $F(x)$  a function of  $x = k/k_1(t)$ , independent of time.

b) The normalised first moment of  $S(k,t)$  is given, as a function of time, by:

$$k_1(t) \propto t^{-a} \quad [9]$$

where the exponent  $a$  is temperature and composition dependent.

The scaling property can be applied in the spinodal region and also in the nucleation and growth region of the miscibility gap. In these statistical theories, there is no definite boundary between the spinodal and nucleation and growth regions (Gunton, 1981) and they do not show a "linear" regime (*i.e.* the linear classical theories would be only approximations even in the early stages).

#### II.5. - The effects of amorphous phase separation on crystal nucleation and growth

It has long been known from phase diagrams that liquid-liquid phase separation can have a marked influence on the course of crystallization in a system. Thus, unmixing may produce two compositions one of which has a greater tendency to crystallize than the initial non-separated glass. However, it is also known that liquid phase separation is not essential to produce

internal crystal nucleation in glasses; e.g.  $\text{BaO} \cdot 2\text{SiO}_2$ ,  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ ,  $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$  and other glass compositions do not show phase separation and still crystallize internally. Also, several glass compositions in the  $\text{Na}_2\text{O} \cdot \text{SiO}_2$ , alkali oxide- $\text{B}_2\text{O}_3$  and other systems show extensive unmixing and do not crystallize internally. At this stage it should be mentioned that the great majority of glasses crystallize from the external surface when heated, yielding coarse-grained polycrystalline materials of poor mechanical strength. For the production of the well known glass-ceramic materials, which have many unusual physical properties, internal nucleation of crystals is essential and this is generally achieved by means of nucleating agents which may be metallic or non metallic additions to the glass composition. Among the most important nucleating agents used in commercial glass-ceramics are the oxides  $\text{TiO}_2$ ,  $\text{P}_2\text{O}_5$  and  $\text{ZrO}_2$ , which are typically used in quantities of several mol %. These agents appear to operate in various ways in catalysing internal nucleation but their roles are often complex and not fully understood. In certain cases (e.g. metallic nucleating agents) precipitation of the nucleating agent in the glass leads to heterogeneous nucleation of the major crystalline phases in the glass-ceramic. In other cases their catalysing action can best be understood in terms of the classical nucleation theory (Zettlemoyer, 1969). According to this theory an increase in the nucleation rate may be due to the following:

- i) an increase in the diffusivity of the appropriate species,
  - ii) a decrease in the crystal-glass interfacial energy and
  - iii) an increase in the thermodynamic driving force.
- Therefore the nucleating agent must produce one or more of these effects.

Theoretically, amorphous phase separation (APS) could influence crystal nucleation in several ways but most of the possibilities fall into two main categories associated either with i) the different compositions of the separating liquid phases or with ii) the interfaces between the glassy phases. These points have been fully discussed by several authors, including Tashiro (1968) and Hammel (1969).

Extensive discussions were presented at a meeting on "The Vitreous State" in 1970, University of Bristol, by Scholes (1970), Uhlmann (1970) and Zarzycki (1970). Recently, James (1982) summarized the present state-of-art on the subject. The compositional changes resulting from liquid phase separation may affect both the thermodynamic and kinetic barriers for nucleation. For instance, phase separation could also result in one of the amorphous phases being closer to the composition of the crystallizing phase, decreasing both the thermodynamic and kinetic barriers to crystal nucleation. Also, the crystal-liquid interfacial energy could be lower for one of the liquid phases than for the parent phase, which could have an important ef-

fect on the nucleation rate of crystals.

The mechanisms for the enhancement of crystal nucleation associated with the interface between the amorphous phases could be of various types. The first possible mechanism is "direct" heterogeneous crystal nucleation at the interface. The second possibility is an enrichment of some component, perhaps a "nucleating agent", at the boundaries between the amorphous phases causing a locally higher thermodynamic driving force or atomic mobility or even a lower interfacial energy. It has been further suggested that a sparingly soluble component might crystallize out at the interface and promote heterogeneous nucleation in the bulk of the glass (Scholes, 1970). A third possible mechanism, suggested by Tomozawa (1972), is preferential nucleation in the diffusion zones around liquid phase droplets.

### III. - EXPERIMENTAL METHODS

#### III.1. - Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is the most direct method for studying the morphology of phase separation in glasses. It is particularly useful in distinguishing between a microstructure of discrete droplets and one of interconnected phases. Two main techniques are used. In the first, surface carbon replicas are prepared of fractured and etched glass specimens.

Stereological analysis can be applied to electron micrographs of the replicas to derive various parameters including the mean radius  $\bar{r}$  and the number of particles per unit volume  $N_V$  (in the case of a "droplet" microstructure), the total surface area per unit volume  $S_T$  and the volume fraction of a given phase  $V_f$ .

In the second technique, thin specimens about 2,000 Å thick are prepared by chemical or ion beam thinning from the bulk glass, and examined directly. Although often giving a higher resolution of fine droplets than is possible by using replicas (say down to 30 Å or less) this method is more difficult to use in quantitative studies. Two TEM micrographs of a phase separated  $\text{BaO} \cdot \text{SiO}_2$  glass near the edge of the miscibility gap are shown in figure 3 (Zanotto, 1982).

Using these techniques much valuable information has been obtained on the morphology and kinetics of phase separation including nucleation and growth and particle coarsening. This information is complementary to the data provided by small angle X-ray scattering (SAXS), which has been applied extensively to the kinetics of decomposition inside the unstable region of the miscibility gap.

