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Crystal growth model with stress development and relaxation

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Abstract – During crystallization of glass-forming melts an important amount of stress energy may develop. The reason for this development is the difference in volume of the new system and that in the ambient phase. Therefore, the growth rate decreases with time. Here we develop an algorithm for the process of crystallization using Monte Carlo simulation techniques that takes into account the stress energy. We find that there is a short period of initial fast growth stage followed by a second period of much slower growth, controlled by the relaxation rate. This picture has also been recently observed experimentally. Additionally, we find that during the growth process the shape of the crystal is changing. Although we start from a highly symmetric crystal with flat ⟨10⟩ interfaces, a shape with a large number of facets is soon created.

Introduction.

Crystal growth has been a very challenging topic over the years. Therefore, a large number of models and approaches were developed in the effort to better understand the microscopic mechanisms of growth, refs. [1–3]. Recently, a new model was suggested combining ideas from percolation theory and the glass-forming ability of silicates, refs. [4–7]. Most glass-forming systems consist of networks in which the network formers, NF, are connected via oxygen bridges. The network is "floppy" or "rigid", depending on the number of broken oxygen bridges (NBO) per NF. According to the theoretical model developed in refs. [8–12], as well as from experimental estimations, refs. [4–7], the threshold number for the floppy-to-rigid transition is $NBO_c = 1.6$ for glasses composed by network formers with coordination number 4. If NBO is less than this critical value, the network is rigid. However, in such networks there are still some tiny floppy regions as this was experimentally proved in refs. [4,5]. Recently, ref. [13], it was shown that the exact threshold conditions for the rigid/floppy transition depend on the dimensionality of the space and on the coordination number. Moreover there is a NBO concentration interval, although relatively narrow, in which both rigid and floppy clusters percolate simultaneously in the system. In this concentration interval the system behaves as floppy with respect to the diffusion of ions. At the same time, the existing rigid skeleton will make the system to behave as rigid with respect to the retaliation of deformations. Studying this behavior is one of the objectives of the present investigation.

The present investigation aims to describe crystallization in multicomponent systems. Our basic starting assumption is that we expect some stress energy to develop, impeding the crystal growth. At a first stage, as the crystal grows, nuclei are formed inside the floppy regions of the glass. The size and concentration of these floppy regions in a rigid matrix is a type of percolation problem. We expect that the crystal can grow relatively fast until the entire floppy region is occupied. Further crystallization has to propagate inside the rigid region and it is to be accompanied by stress development. This is of particular importance if the chemical composition of the growing crystal is different from that of the ambient phase. Viscous relaxation could reduce, or even eliminate, the inhibiting effect of elastic stresses. This is why in most cases the effect of internal stress is neglected. The common argument is that stress energy is relaxing too fast to affect crystal nucleation or crystal growth. If the two scales (of growth rate and of relaxation rate) are comparable, the stress energy will not have enough time to dissipate completely during the crystallization. Although the relaxation time is long near the glass transition temperature,

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the crystallization time is long as well. On the other hand, at elevated temperatures the relaxation time is short, just like the crystallization time. Therefore, during the crystallization, the possibility of appearance of certain residual stress energy cannot be neglected *ad hoc*.

In the present work we use Monte Carlo, MC, methods to simulate crystallization. The process initiates in the floppy region and then propagates to the rigid one. By use of these simulations we obtained such quantities as the crystal growth rate and the stress energy. Similar MC techniques have been extensively used in the past for studying crystal growth phenomena and for modeling glass materials, refs. [14–20]. Finally, we compare the results of the numeric simulations with experimental data obtained for the growth of BaF_2 crystals, and we find good quantitative agreement.

Model description. – In our model we take into account two main features: the number of bonds that are realized at each incorporation step and the stress energy that is developed in the vicinity of the new interface. Almost a century ago Kossel and Stranski, refs. [21,22], first realized the necessity of consideration of elementary acts of attachment and detachment of single particles to the crystal. In this respect of special importance happened to be the so-called "kink" position, refs. [23]. It was the main point for the theory of linear crystal growth developed later, refs. [24]. Due to the differences in the specific volumes of the ambient phase and the new phase, certain strain appears leading to stress development and stress relaxation refs. [25–27]. The latter we account for by the Maxwell equation, as this is the widespread first approximation for the relaxation kinetics in glasses (see for instance refs. [25,28]).

In the current investigation we consider a mesh, which consists of a central floppy region, surrounded by a wider rigid one. The crystallization process is initiated in the floppy region, where it proceeds at a high growth rate. Once the crystal has covered this region, it will start expanding in the adjacent rigid one. In this case, the growth rate can be strongly affected by the stress energy, which develops in the periphery of the crystal.

