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Crystallization at the glass transition in supercooled thin films of methanol

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The stability of an amorphous material depends on how fast and by what mechanism crystallization occurs. Based on crystallization rate measurements through optical reflectivity changes in supercooled methanol thin films, it is observed for the first time that there is a definitive and detectable change of the crystallization mechanism at the glass transition temperature \( T_g \). For methanol glasses below \( T_g=103.4 \) K, crystallization occurs as an interface controlled, one-dimension process at frozen-in embryo sites, while in the deep supercooled liquid phase above \( T_g \) crystallization is diffusion controlled in two dimensions with a constant nucleation rate and an activation energy of 107.8 (±4.7) KJ/mol. © 2007 American Institute of Physics.

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Many recent studies on dynamics in supercooled systems aim to answer the questions how fast and by what mechanism does a metastable amorphous solid move toward its equilibrium structure over time. A fundamental characteristic of a supercooled system is its glass transition temperature \( T_g \), which is correlated to a reversible transformation between the supercooled liquid and amorphous solid forms. Approaching \( T_g \), the dynamics in the supercooled system show a marked change in time scales. Below \( T_g \), the dynamics are nearly arrested and thus relaxation can be extraordinarily slow. At temperatures above \( T_g \), there is an activation (sometimes sudden as for fragile glass formers) of molecular motions which may have a profound effect on kinetic processes such as the nucleation and crystal growth rates.

In poor glass-forming molecular liquids such as methanol,\(^1\)\(^2\) nucleation and crystallization rates often are fast enough for detection on laboratory time scales even at relatively low temperatures. Studies have shown that nucleation can be detected even for some glasses below \( T_g \).\(^3\) For large organic molecules crystal nuclei can exist hundreds of degrees below \( T_g \).\(^3\)\(^4\) These systems afford opportunities to probe the effect of different dynamics on crystallization above and below \( T_g \).

Crystallization is a process that starts by the formation of critical sized nuclei of crystallites followed by growth of these nuclei. In a typical liquid with fast molecular relaxation times, nuclei are formed by rapid local density fluctuations. If a nucleus is large enough to surmount the free energy barrier, it can then grow spontaneously. Viscous liquids and, in particular, glasses, however, are expected to behave very differently since structural fluctuations are slow due to restricted rotational and translational motions. In such a system, a marked change in the rate, and perhaps mechanism, of nucleation at \( T_g \) is expected. Although crystallization in supercooled molecular fluids has been studied,\(^6\)\(^7\)\(^8\)\(^9\)\(^10\) no system has been examined in terms of its nucleation and crystallization behavior at temperatures both above and below \( T_g \). The influence of the glass transition on the crystallization mechanism and rate has not been characterized.

Methanol affords a unique opportunity to examine the crystallization process in relation to the glass transition. This is due to the close proximity of methanol’s \( T_g \) (reported at 103 K) (Ref. 1) and its crystallization temperature (105 or 108 K).\(^1\)\(^11\) The proximity of the two temperatures suggests that crystallization can be detected on laboratory time scales both above and below \( T_g \).

Such a study can be performed using deeply supercooled glasses formed by vapor deposition of thin molecular films,\(^5\) with sufficient thickness to mimic bulk properties, onto a cold substrate. Heating the metal substrate provides an efficient way to change the film temperature. In this letter, we report for the first time a correlation between changes in nucleation mechanism with the glass transition, i.e., different kinetics for crystallization from the glassy versus supercooled liquid states stemming from different nucleation mechanisms.

In this study an experimental technique that is sufficiently sensitive to detect crystallization occurring in the thin film deposited on a metal substrate under vacuum conditions is needed. We have devised such a technique based on the refractive index change induced by the change of crystalline/amorphous composition in the film. The change in refractive index can be measured through the change in reflectivity of a laser beam passing through the film. The film is first deposited at 85 K on Ag and then heated to a specific temperature above or below the methanol \( T_g \) (102.5–107.5 K). Reflectivity change is then recorded as a function of time for monitoring crystallization in the film.