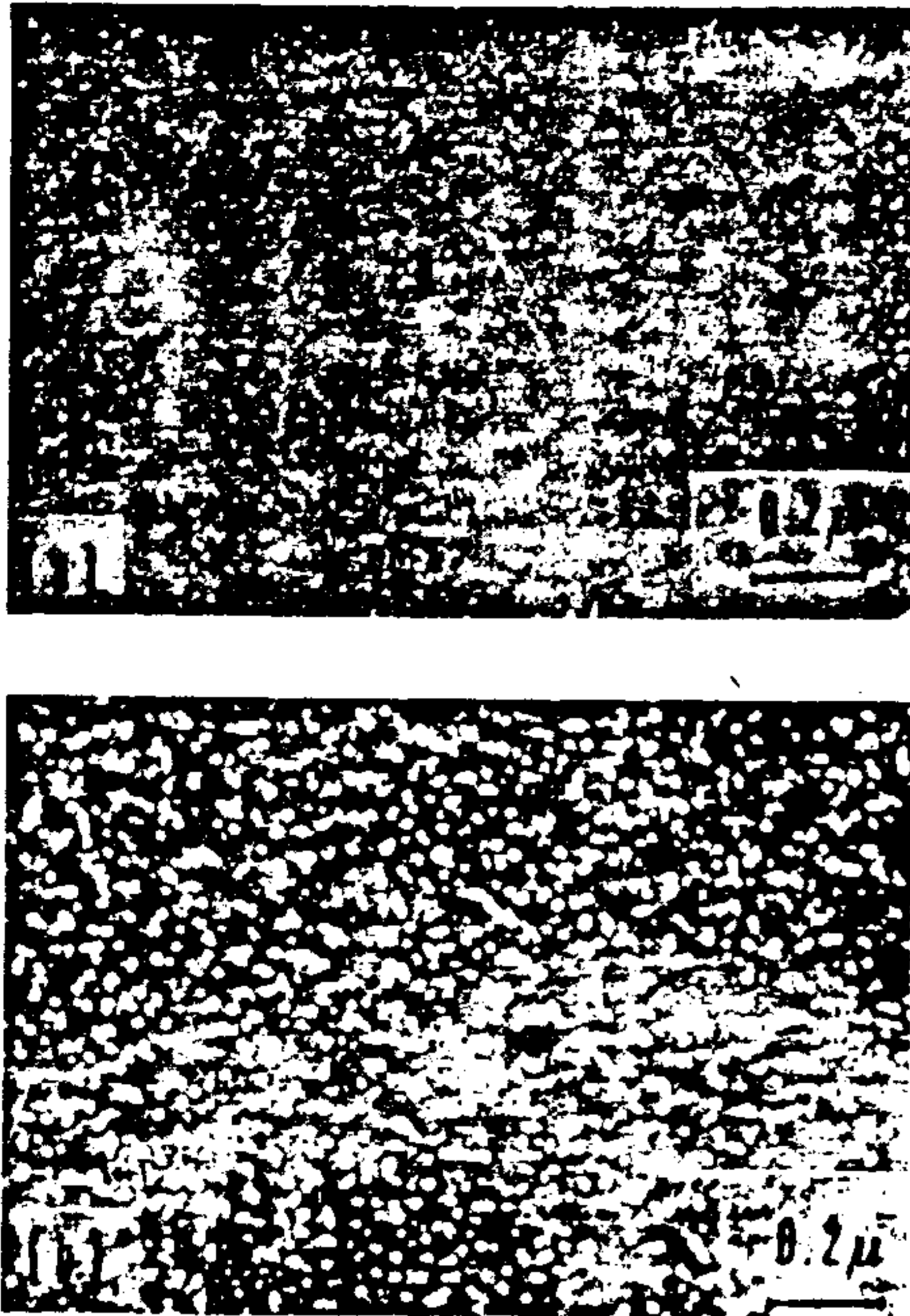


FIG. 3. — Transmission electron micrographs (Zanotto, 1982) of a 28.3 BaO-SiO<sub>2</sub> (mol %) glass heat treated at 760 °C for (a) 3.7 hours and (b) 8.4 hours. Nucleation and growth region of the miscibility gap.

### III.2. - Small angle X-ray scattering (SAXS)

Small angle X-ray scattering is an experimental technique which gives informations on fluctuations in electronic density on a submicroscopic scale (Guinier and Fournet, 1955). It is often used to study heterogeneous materials such as segregating alloys, partially crystalline polymers and phase separated glasses. The SAXS method is not very sensitive to electron density variations on an atomic scale: this structural information is concentrated at higher scattering angles.

The amplitude of the waves scattered by a medium with electronic density  $\rho(\vec{r})$  is given, as a function of the scattering vector  $\vec{q}$ , by :

$$A(\vec{q}) = \int \rho(\vec{r}) e^{i\vec{q}\cdot\vec{r}} d\vec{r}$$

where  $|\vec{q}| = \frac{4\pi \sin \theta}{\lambda}$ ; the Bragg angle  $\theta$  is half the scattering angle,  $\epsilon$ , and  $\lambda$  the wavelength of the X-ray radiation. At small angles  $|q| = 2\pi \frac{\epsilon}{\lambda}$ . Different sym-

bols are used in the literature for the scattering vector ( $\vec{q}$ ,  $\vec{k}$ ,  $\vec{\beta}$  or  $\vec{h}$ ). In some cases the SAXS intensity is given as a function of the scattering angle ( $\epsilon \propto q$ ).

Instead of the amplitude  $A(\vec{q})$ , the function which is obtained from experiments is the scattered intensity  $I(\vec{q})$  :

$$I(\vec{q}) = |A(\vec{q})|^2$$

The scattering intensity  $I(q)$  from isotropic systems is related to the Fourier amplitude  $\eta(k,t)$  of the composition fluctuations of classical theories and to the structure function  $S(k,t)$  of statistical theories by :

$$I(q,t) \propto |\eta(k,t)|^2 \quad [10]$$

and

$$I(q,t) \propto S(k,t) \quad [11]$$

for  $q$  (modulus of the scattering vector) =  $k$  (wavenumber of the composition wave).

It is apparent from equation [10] that the original theory of Cahn (equations 4 and 5) can be tested directly with SAXS data. The criteria are :

- Maxima in the  $I(q,t)$  vs  $q$  curves, for different  $t$ , at constant  $q = q_m$ .
- Exponential growth of  $I(q,t)$  as a function of  $t$  or linearity of  $\log I(q,t)$  vs  $t$  plots, for different  $q$ .
- Cross-over of the SAXS curves  $I(q,t)$ , for different  $t$ , at  $q_c = \sqrt{2} q_m$ .

These criteria are summarised in figure 4.

The existence of a maximum in the SAXS curve is also expected for systems within the nucleation and growth region of the miscibility gap. The maximum may be due to interferences of the scattered waves from different droplets in dense systems or to the complex structure or the segregation "particles" (droplets and surrounding depleted zones) in dilute systems, as described by Guinier (1964). Therefore, accurate SAXS data are necessary to establish the nature of the mechanism of phase separation.

Equation [11] allows an experimental test in real systems of the simulation results (equations 8 and 9). The conditions to be satisfied experimentally are :

- Dynamical scaling, i.e. invariance of the product  $[q_1(t)]^3 I(q/q_1,t) = F(q/q_1)$  [12]

where

$$q_1(t) = \frac{\int q I(q,t) dq}{\int I(q,t) dq}$$

- Linearity of  $\log q_1$  vs  $\log t$  plots.

The above mentioned conditions are schematically represented in figure 5. More detailed, critical, tests should include the comparison of theoretical and experimental results as a function of composition and temperature.