Calculations are performed on 2D square lattices, of size $N \times N$. This is the lattice in which the nodes are occupied by the atoms, but they do not correspond to the exact positions that they may have in the ambient phase. Although the glass is in a condensed phase with relatively high density and the atoms are somewhere close to the lattice nodes, their exact positions are not specified in the model. In the initial configuration, just a small fraction of the lattice sites are occupied. These sites form a square cluster at the central region, of size $n \times n$. Our assumption is that the central $n \times n$ region is a floppy one (although it could appear inside the otherwise rigid skeleton of the system). The crystallization process has already been initialized and has occupied this void. All the particles that belong to the crystal are connected through
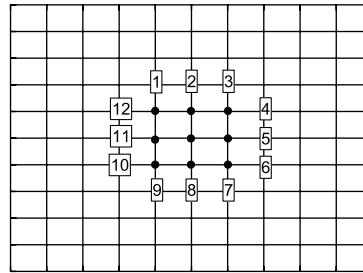

Fig. 1: 2D square $N \times N$ lattice. The gray dots denote the central $n \times n$ cluster and the numbers 1 to 12 the sites that are adjacent to its periphery, which are eligible to receive new particles, as the original $n \times n$ cluster grows.

bonds. The outer region is rigid and we intend to monitor the expansion of the crystal through it. The crystal grows in size when new particles are added to its periphery, and as a consequence bonds are formed with the existing cluster particles. We expect that the crystal growth rate will be affected by the presence of the local regions of stress energy. As the stress relaxation rate is too low in the rigid region, important stress energy can be accumulated.

The initial configuration is illustrated in fig. 1 for a $n \times n = 3 \times 3$ central cluster. The sites 1 to 12 are the nearest neighbors of the periphery sites and a fraction of them will accept particles that will attach to the cluster, allowing the crystallization process to proceed through the rigid region. In this model there is no simulation of the diffusion of the particles, but we assume that particles may attach on the existing cluster. For each one of the cluster neighboring sites we calculate the number of bonds through which a new particle can be attached to the cluster. Then we calculate the local stress energy, which is a sum of the stress energy of each cluster site, adjacent to the site to be attached. We use a Boltzmann exponential equation for the attachment probabilities, according to the formula

$$P = 1 - e^{-\frac{mb - \epsilon}{kT}}, \tag{1}$$

where b is the energy of a bond, k is the Boltzmann constant and T is the temperature. By m we denote the number of the bonds through which a site can be attached to the crystal and by ϵ the stress energy. Thus, $m \cdot b$ denotes here the energy of the bonds that is gained, while ϵ is the stress energy that is not favorable for the process. We apply the Metropolis algorithm with an attachment probability for each site of the periphery, accounting for both the bond energy b and the stress energy ϵ. In case of the initial configuration of fig. 1, for each one of the 12 sites we have $m = 1$. At time $t = 0$, the stress energy is 0 for all periphery sites.

The stress energy is not constant during the simulation and its value depends on whether a site is attached to the cluster, according to the probability P and on the relaxation time τ. It follows a simple Maxwell relaxation

kinetics with a single τ, given by the equation

$$\frac{\mathrm{d}\epsilon}{\mathrm{d}t} = -\frac{\epsilon}{\tau}. \tag{2}$$

The change $\frac{\Delta\epsilon}{\Delta t}$ in the stress energy is given by the following formula:

$$\frac{\Delta\epsilon}{\Delta t} = \begin{cases} -\dfrac{\epsilon}{\tau} + \epsilon_0, & \text{if a site is attached,} \\ -\dfrac{\epsilon}{\tau}, & \text{if a site is not attached,} \end{cases} \tag{3}$$

where τ is a constant for the relaxation time. By ϵ we denote the current value of the stress energy and by ϵ_0 a constant value that is added instantaneously when a new atom is attached to the crystal. It is seen that ϵ_0 accounts for the change of the system volume caused by the crystallization. The value of ϵ_0 is independent of the the number of the new m bonds which were created, just like the volume of the unit cell. The term $-\frac{\epsilon}{\tau}$ in eq. (3) accounts for the elementary step of a Maxwell relaxation process.