The experiments were performed in a ultrahigh vacuum chamber (base pressure \( 1 \times 10^{-10} \) Torr). Cleanliness and flatness of the Ag(110) surface were maintained by routine cycles of Ar\(^+\) bombardment followed by annealing at 685 K. The films were deposited by condensing methanol vapor (Aldrich, purified by several freeze-pump-thaw cycles) at a pres-
The indices of refraction are \( n_1 = 1 \) in a vacuum, \( n_2 = n_2 \) for a nonabsorbing film, and \( n_3 = 0.27 + 4.18i \) for silver at a wavelength close to 2 eV.\(^1\) Due to multiple reflections inside the film, a change in film thickness will result in an oscillatory optical interference pattern with the periodicity corresponding to a change of \( \beta \)—the phase difference after one round trip of reflection in between the two film boundaries that can be related to the film thickness \( d_2 \). The methanol film thickness \( d_2 \) increases linearly with growth rate \( G \) as \( d_2 = G \times t \). The interference pattern measured in differential reflectivity as a function of exposure time (or equivalently \( d_2 \)) during isothermal film growth at 85 K is displayed in Fig. 1. The parameters \( G \), \( d_2 \), and \( n_2 \) can be determined by fitting the experimental data.

After isothermal growth of the methanol film, the change in the differential reflectance can be related to the extent of crystallization in the film. The refractive index of the film is related to the dielectric constant which in turn is related to crystallization in the film. The refractive index of the film is fit to the experimental data.

The reflectivity changes from a metal surface during the crystallization process can be related to the Avrami parameters: growth rate, mechanism, and crystal shape, respectively. Thus the refractive index change during the crystallization process can be related to the Avrami parameter as:

\[
\chi^{(1)} = \alpha_0 f_{\text{cry}}^{1/2} + \alpha_d (1 - f_{\text{cry}}) = \alpha_0 + (\alpha_d - \alpha_0) \exp(-k t^\beta),
\]

\( f_{\text{cry}} = 1 - \exp(-k t^\beta), \)

where \( f_{\text{cry}} \) indicates the crystallized fraction, \( k \) the rate constant, and \( n \) the Avrami parameter which relates to the nucleation rate, growth mechanism, and crystal shape, respectively. The differential reflectivity changes as functions of time measured at fixed temperatures in the ranges of 102.5–104 K and 105–107.5 K are displayed in Figs. 2(a) and 2(b), respectively. In each case the films were deposited to a thickness of 610 nm. The crystallization rate dramatically increases with the crystallization temperature, as indicated by the appearance of the crystallized fraction which causes the \( \Delta R / R \) signal to fall. There is a marked difference in the shape of the crystallization curves between 103 and 103.5 K [Fig. 2(a)]. The isothermal crystallization data can be fitted by Eqs. (2)–(4) for extraction of the parameters \( \alpha_d, (\alpha_d - \alpha_0), k, \) and \( n \).

Figure 3 shows a plot of the Avrami parameter \( n \) as a function of the crystallization temperature. The seven measurements from 102.7 to 103.3 K (\( n \) values ranging from 0.928±0.006 to 1.081±0.008) result in \( n = 0.963±0.053 \), while the nine measurements from 103.5 to 107.5 K (\( n \) values from 1.955±0.002 to 2.265±0.006) give \( n = 2.110±0.120 \). An abrupt change is observed at 103.4 K at which \( n \) is measured as 1.352±0.011. The change in \( n \) corresponds to a change in nucleation or growth mechanism.\(^1\) Remarkably, this abrupt change is coincident with methanol's \( T_g \) of 103 K.\(^1\)
The parameter \( k \) is plotted in Fig. 4 as a function of temperature. Since \( k \) should follow Arrhenius behavior for a given \( n \) value such that
\[
k = k_0 \exp\left(-\frac{E_a}{RT}\right)
\]
and changes with \( n \) in units of \( \text{sec}^{-n} / \text{K} \), Fig. 3 is plotted as \( \ln(k_0^n) \) vs \( 1/T \). This plot should give a straight line with the slope as activation energy \( E_a^* \) for temperatures with the same crystallization mechanism.\(^{17}\) (Note that \( E_a^* \), other than the generic \( E_a \), is used for the activation energy associated with the specific Avrami parameter \( n \).) The low temperature \( k \) values indicate a very small activation energy that does not allow accurate determination while the points at \( T > 103.4 \) K result in
\[
E_a^* = 107.8 \pm 4.7 \text{ kJ/mol}
\]
This somewhat large crystallization activation energy is consistent with the slow diffusivity and/or the highly cooperative nature of molecular motion in supercooled liquids.