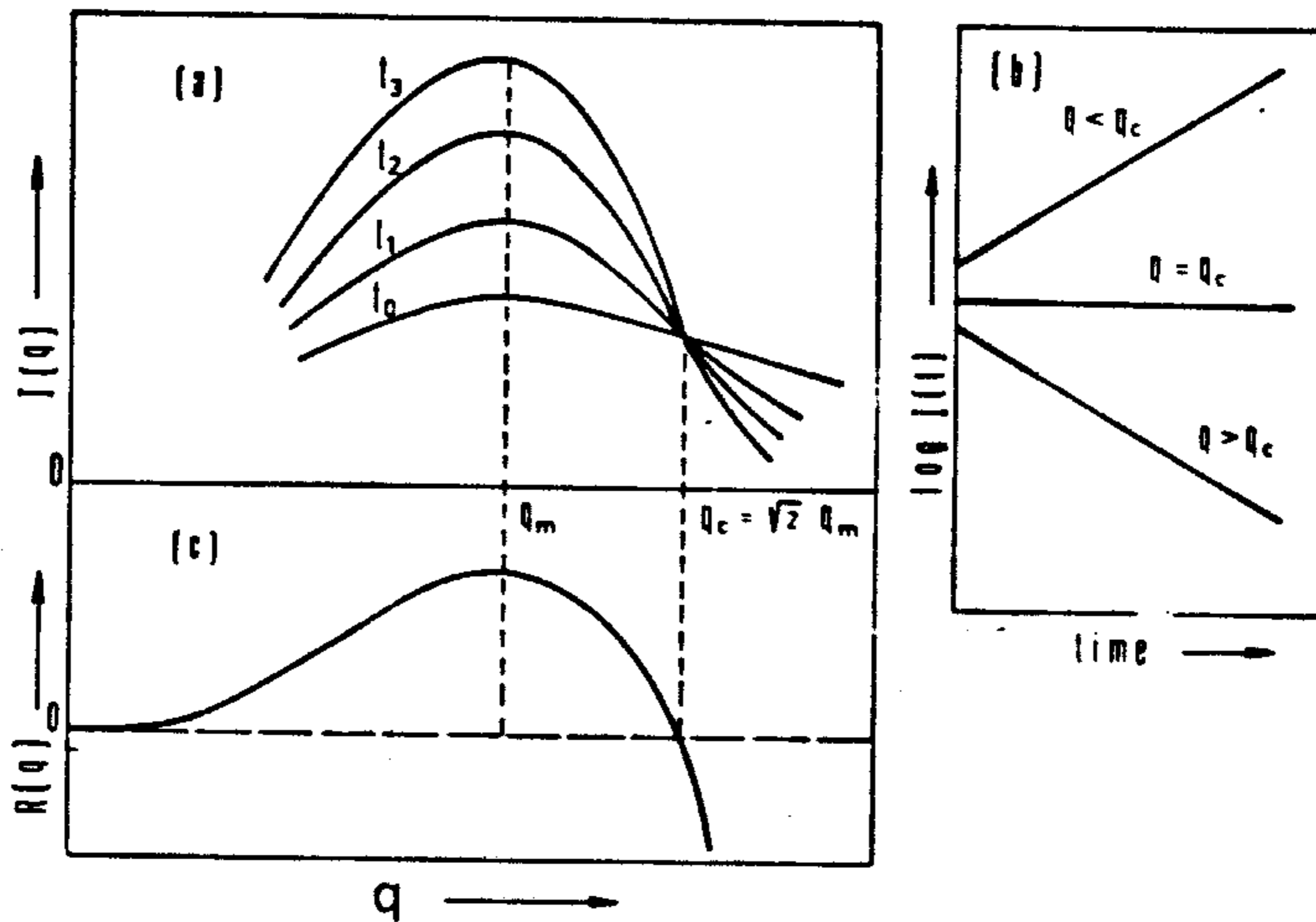


FIG. 4. — Schematic (a) SAXS curves  $I(q)$  for different times  $t$ , (b)  $\log I(t)$  for different wavenumbers  $q$  and (c) amplification factor as predicted by the linear theory of Cahn.

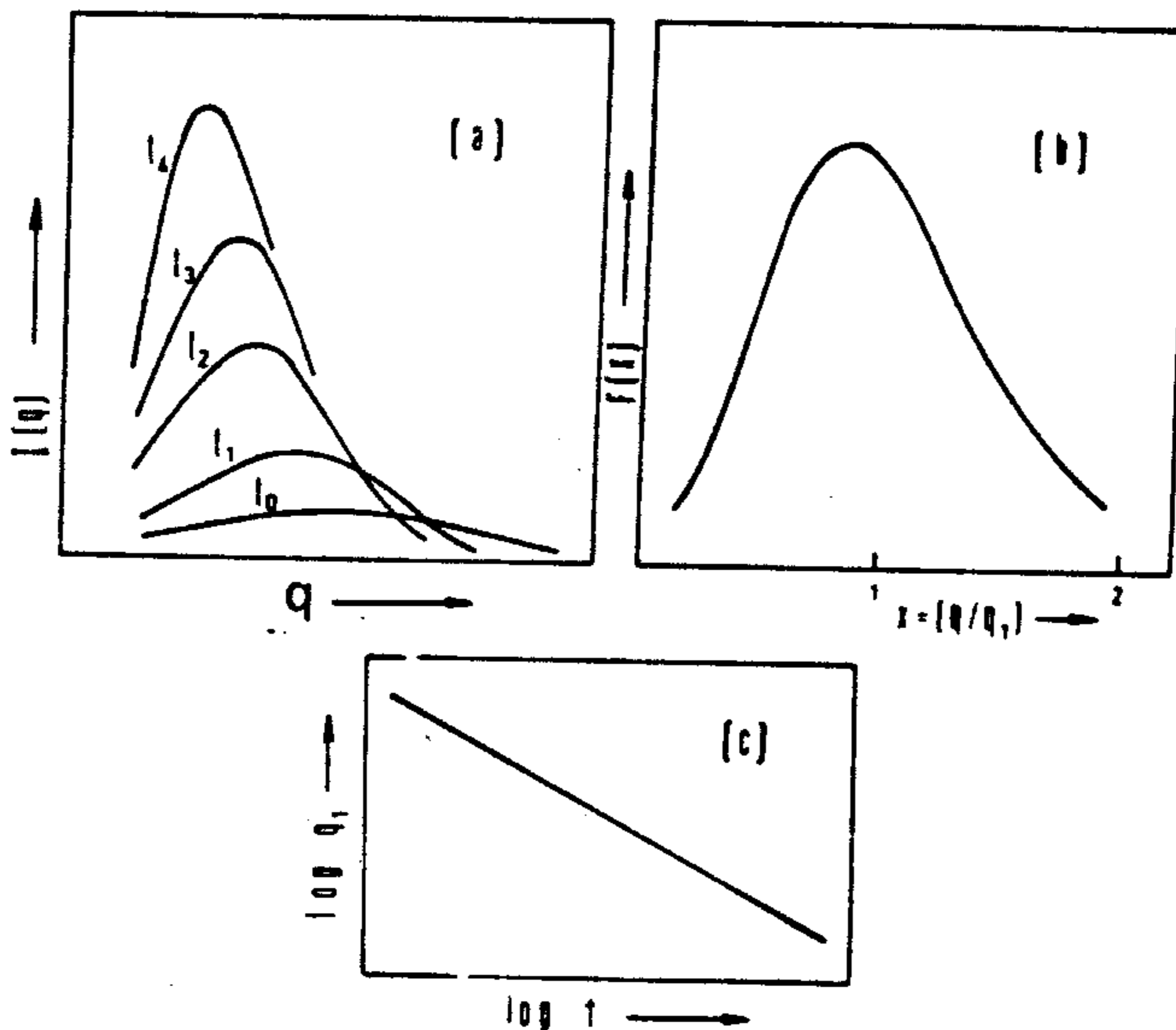


FIG. 5. — Schematic (a) SAXS curves  $I(q)$ , for different  $t$ , having the scaling property  $F(x) = [q_1(t)]^3 I(q/q_1, t)$ , (b) scaled function and (c) variation with time of  $q_1$  according to the computer simulation of Marro et al. (1979).