After the attachment probabilities P have been calculated for all the sites that are adjacent to the periphery of the crystal, the attachment decision for each one of them is made according to the Metropolis algorithm. Therefore, in fig. 1, if the particle found in site 1 will be attached, then it will not influence the decision for the one in site 2, which still has $m = 1$. This is done in order to avoid the influence of the order of counting the sites. In one MC step the attachment of a particle to one site is taken not to influence the attachment to a neighboring site because it is assumed that they are taking place at the same moment. On the other hand, the attachment of a particle to one site is very important for the attachment of a particle of the neighboring site in the next MC steps. The MC step is completed only after the possible attachments to the periphery have been completed. Therefore, the time step is always the same, no matter how large the crystal is. It accounts for the time during which one atom can attach to a given position of the periphery, provided a positive decision is made by the Metropolis algorithm. Actually, this corresponds to the time needed by a building unit of the melt to diffuse at a distance equal to a unit cell. Evidently, if the crystal and the ambient matrix have the same composition, the MC time step is approximately equal to τ. On the other hand, for multicomponent systems the MC time step is about the diffusion time, namely much shorter than τ.

Simulation results. – Computer simulations are performed on 2D square lattices of size 1000×1000. The parameters for the simulations were $b = 1$ and $T = 1$. We always start from a cubic 3×3 crystal, with no stress energy accumulated around it. (If only the bonds between the first neighbors are taken into account, the equilibrium form is cubic.) As the cluster gets larger, we observe that the crystal is getting faceted. This change of shape of the crystal leads to an increase of the places at "kink" positions and to higher growth possibilities. Note that
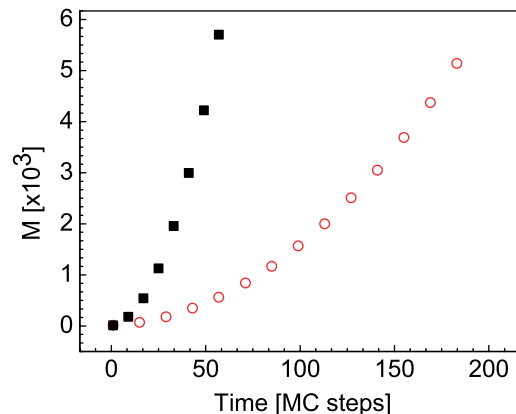

Fig. 2: (Colour on-line) Size M of the cluster *vs.* time for two different cases, one with stress $\epsilon_0 = 1$ (open circles) and a second without stress, $\epsilon_0 = 0$ (full squares). The growth rate of the cluster is much lower in the case of $\epsilon_0 = 1$.

the attachment probabilities are not the same along the periphery. The outer protrusions cause local increase of the stress. Therefore, the Bales-Zangwill instabilities are not observed.

The cluster size at each time step is defined as the number of particles that belong to it. Figure 2 illustrates the dependence of the size M on time. The linear size of the cluster can be thought of as $L = M^{\frac{1}{2}}$. Results are for two values of the constant ϵ_0, namely $\epsilon_0 = 0$ and $\epsilon_0 = 1$. The first one accounts for the case of crystallization without stress energy development. The size M of the crystal grows parabolically with time. This corresponds to a linear increase of the size L with time as expected, refs. [2,24,25]. It is here obvious that the stress energy will definitely affect the growth of the crystal, since the rate is much slower than in the case of $\epsilon_0 = 0$.

The growth rate can be determined by the slope of L *vs.* time and it depends on the steady-state value of the stress energy ϵ, which is developed after a short time. The effective steady-state value depends on the parameter ϵ_0. If a high value is chosen for ϵ_0, then ϵ will also grow to be relatively large and as a result the corresponding slope on the L *vs.* time line will be lower. Moreover, the effective stress energy value that reduces the growth rate also depends on the relaxation time. Evidently, for $\tau \to 0$ no stress can be developed. Increasing τ causes an increase of the effective steady-state ϵ value and a decrease in growth rate as shown in fig. 3. The relaxation time is given as a parameter for each curve. Additionally, it is necessary to focus on the initial stages of the process. A zoom of the early time steps is shown as an inset in fig. 3.