The abrupt change in the \( n \) values near \( T_g \) is significant. It represents a change in one or more of the following factors—the control mechanism of growth (i.e., interface versus diffusion control), the nucleation rate/mechanism (i.e., constant versus rapid nucleation rate), or the dimensionality of the growth. There are several possible known crystallization mechanisms that are correlated to the Avrami parameter \( n = 1 \) and \( 2.\text{\textsuperscript{14–16}}\)

An Avrami parameter of 1.0, obtained for crystallization below the glass transition, may arise from two scenarios. Scenario A is interface controlled crystallization in one dimension with a rapid nucleation rate (i.e., constant number of nuclei). Scenario B is diffusion controlled in two dimensions with a rapid nucleation rate. The latter, however, is not plausible since long range diffusion on laboratory time scale should be arrested below \( T_g \).

An Avrami parameter of 2.0, obtained for crystallization above \( T_g \), is consistent with three scenarios. Scenario C is diffusion controlled in two dimensions (2Ds) with a constant nucleation rate. Scenario D is interface controlled in 2Ds with a rapid nucleation rate. Scenario E is interface controlled in one dimension (1D) with a constant nucleation rate.

In comparing the crystallization mechanisms below and above \( T_g \), we rule out the combination A → D. This case entails a change only in dimensionality without accompanying changes in mechanism. There can therefore be two possible sets of mechanisms: A → C and A → E. In the A → C case, the growth process is interface controlled below \( T_g \) and...
diffusion controlled above. There is also an increase in growth dimension. This could be possible if one considers that arrested relaxation below \( T_g \) results in 1D chains while increased diffusion above \( T_g \) allows for 2D growth in the form of branched chains. Conversely, there is no change in the dimensionality of the growth in going from A → E. Here, growth is interface controlled on both sides of \( T_g \). Interface control is reasonable in a glass or viscous liquid where reorientations of molecules at a nucleus interface are much faster than long range diffusion.

It is important to recognize that in both cases A → C and A → E, there is a change in the nucleation mechanism near \( T_g \). In fragile glass formers such as methanol, small nucleus embryos can be frozen in during the initial deposition of the amorphous film. \(^{16,18,19}\) It appears that below \( T_g \), where molecular relaxation and diffusion processes are dramatically slowed and the structure is far from equilibrium, nucleation occurs at preexisting frozen-in cluster sites (athermal nuclei\(^{16}\)). This condition corresponds to a rapid nucleation rate\(^{16}\) where during crystallization, growth at these frozen-in embryo sites results in depletion of the constant number of nuclei. On the other hand, above \( T_g \) the film behaves like a viscous liquid and nuclei can be formed by density fluctuations. This allows steady-state nucleation to occur throughout the growth phase.

The activation energy determined in association with the crystallization mechanism supports more strongly scenario C for crystallization above \( T_g \). The interface controlled mechanism can be facilitated by rotational motion only, while the diffusion controlled mechanism requires translational mobility of molecules. The value of 107.8 kJ/mol would be conspicuously large for rotation but reasonable for translational diffusion in the vicinity of \( T_g \). Though the activation energy cannot be determined for temperatures below \( T_g \) as these points have larger fluctuations, it is definitely smaller in value than the one above \( T_g \). This observation is consistent with the assignment that crystallization in the glass is interface controlled but diffusion controlled in the viscous liquid.

The observations on methanol provide the first experimental evidence indicating a strong correlation between a change in the nucleation mechanism and \( T_g \). Based on Avrami analysis of nucleation rates determined from linear reflectivity measurements of crystallized fractions, we can clearly identify a change of crystallization mechanism at the refined \( T_g \) of 103.4(±0.1) K for methanol. The measured Avrami parameters and temperature dependent rate constants suggest that in the methanol glass, crystallization occurs as an interface controlled, one-dimension process with a rapid nucleation rate at frozen-in embryo sites, while in the deep supercooled liquid phase, crystallization is diffusion controlled in two dimensions with a constant nucleation rate and an activation energy of 107.8(±4.7) kJ/mol.

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