#### IV. - ELECTRON MICROSCOPY RESULTS

In the following survey of results only a selection of references is given. For more comprehensive lists the reader is referred to the reviews by James (1975), Uhlmann and Kolbeck (1976) and Tomozawa (1979).

##### IV.1. - Earlier work

Some of the earliest kinetics studies were those of Ohlberg *et al.* (1965), Haller (1965) and Moriya *et al.* (1967). Ohlberg *et al.* (1965) found, using surface replicas, that the average radius of the silica rich droplets  $\bar{r}$  in a 13 Na<sub>2</sub>O - 11 CaO - 76 SiO<sub>2</sub>\* was proportional to  $t^{1/2}$  ( $t$  is the duration of the heat treatment at a given temperature), indicating growth controlled by diffusion. This result was confirmed by comparison of light scattering data with the theory of scattering for diffusion controlled phase separation (Goldstein, 1963). Also light scattering measurements on a CaO-Al<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> glass (Hammel and Ohlberg, 1965) indicated that compositional gradients occurred around the growing droplets in agreement with the theory of diffusion controlled growth. It appears that these studies were concerned with the early stage growth of the droplets before the onset of coarsening. Moriya *et al.* (1967) studied the phase separation in a number of binary and ternary alkali silicate glasses using TEM of replicas and thin glass films. The average radius of the droplets  $r$  was proportional to  $t^{1/3}$  indicating a later stage diffusion controlled coarsening. Little could be inferred about the initial mechanism of separation.

##### IV.2. - Studies of later stages (coarsening)

A very thorough quantitative study of late stage coarsening was made by McCurrie and Douglas (1967) for a 1 K<sub>2</sub>O - 26 Li<sub>2</sub>O - 73 SiO<sub>2</sub> glass. Glass samples were isothermally treated at various temperatures for a series of times and examined using surface replicas. The relations  $\bar{r} \propto t^{1/3}$ ,  $N_V \propto t^{-1}$ ,  $S_T \propto t^{-1/3}$  and  $V_f = \text{constant}$  were observed, as predicted for diffusion controlled coarsening ( $\bar{r} \propto t^{1/3}$  since experimentally  $\bar{r} \gg r_0$ ). The growth rates for various particle sizes were in good agreement with theory.

A detailed study of particle coarsening in a 30 Li<sub>2</sub>O - 70 SiO<sub>2</sub> glass and in P<sub>2</sub>O<sub>5</sub>-Li<sub>2</sub>O-SiO<sub>2</sub> glasses was made by James and McMillan (1970). Instead of re-

plicas, thin samples of the glasses were prepared from bulk material by chemical thinning. The true size distributions of particles were determined from the apparent size distributions on the micrographs, using stereo pairs of micrographs to determine the thickness of the thin films directly. The size distributions were in general agreement with theory although some deviations from theory were apparent. However there was very little systematic change in the shapes of the distributions with time, suggesting that the equilibrium shape of the steady state size distribution was achieved at an early stage in the coarsening process. Values of  $\bar{r}$ ,  $N_V$  and  $V_f$  were also determined from the micrographs. The initial separation was essentially complete after a very short period, as observed in other studies, and thereafter the particles coarsened with  $\bar{r}^3 \propto t$  and  $N_V \propto t^{-1}$  as observed for other compositions. One advantage of the thin foils over replicas is the better resolution, which is particularly useful for studying distributions of very fine droplets. The effect of adding P<sub>2</sub>O<sub>5</sub> to the lithia-silica system is to produce a higher degree of connectivity in the phase separation due to the greater volume fraction of the silica rich phase. This effect can be attributed to an increase in the immiscibility temperature (Moriya, 1971; Tomozawa, 1971) and may also be connected with a tendency of P<sub>2</sub>O<sub>5</sub> to associate with Li<sub>2</sub>O in the continuous lithia rich phase in these glasses.

Studies of particle coarsening using SAXS (Zarzycki and Naudin, 1967; Neilson, 1972), have also shown that  $\bar{r}^3 \propto t$ , indicating diffusion controlled coarsening in agreement with the TEM work.

Mahoney *et al.* (1974) have examined the kinetics of coarsening of a highly interconnected microstructure, in a study of the effect of phase separation on the viscosity of a sodium borosilicate glass. To characterize the "scale" of the separation, a "correlation length"  $\Lambda$  was defined which was related to the average distance between boundaries  $\bar{d}$  measured from replica electron micrographs ( $\Lambda = 0.63 \bar{d}$ ). They found that  $\Lambda^3 \propto t$ , where  $t$  is the heat treatment time, demonstrating that the kinetics of diffusion controlled coarsening of a highly interconnected microstructure obeys the same power law as that of a distribution of discrete spheres.

##### IV.3. - Phase separation in the soda-lime-silica system

Important studies using TEM were carried out on the ternary soda-lime-silica system by Ohlberg and Hammel (1965), Hammel (1967) and Burnett and Douglas (1970). Immiscibility temperatures ( $T_m$ ) were determined for compositions between 50 and 85 SiO<sub>2</sub> by observing the temperatures above which opalescent samples "clear".

\* All compositions are given in mole %.



Burnett and Douglas (1970) very carefully examined the errors associated with the TEM replica method. They found that the etching *time* (prior to depositing the surface carbon layer) has a marked effect on quantitative measurements. Thus excessive etching caused serious errors in the measured values of  $N_V$  and  $V_f$ . However by using controlled light etching these errors were small.

Two compositions were studied in detail by Burnett and Douglas: glass 80 (10 Na<sub>2</sub>O - 10 CaO - 80 SiO<sub>2</sub>) and glass 75 (12.5 Na<sub>2</sub>O - 12.5 CaO - 75 SiO<sub>2</sub>). Glass 80 was representative of compositions well within the region of immiscibility and just below  $T_m$  separated very rapidly into droplets which coarsened according to  $\bar{r} \propto t^{1/3}$ . At lower temperatures this glass produced a more connected microstructure. The scale of separation increased with time but the degree of connectivity *decreased*, showing that the structure was tending towards a configuration of minimum interfacial area, *i.e.* a collection of spheres. From the replicas  $V_f$  was constant with time but  $S_T \propto t^{-1/3}$ , indicating volume diffusion controlled coarsening (Haller, 1965).

<sup>2</sup> Glass 75 had a lower  $T_m$  than Glass 80 and separated sufficiently slowly as droplets, to enable the early stages of separation to be studied. It was possible to determine the rate of *nucleation* of droplets by heating glass samples at temperatures within the nucleation range for various times followed by a "development" heat treatment *just below*  $T_m$  to grow the particles which can be then studied by replica TEM. The nucleation rate of droplets *just below*  $T_m$  at the development temperature was negligible. The results showed that the nucleation rate was not constant but increased with time until a steady state constant value was obtained after a certain *induction period*, in agreement with the work of Hammel (1967). According to theory (Zettlemoyer, 1969) this behaviour arises from the finite time required to achieve a steady state distribution of subcritically sized embryos in the glass. Such transient nucleation effects become progressively more important at lower temperatures as the transformation range is approached and have been observed also for crystal nucleation (James, 1982).