It is a widespread assumption that relaxation time is proportional to viscosity of the ambient system. Therefore it changes fast with temperature. In figs. 2 and 3, one can easily observe the scaling behavior of the steady growth rate even for long times. Concerning the early growth stages, it can be seen in the inset of fig. 3, that the crystal starts to grow very fast since the slope is
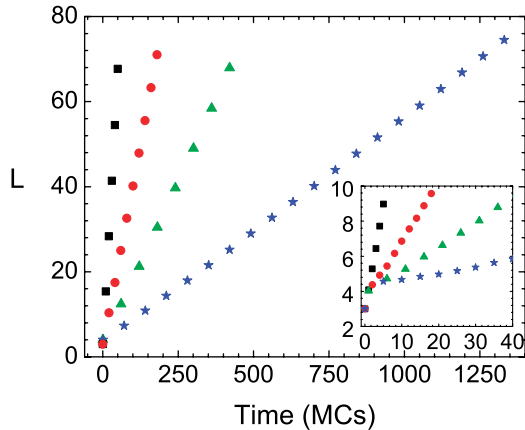
Fig. 3: (Colour on-line) Linear size L of the cluster *vs.* time for different relaxation times. Relaxation time $\tau = 0$ (squares) is equivalent to stress $\epsilon_0 = 0$. The other cases shown include $\epsilon_0 = 1$ with $\tau = 10$ (circles), $\tau = 100$ (triangles) and $\tau = 1000$ (stars). The growth rate slows down as the relaxation time increases. In the inset the change of L is presented for the early time steps.
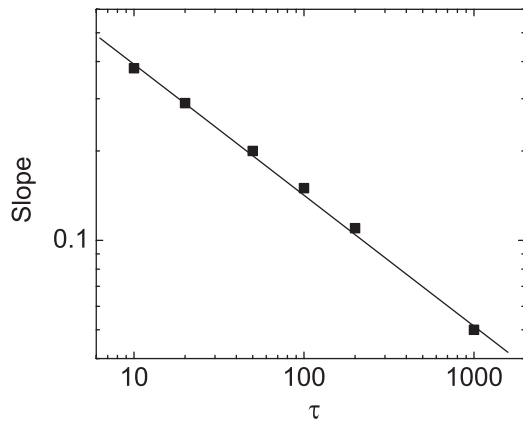

Fig. 4: Slopes after the crossover point *vs.* the relaxation time τ. The black squares denote the slopes derived from fig. 3. The solid line is a power law fit. The slope is -0.44 ± 0.01.

initially very high, as if there were no stress. As soon as a couple of mono layers are deposited, stress is developed and the growth rate drastically decreases. The linear dependence of size against time observed after the break indicates that a steady state with constant value of the average concentration of stress energy on the periphery is fast established. This is in agreement with the analytical solution given in ref. [27]. This change of the growth rate could be very important. It means that there is a range of compositions in which crystals remain tiny (nanocrystals) while away from them the matrix is stress free and a new nuclei can be formed. In this way nanocrystalline glass ceramics could be produced.

All lines in the inset of fig. 3 go through a crossover point at this early stage of growth and then they have various slopes that strongly depend on relaxation time. These slopes are plotted *vs.* the relaxation time τ in fig. 4.
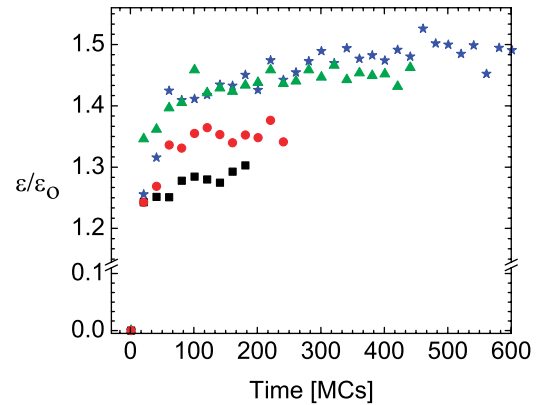

Fig. 5: (Colour on-line) Mean value of the normalized stress energy *vs.* time for different relaxation times. As the relaxation time increases, the mean value increases, until it reaches a constant, for $\epsilon_0 = 0$ (squares) and $\epsilon_0 = 1$ for different relaxation time, namely $\tau = 10$ (circles), $\tau = 100$ (triangles), $\tau = 1000$ (stars).

We observe a straight line in log-log axes giving a slope of -0.44 ± 0.01. Thus, the linear size L is proportional to: $L \approx 1/\tau^{0.44}$.

Since at each MC step we calculate the stress energy at every point of the periphery, we estimate the average stress energy per atom of the periphery and plot it against time in fig. 5 for the same parameters as in fig. 3. It is obvious that the steady-state average values do not increase sharply when the relaxation time increases, unlike the slopes displayed in the same figures. This phenomenon is due to the fact that the effective steady-state value that controls the growth process is different from the average stress value on the periphery.

Comparison with experimental data. – Crystallization kinetics of BaF_2 crystals from a glass with the composition

$$1.88Na_2O \cdot 15.04K_2O \cdot 7.52Al_2O_3 \cdot 69.56SiO_2 \cdot 6BaF_2$$
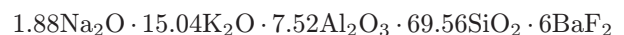
was studied in ref. [28]. The mean sizes of the respective crystals after thermal annealing for 5 to 160 h were calculated by Scherrer's equation from XRD line broadening. The values obtained were in agreement with mean crystal sizes determined using transmission electron microscopy.