At constant temperature the droplets in glass 75 grew initially with  $\bar{r} \propto t^{1/2}$  but at longer times  $\bar{r} \propto t^{1/3}$ . This is expected for diffusion controlled growth followed by coarsening. The onset of coarsening corresponded to an approach to a constant volume fraction  $V_f$ . The number of droplets  $N_V$  increased initially due to nucleation but reached a maximum and then decreased due to coarsening. In contrast, for glass 80 separation occurred much more rapidly and only the coarsening stage was observed.

Very similar results have been obtained by Neilson (1972) who used SAXS to study the early growth and later coarsening of droplets in a Na<sub>2</sub>O-SiO<sub>2</sub> glass.

#### IV.4. - Comparison of experimental nucleation rates with theory

The work of Hammel (1967) is worthy of particular note since it represents one of the few attempts to test classical homogeneous nucleation theory quantitatively (equation 1). Hammel determined nucleation rates of droplets in a 13 Na<sub>2</sub>O - 11 CaO - 76 SiO<sub>2</sub> glass composition, near the edge of the miscibility gap where the classical theory should apply, using replica electron micrographs of samples heated for various times at temperatures below  $T_m$ .  $\Delta G_V$  (see equation 1) was calculated at various undercoolings by fitting a thermodynamic model to the experimental miscibility gap data. By measuring the variation of solubility temperature with particle radius, a value of 4.6 mJ m<sup>-2</sup> was found for the interfacial energy  $\sigma$ , and  $\Delta G_D$  was obtained from measured particle growth data. When these values were substituted in equation [1], the calculated nucleation rates were within an order of magnitude of the experimental results. This is good agreement but does not constitute a critical test of the classical theory, as was pointed out by Hammel. Thus there are uncertainties in the calculation of  $\Delta G_V$  using thermodynamic models and only a small error in the value of  $\Delta G_V$  would alter the calculated nucleation rates very considerably, since  $J$  is very sensitive to the value of  $\Delta G_V$  (and also  $\sigma$ ).

For more critical tests of the classical theory of homogeneous nucleation, it is necessary to consider systems other than glasses. A thorough experimental test was carried out by Heady and Cahn (1973) in the C<sub>7</sub>H<sub>14</sub>-C<sub>7</sub>F<sub>14</sub> liquid-liquid miscibility gap system. A large discrepancy was found between classical theory and experiment for a wide range of initial compositions. For example, the observed undercoolings below  $T_m$  for detectable nucleation were much greater than predicted by classical theory (typically four times those predicted). Heady and Cahn (1973) could not explain the discrepancy either in terms of heterogeneous nucleation or by using the diffuse nucleus theory of Cahn and Hilliard (1959), and concluded that their result challenged the basis of classical theory.

Recently James (1982) reviewed the evidence on *crystal* nucleation in glasses and concluded that the classical theory gave a satisfactory explanation of many of the experimental results as for example the general dependence of nucleation rate  $J$  on temperature and composition (equation 1). However, there are certain quantitative discrepancies between experiment and theory which are still unresolved.

One of the main obstacles to experimental tests of the classical theory in silicate and borate systems exhibiting liquid-liquid immiscibility is the present lack of sufficiently accurate thermodynamic data ( $\Delta G_V$  values). There is considerable scope for further experi-

mental work similar to that of Hammel (1967) and Burnett and Douglas (1970) but in simpler binary systems such as  $\text{Li}_2\text{O-SiO}_2$  or  $\text{Na}_2\text{O-SiO}_2$ , provided accurate thermodynamic free energy data can be obtained for these systems.

#### IV.5. - Other evidence for phase separation mechanisms

The highly interconnected microstructures revealed in many phase separated glasses by electron microscopy was taken as evidence, in many earlier studies, for spinodal decomposition. The morphologies appeared very similar to the interconnected morphologies predicted theoretically for spinodal decomposition using computer modelling (Cahn and Charles, 1965). However it is now clear that morphology alone is not a sufficient criterion to decide the mechanism. Haller (1965) has shown that an interconnected microstructure can be produced by classical nucleation leading to a distribution of discrete spherical particles, which then grow radially until impingements occur. The important quantities governing interconnectivity are then the volume fractions of the two phases; the closer they are to 50% the greater will be the tendency for interconnectivity.

An objection to the impingement and coalescence of particles based on the theory of diffusion controlled growth has been advanced. This and counter arguments suggesting possible mechanisms of impingement are fully discussed by James (1975) and Uhlmann and Kolbeck (1976).

The intersecting growth model of Haller has received support from the work of Seward *et al.* (1968) who examined thin films of  $\text{BaO-SiO}_2$  glass which had been vapour deposited on a cold substrate. The films were electron beam heated and the separation process was observed directly. For compositions near the centre of the miscibility gap, fine isolated droplets (30-50 Å diameter) were observed during the early stage. However at a later stage two interconnected phases were observed. This appeared to indicate nucleation and intersecting growth for a composition within the spinodal region. However these observations cannot be regarded as conclusively against a spinodal decomposition mechanism. With an electron microscope it is difficult to determine if very fine "droplets" (< 50 Å diameter) are really discrete particles with sharp interfaces or are more gradual compositional fluctuations. Also, observations of morphology alone, even when obtained as a function of time, may be of limited value in deciding the mechanism, especially if the temperature of heat treatment is not far below the spinodal. Here fluctuations rapidly sharpen and begin to coarsen and the process is not readily distinguished from nucleation and growth.

An attempt to overcome these difficulties and to distinguish between nucleation and growth and spinodal decomposition using replica electron microscopy has been made by Srinivasan *et al.* (1976). They suggested that for nucleation and growth the volume fraction transformed should increase with time, but for spinodal decomposition the volume fraction  $V_f$  would tend to decrease with time. They studied the early stages of separation in a sodium borosilicate glass in a composition near the centre of the miscibility gap, for which the immiscibility temperature  $T_m$  was about 5 °C higher than the spinodal temperature  $T_s$ . Replica micrographs indicated that for temperatures between  $T_s$  and  $T_m$  the volume fraction increased with time (suggesting nucleation and growth) and for temperatures just below  $T_s$  the volume fraction decreased with time (suggesting spinodal decomposition). This appears an interesting approach, but has been criticized by Uhlmann and Kolbeck (1976) and Tomozawa (1979) on the grounds that volume fractions determined from replicas are influenced by the etching conditions (Burnett and Douglas, 1970). Hence uncertainties could arise for the early stages of spinodal decomposition when the compositions of the separating phases (and their etching behaviour) are changing with time.

Tomozawa (1978 and 1979) has suggested an entirely different approach to distinguish the above mechanisms. He measured various properties such as viscosity and chemical durability as a function of heat treatment time for glasses undergoing phase separation inside the spinodal region. He interpreted the results in terms of a simultaneous gradual composition variation of both phases, indicating that spinodal decomposition was taking place.

## V. - EXPERIMENTAL SAXS STUDIES

### V.1. - Comparison of experimental results with the theory of spinodal decomposition

SAXS studies of many phase separated glasses have been reported. Nevertheless, two systems have received particular attention from a number of authors: the  $\text{PbO-B}_2\text{O}_3$  system containing minor additions of  $\text{Al}_2\text{O}_3$  and the  $\text{Na}_2\text{O-SiO}_2$  system.  $\text{PbO-B}_2\text{O}_3$  glasses were chosen because of the high electronic contrast produced by the chemical heterogeneities. The addition of some  $\text{Al}_2\text{O}_3$  is necessary to reduce phase separation during the quenching.