The reason to consider these results together with the present model is because in the present case the particles creating the new crystal are moving inside the melt much faster than the main building units of the melt. The mean jump frequency of the main molecules is established from the viscosity (η) data according to

$$\tau \approx \frac{\eta}{G}, \tag{4}$$

where the shear modulus is $G = 10^{10}\,\mathrm{Nm^{-2}}$. The time Δt of one Monte Carlo step is determined via the lattice
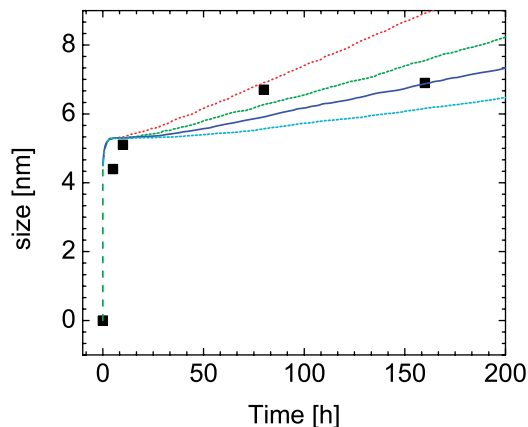
Fig. 6: (Colour on-line) Size of the crystals in nm *vs.* time in hours. The black squares are the experimental results for the growth of BaF_2 crystals. The lines are the simulation results for $\epsilon_0 = 1$ and for relaxation times $\tau = 1000$ (red dotted line), $\tau = 2000$ (green dashed line), $\tau = 4000$ (blue solid line), and for $\tau = 10000$ (cyan dash-dotted line).

constant d_0 and the diffusion coefficient D as follows:

$$\Delta t = \frac{d_0^2}{D}, \tag{5}$$

so that in Δt units the relaxation time is

$$\tau_\eta \approx 10^{-10} \frac{\eta D}{d_0^2} \approx 10^8 \eta D. \tag{6}$$

In order to compare the Monte Carlo results to experimental data we need to start from the estimated size (in nm) of the floppy region and to consider the length propagation of one attachment as d_0 (in nm). Results are shown in fig. 6. Experimental data are solid points. The size of the floppy region was assumed to be 4.5 nm, so that the crystal grows very fast, without stress development, from zero to about this size. From these considerations we see that the correspondence of the simulation time to real experimental time is that 1 Monte Carlo step is approximately equal to 1 hour.

Recently, refs. [29,30], some other systems were reported, in which a strong dependence of the crystallization kinetics on time was observed. In these works oxyfluoride glasses were considered, from which CaF_2 is crystallized by annealing the samples at about 10 K above the glass transition temperature. As shown in refs. [28–30], after the initial fast growth stage, the crystallite sizes did not depend much on the annealing time. This means that in an initial state of crystallization, the crystal growth velocity was much larger than in a later state. This is exactly the behavior shown in fig. 6.

In ref. [29], the chemical composition of the glasses was altered and particularly the Na_2O concentration was changed. This means that if the concentration of the network modifiers is increased, then also the size of the floppy regions gets larger. As already shown in ref. [29] the crystallite size is proportional to the size of the floppy

regions after annealing. Hence, the assumption that the crystal growth velocity is large until the crystals have a size equal to that of a floppy region is in agreement with these experiments.

Discussion and summary. – We developed here a model that describes crystal growth that starts with a small crystal seed and proceeds to a full size crystal based on considerations of the stress energy developed during the process. The method shows a fast initial increase in size of the order of a few nm, which then slows down to a more moderate rate, which is strongly dependent on the relaxation time allowed for the system. We find that the rate of increase of the crystal diameter scales with the relaxation time with a scaling exponent of -0.44 ± 0.01. This fast/moderate crossover is also observed experimentally during growth of BaF_2 crystals from a glassy matrix.

In many systems the crystal growth rate remains approximately constant or in some cases even increases during the course of the crystallization. In these systems the components that crystallize are usually silicates or aluminosilicates. This, however, leads to a depletion of the glassy phase near the crystals in network formers which results in a decrease in viscosity. Then the relaxation processes are enhanced and a crystal growth process according to figs. 3 to 6 is not observed. Hence, depending on the temperature, the chemical composition of the glasses and the precipitated crystal phases, the crystal growth might be controlled by stress development and stress relaxation or, however, might not depend on such effects.

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