Zarzycki and Naudin (1969) studied 4  $\text{Al}_2\text{O}_3$  - 7  $\text{PbO}$  - 89  $\text{B}_2\text{O}_3$  glasses during phase separation at 350 °C and 450 °C. The scattering curves from the

specimen heat treated at 350 °C, showed a maximum at constant  $q$  for the early stages of decomposition. Displacement to lower  $q$  was observed at more advanced stages. The linearity of the  $\log I(q,t)$  vs  $t$  plot was found in the early stages, but a single cross-over point of the SAXS curves was not found. A glass of similar composition was also studied by the same authors (1971) by "in-situ" heat-treatment. The reported  $I(q,t)$  vs  $t$  curves show a sudden increase in the earliest stages and, consequently, a clear deviation from linearity of the  $\log I(q,t)$  vs  $t$  plot. The linear behavior was verified for the later stages. According to these authors their borate glasses were quenched at a rate high enough to retain the quasi homogeneous high temperature structure. Zarzycki and Naudin argued that the deviations from the Cahn theory may be due to its intrinsic inadequacy to describe phase separation even in the early stages.

Srinivasan *et al.* (1973) also studied a  $\text{Al}_2\text{O}_3$ - $\text{PbO}$ - $\text{B}_2\text{O}_3$  glass. They did not find the cross-over point predicted by Cahn theory. They attributed this absence to thermal fluctuations in composition (Cook, 1970). These authors observed secondary peaks in the scattering curves which they associated with contributions from higher harmonics of the spinodal wavelength.

Another SAXS study with "in-situ" heat treatment, in a  $4\text{Al}_2\text{O}_3$ - $5\text{PbO}$ - $91\text{B}_2\text{O}_3$  glass was carried out by Craievich (1975b). His experimental results confirmed that the position of the maximum of the SAXS curves did not change in the early stage. Deviations from linearity in the  $\log I(q,t)$  vs  $t$  plots were also found for the very early stage and no definite cross-over point was observed. A time constant SAXS intensity was found for the  $I(q,t)$  vs  $t$  plot in the high  $q$  domain. The deviations from linearity of the  $\log I(q,t)$  vs  $t$  curves were explained in terms of structural relaxation during the very first stage of phase separation (Craievich, 1975a).

A SAXS study of binary  $\text{Na}_2\text{O}$ - $\text{SiO}_2$  glasses was made by Neilson (1969) in two samples containing approximately 13 %  $\text{Na}_2\text{O}$ . One of the glasses was rapidly quenched and the other cooled at a lower rate. The SAXS curves showed a maximum at a constant  $q = q_m$  value for the first stage of phase separation and a lowering of  $q_m$  in the more advanced stages. The  $\log I(q,t)$  vs  $t$  plot was linear for the very early stage. A well defined cross-over point of the SAXS curves was found for the glass quenched at the lower rate but, surprisingly, no cross-over was observed in the more rapidly cooled glass. Neilson (1969) pointed out that the initial state of the glass can affect the kinetics of phase separation. The observed deviations from Cahn's theory were attributed to a competitive mechanism of nucleation and growth.

Another study of  $\text{Na}_2\text{O}$ - $\text{SiO}_2$  glasses of similar composition was carried out by Tomozawa *et al.* (1970). The  $\log I(q,t)$  vs  $t$  plots were not linear. The curves obtained were approximated by several straight lines. In the early stages, the amplification factors  $R(q)$  showed two peaks, instead of one as predicted by Cahn's theory (equation 5). Only one peak was found in the later stage. These experimental observations are not compatible with the linear theory of Cahn. Tomozawa *et al.* (1970) showed that their results can be described by the late stage non linear solution of Cahn's equation (De Fontaine, 1967) and they suggested that in practice the early stages cannot be observed in the  $\text{Na}_2\text{O}$ - $\text{SiO}_2$  system.

These experimental studies have in common that for the early stages they show only a qualitative agreement with the theory of Cahn. The  $q_m$  values, associated with the maximum of the scattering curves, were found to be approximately independent of time and, disregarding the very first stage of separation, a linear dependence of  $\log I(q,t)$  on  $t$  was observed. In general, the experimental dependence of  $R(q)$  showed clear deviations from the theoretical predictions and no definite cross-over point was found. It should be stressed that each author used a different argument to justify the deviations from the original theory of Cahn. These arguments are related to contributions from: statistical fluctuations in composition, non linear terms, structural relaxation and competitive nucleation and growth mechanism. These additions to the linear equation of Cahn justified qualitatively the observed deviations from theory. Nevertheless no unified quantitative theory was used to explain the SAXS results.

## V.2. - Comparison of SAXS experiments with statistical theories

Recently, Craievich and Sanchez (1981) analyzed experimental SAXS curves of a  $4\text{Al}_2\text{O}_3$  -  $5\text{PbO}$  -  $91\text{B}_2\text{O}_3$  glass, heat treated at 450 °C for different times, in terms of the predictions of the statistical theories. These experimental curves correspond to a glass in advanced stages of phase separation. The plots of  $[q_1(t)]^3 S(q,t)$  vs  $q/q_1$  for different times  $t$ , showed a good quantitative agreement with the scaling relation (equation 12). The  $\log q_1(t)$  vs  $\log t$  plot has the predicted linear behavior giving an exponent  $a$  of 0.23 (see equation 9), in agreement with the computer simulation calculations for the centre of the miscibility gap. This quantitative agreement between the computer simulation calculations for a model alloy and the experimental SAXS results suggests that the statistical theory of phase separation is valid in glasses.

## VI. - EXPERIMENTAL STUDIES OF THE EFFECTS OF AMORPHOUS PHASE SEPARATION ON CRYSTAL NUCLEATION AND GROWTH

### VI.1. - Amorphous phase separation and crystal nucleation

There are many experimental studies on the relationships between phase separation and crystallization (especially nucleation) but only a number of the most important will be discussed. In a review on catalyzed crystallization of glass, Stockey (1959) suggested that liquid phase separation could help subsequent crystallization because homogeneous crystal nucleation could occur in one of the separated amorphous phases. In much of the earlier work, complex compositions were used and only qualitative studies with optical and electron microscopy were carried out (see for example Vogel, 1971). Excellent micrographs showed crystals growing in the amorphous matrix or within the droplets, but no positive evidence of crystallization starting at the interfaces of the amorphous phases was ever presented, although some authors have claimed such evidence.

The first quantitative attempts to test the relationships between amorphous phase separation (APS) and crystal nucleation and growth were by Harper *et al.* (1970) and Harper and McMillan (1972) with glasses of the systems  $\text{Li}_2\text{O}-\text{SiO}_2$  and  $\text{Li}_2\text{O}-\text{P}_2\text{O}_5-\text{SiO}_2$ . They observed that the finest crystals were produced in glasses which contained both  $\text{P}_2\text{O}_5$  and a phase separated microstructure. In later work McMillan (1974) studied the crystallization of a  $1\text{P}_2\text{O}_5-30\text{Li}_2\text{O}-69\text{SiO}_2$  glass. Specimens were nucleated at  $550^\circ\text{C}$  from 0.1 to 6 hours and "developed" at  $750^\circ\text{C}$  for 1 hour. A maximum crystal nucleation density was found for 20 minutes of heat treatment at  $550^\circ\text{C}$ . There was no simple correlation between this observation and the phase-separated microstructure, since the number density of amorphous particles and the total interfacial area decreased throughout the heat treatment period. This result did not support the idea that the interface of the amorphous particles provides nucleation sites for subsequent crystallization.

Studying a  $28.6\text{Li}_2\text{O}-71.4\text{SiO}_2$  glass, Nakagawa and Izumitani (1969) observed that the difference in the number density of  $\text{Li}_2\text{O}.2\text{SiO}_2$  crystals formed in a previously phase separated specimen and in a quenched specimen was negligible. For a  $9.5\text{Li}_2\text{O}-22.5\text{TiO}_2-68\text{SiO}_2$  glass, micrographs showed lithium titanate crystals around the amorphous droplets. These crystals apparently acted as nucleation sites. These authors concluded that crystal nucleation was independent of amorphous phase separation.

A very detailed study was carried out by Tomozawa (1972) who compared the kinetics of amorphous separation for  $\text{LiO}_2-\text{SiO}_2$  glasses with the nucleation of lithium disilicate crystals as a function of temperature and time. The nucleation rate of crystals, in a glass outside the immiscibility gap was constant with time, but for glasses inside the gap a marked increase in crystal nucleation rate was observed in the initial stage of amorphous phase separation. This increase was attributed to the presence of a diffusion zone (depleted in silica) surrounding the silica-rich droplets, which acted as a favourable site for crystal nucleation by lowering the effective surface energy. Straightforward heterogeneous nucleation did not provide a complete answer since the period of enhanced crystal nucleation at a given temperature did not correspond to the period during which the interfacial area of the liquid droplets attained a maximum.

A similar study was made recently by Zanotto and Craievich (1981) using splat cooled glasses and a more rigorous technique for measuring crystal nucleation densities. Although the general conclusions were in agreement with Tomozawa's work, the observed increase in crystal nucleation rate was smaller. It was also shown that the crystal nucleation density ( $N_c$ ) vs time curve for glass samples previously phase separated at  $500^\circ\text{C}$  and then nucleated at  $475^\circ\text{C}$  was different from that of non phase separated quenched samples nucleated at  $475^\circ\text{C}$ . These results did not agree with those of Nakagawa and Izumitani (1969).

Matusita and Tashiro (1973) determined the effect of a series of oxide additives on the crystal nucleation and growth of a  $\text{Li}_2\text{O}.2\text{SiO}_2$  glass. They showed that the nucleation rate was inversely proportional to the viscosity of the glass, except for additions of  $\text{P}_2\text{O}_5$  and  $\text{V}_2\text{O}_5$ . They also suggested that  $\text{P}_2\text{O}_5$  and  $\text{V}_2\text{O}_5$  influenced the nucleation kinetics by inducing liquid phase separation.

Matusita *et al.* (1974) examined the effect of oxide additions ( $\text{RO}_n$ ) on the crystal nucleation and growth kinetics of  $\text{Li}_2\text{O}.2\text{SiO}_2$  crystals in  $\text{Li}_2\text{O}.3\text{SiO}_2$  ( $\text{RO}_n$ ) and  $\text{Li}_2\text{O}.2\text{SiO}_2$  ( $\text{RO}_n$ ) glasses. The ratios of the number of crystals between glasses  $\text{Li}_2\text{O}.3\text{SiO}_2$  ( $\text{RO}_n$ ) and  $\text{Li}_2\text{O}.2\text{SiO}_2$  ( $\text{RO}_n$ ) and also the ratios of the crystal growth rates were shown to increase with  $T_m$ , the immiscibility temperatures of the  $\text{Li}_2\text{O}-3\text{SiO}_2$  ( $\text{RO}_n$ ) glasses. The results were partly explainable on the basis that immiscibility in the higher  $T_m$  glasses produced a liquid phase closer to the  $\text{Li}_2\text{O}.2\text{SiO}_2$  composition. However, the growth rate ratios were always less than the nucleation rate ratios. From the classical nucleation and growth theories they showed that nucleation rates should be more sensitive than the growth rates to composition shifts in the matrix produced by phase separation. Thus, the nucleation ratios should be lower than the growth ratios. It was suggested that the nucleation ratios in the phase separated glasses were higher than expected because crystals

nucleated at or near the interfaces between the two glassy phases.

Hautojärvi *et al.* (1978) studied  $\text{Li}_2\text{O-SiO}_2$  glasses with positron life-time, annihilation line-shape and electron microscopy. They showed that phase separation increased the number of crystals and the rate of volume crystallization.

Another very extensive study was carried out by Ramdsen (1977). He studied the nucleation kinetics of the barium disilicate crystal phase for glass compositions in the range 25 to 34 % BaO. Three sets of specimens from a glass containing 25.3 % BaO (and having a miscibility temperature  $T_m$  of 1.140 °C) were prepared as follows: glass A was rapidly cooled in air, glass B was heated at 800 °C for 1 hour and glass C was heated at 900 °C for 10 minutes. This resulted in three glasses in which the number and size of the exsolved  $\text{SiO}_2$ -rich droplets were completely different. Then, all the glasses were nucleated at 700 °C for various times and given a crystal growth treatment at 840 °C so that the number densities of crystals could be determined by optical microscopy. The effects of the different heat treatments prior to the crystal nucleation treatments were striking (nucleation produced in the prior treatments was negligible compared with crystal nucleation at 700 °C). The crystal nucleation rate was significantly higher in glass B than in glass C or A. This was attributed to the greater degree of phase separation initially present in glass B and hence to the significant shift in matrix composition that had already occurred in this glass.

Estimations of the interfacial area per unit volume of the phase separated glass, using replica electron microscopy, showed that this quantity changed only very slowly at 700 °C for glasses A, B and C. However, the crystal nucleation rates changed considerably with time at 700 °C indicating that the interfacial area was *not* affecting crystal nucleation directly. Also the number of droplets per unit volume in glass A was about ten times greater than in glass C, but initially A had a crystal nucleation rate less than, but similar to C. It was concluded that the morphology of the phase separation had little or no influence on crystal nucleation.

The importance of compositional shifts due to liquid phase separation in the baria-silica system has recently been confirmed by Zanotto (1982). The kinetics of amorphous phase separation in baria-silica glasses with well characterized impurity contents were studied by SAXS and TEM and related to the kinetics and morphology of crystal nucleation and growth determined by quantitative optical microscopy and TEM. Zanotto used various crystal nucleation temperatures higher than 700 °C (Ramdsen used 700 °C). Amorphous phase separation caused a marked increase in crystal nucleation rates with time due to gradual compositional changes occurring in the baria-

rich matrix. Also, in agreement with Ramdsen, the highest nucleation rates were observed in the stoichiometric  $\text{BaO} \cdot 2\text{SiO}_2$  glass, which did not phase separate.

Zanotto (1982) has also observed the compositional effect of phase separation on crystal nucleation rates in the  $\text{Li}_2\text{O-SiO}_2$  system. However, the nucleation rates in phase separated glasses were *higher* than in the stoichiometric  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  glass, in contrast to the  $\text{BaO-SiO}_2$  system. This was shown to be due to the crystallization of a solid-solution phase in the phase separated  $\text{Li}_2\text{O-SiO}_2$  glasses rather than the stoichiometric  $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$  crystal phase.

Again, no correlation was found between crystal nucleation and phase separation morphology in the lithia-silica and baria-silica systems. However, there was some evidence of a small additional nucleation in the early stages of phase separation similar to that observed by Tomozawa (1972) in the lithia-silica system, and possibly due to nucleation in the diffusion zones around the droplets, as described earlier.

## VI.2. - Amorphous phase separation and crystal growth

Before proceeding it is convenient to consider very briefly the theory of crystal growth. There are various possible mechanisms for crystal growth but the simplest applicable to glass systems is the "normal" growth mechanism, in which the growth rate at a given temperature is constant and controlled by the atomic movements near the crystal-melt interface. At high undercoolings below the melting point (which is most relevant to the present discussion) the growth rate  $v$  can be expressed in the form

$$v = B \exp(-\Delta G'_D/k_B T) \quad [13]$$

where  $B$  is essentially a constant and  $\Delta G'_D$  the activation free energy for atomic transport across the interface (kinetic barrier).  $\Delta G'_D$  can also be expressed as  $\Delta H'_D - T\Delta S'_D$  where  $\Delta H'_D$  and  $\Delta S'_D$  are the enthalpy and entropy of activation, respectively. Thus a plot of  $\log v$  vs  $1/T$  will yield a straight line of slope  $\Delta H'_D/k_B$  according to equation [13]. It should be noted that  $\Delta G'_D$  is not necessarily identical to the kinetic barrier for nucleation ( $\Delta G_D$ ) in equation [1]. A review of crystal growth in glasses is given by Uhlmann (1971).

Phase separation can affect crystal growth rates. However, experimental studies on the subject have yielded conflicting results. Some authors suggested that "mechanical" interference could occur between the growing crystals and amorphous droplets resulting in an overall decrease in growth rates (Harper and McMillan, 1972).

Ogura *et al.* (1968), Tomozawa (1973) and Komppa (1981) have measured the crystal growth

rates  $v$ , and activation enthalpies,  $\Delta H_b$  in several  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  glasses with compositions inside and outside the miscibility gap. These studies show that, for all glasses inside the gap, both crystal growth rates and activation enthalpies are very similar. For glasses outside the gap the crystal growth rates and activation enthalpies increased as the stoichiometric  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  composition was approached (with increasing  $\text{Li}_2\text{O}$  content). These results demonstrate that the compositional shifts caused by the amorphous phase separation have a marked influence on the growth of  $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$  crystals. Otherwise, the crystal growth rates in the several phase separated glasses would be different due to differences in initial compositions (and diffusivities) of the parent glasses.

Ramsden (1977) made a study of crystal growth in phase separated and homogeneous  $\text{BaO}\cdot\text{SiO}_2$  glasses. He showed that induction periods were caused by a change in growth morphology and crystal form, from spheres to rapidly growing needles nucleated at the sphere-glass interfaces. The induction time decreased with rise in temperature. Phase separation increased the growth rates due to an accompanying shift in composition of the  $\text{BaO}$ -rich phase during heat treatment. This shift also caused an apparent reduction in the measured activation enthalpies for growth in the phase separated glasses. The morphology of the two liquid phases had no influence on crystal growth rates.

Scherer and Uhlmann (1976) in a detailed study of the crystallization kinetics of cristobalite in  $\text{Na}_2\text{O}\cdot\text{SiO}_2$  glasses with 1.5, 10.0 and 15.0 %  $\text{Na}_2\text{O}$  found no significant effect of phase separation on crystal growth kinetics. This work was later criticized by Tomozawa (1979) who replotted the data of Scherer and Uhlmann for the glass containing 10.0 %  $\text{Na}_2\text{O}$  in the form  $\log v$  versus  $1/T$ . A kink at 845 °C, approximately the same temperature as the immiscibility temperature for that glass, was clearly observed. Thus, the phase separation did appear to influence the crystal growth rate.

## VII. - CONCLUSIONS

After the initial stage of phase separation the kinetics of coarsening of both droplet and interconnected microstructures are well established and in general agreement with theory.

In the region between the spinodal and binodal boundaries and, in particular, close to the binodal the results are consistent with a classical homogeneous nucleation mechanism. However, there is scope for further quantitative work on nucleation kinetics in simple binary systems to test the predictions of the classical theory of nucleation.

TEM studies of glass compositions within the spinodal region of the miscibility gap have so far yielded

conflicting results and spinodal decomposition has not been conclusively demonstrated by TEM alone.

It is clear that morphological observations by themselves are inadequate for determining the mechanisms of amorphous phase separation. Furthermore, high interconnectivity in the later stages of separation is not a sufficient criterion for spinodal decomposition but may arise also from nucleation and intersecting growth. Here the equilibrium volume fraction of the phases has a very important influence.

The SAXS studies of phase separating glass systems, within the spinodal region of the miscibility gap, are in qualitative agreement with the classical model of spinodal decomposition according to Cahn. Nevertheless, quantitatively there are clear deviations from the predictions of the original theory. These deviations have been only qualitatively explained in each case on the basis of different contributions to the classical model.

Most of the published studies on phase separation have dealt with crystalline solid solutions which generally show anisotropy of the structure function in the advanced stages of segregation. Thus glass systems seem to be better candidates for testing the validity of the statistical theories because of the absence of anisotropic effects. The only reported quantitative comparison of experimental SAXS data with the statistical theories showed a remarkable agreement. A closer experimental test of the validity and generality of the scaling properties in glasses will require a systematic study of binary systems for several compositions and temperatures, and more accurate SAXS measurements. SAXS studies using a X-ray beam with point-like cross-section (instead of linear cross-section) and "in-situ" heat treatment of the specimens, may furnish experimental data with higher precision than previously reported. The increasing availability of high intensity beams from synchrotron radiation sources will help to perform experiments satisfying these conditions.

At present, there is growing evidence of enhanced crystal nucleation in certain glasses undergoing liquid phase separation. From recent detailed work on crystal nucleation kinetics in phase separated and non-phase separated  $\text{BaO}\cdot\text{SiO}_2$  and  $\text{Li}_2\text{O}\cdot\text{SiO}_2$  glasses, it is clear that *compositional shifts* caused by phase separation play a very significant part in increasing crystal nucleation. It should be stressed, however, that nucleating agents have a much more pronounced effect on nucleation rates, increasing it by 5 or 6 orders of magnitude in some cases, while the amorphous phase separation usually produces an increase of less than one order of magnitude.

It is clear from the reported results that liquid-liquid immiscibility also affects crystal growth rates. Again,

this is mainly due to compositional shifts in the amorphous matrix.

For the future, there is no doubt that further studies of the kinetics of amorphous phase separation in glasses

and of the relation between phase separation and crystal nucleation and growth in glasses will continue to be of both fundamental and practical importance.

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