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Citation: *The Journal of Chemical Physics* **126**, 191111 (2007); doi: 10.1063/1.2741506

View online: <http://dx.doi.org/10.1063/1.2741506>

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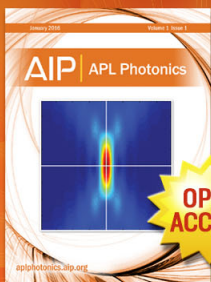
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Crystallization at the glass transition in supercooled thin films of methanol

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(Received 30 December 2006; accepted 19 April 2007; published online 21 May 2007)

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 $107.8(\pm 4.7)$ kJ/mol. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2741506]

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,^{6–10} 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 an ultrahigh vacuum chamber (base pressure 1×10^{-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-

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sure of 2×10^{-6} Torr. Sample temperature was controlled to ± 0.1 K by a temperature controller (Eurotherm 2404) through resistive heating and liquid nitrogen cooling.

In the optical setup for the reflectance measurements, the 632.8 nm output of a He-Ne laser (Melles Griot, 1 mW, polarized), mechanically chopped at 450 Hz, passes through a rotatable polarizer which allows the relative intensities of *s*- and *p*-polarized incident light to be adjusted. The beam then enters the UHV chamber and is incident on the Ag(110) surface at a 60° angle relative to the surface normal and along the $[1\bar{1}0]$ direction. The reflected beam exits the chamber and passes through a polarizing beam splitter which separates the *s*- and *p*-polarized components, which are detected with photodiodes, respectively. The two signals are subtracted from each other via a differential amplifier, and further amplified by a lock-in amplifier. Each experiment begins with the nulling of the differential signal reflected off a clean surface at 85 K by rotating the first polarizer. The resulting optical signal, monitored during the crystallization for a maximum of 3 h, is reported as $\Delta R/R$ described below.

The reflectivity changes from a metal surface during the growth of a thin film overlayer in vacuum can be described by a three media model in which medium 1 is the vacuum, medium 2 the film, and medium 3 the metal substrate. In the experiments, the difference in reflectance of the *p* and *s* components is measured as $\Delta R/R = (\Delta R_p/R_p) - (\Delta R_s/R_s)$. Reflectance of the *s* component R_s (and likewise for the *p* component) is defined through the Fresnel reflection coefficient r_s that can be expressed by the refractive indices of the three media:¹²

$$\frac{\Delta R_s}{R_s} = \frac{R_s(d) - R_s(0)}{R_s(0)} = \frac{|r_{s123}|^2 - |r_{s13}|^2}{|r_{s13}|^2}. \quad (1)$$

The indices of refraction are $\tilde{n}_1 = n_1 = 1$ in a vacuum, $\tilde{n}_2 = n_2$ for a nonabsorbing film, and $\tilde{n}_3 = 0.27 + 4.18i$ for silver at a wavelength close to 2 eV.¹³ 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 β —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 the first order susceptibility as $n_2 = \sqrt{\epsilon_2} = \sqrt{1 + \chi^{(1)}}$. The macroscopic susceptibility can be described by a linear combination of the microscopic polarizabilities of the ordered and disordered phases as $\chi^{(1)} = N_o \alpha_o + N_d \alpha_d$. These relations allow the deduction of the crystallized fraction from the measured change in n_2 .

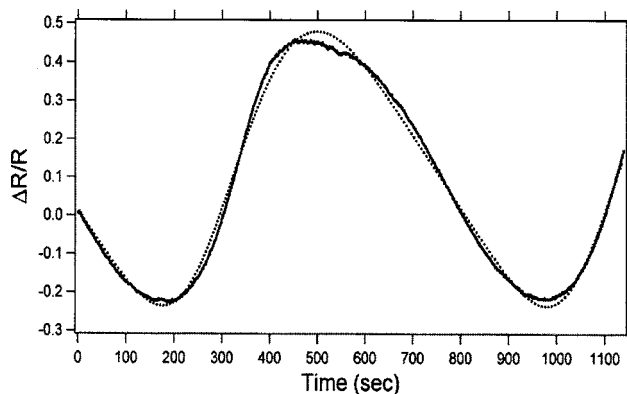


FIG. 1. Differential reflectivity (solid line) measured as a function of exposure time during methanol film growth on Ag(110) at 85 K. The dotted line is the fitting to the three media model in which $n_2 = 1.133 \pm 0.002$.

In the Avrami treatment of isothermal crystallization kinetics,^{14–16} different nucleation and growth mechanisms have correspondingly different time dependences of the crystallization rate. Transformation from the disordered, amorphous phase into the ordered, polycrystalline phase at a fixed temperature can be modeled by the Avrami equation:^{14–16}

$$f_{\text{cry}} = 1 - \exp(-kt^n), \quad (2)$$

where f_{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. Thus the refractive index change during the crystallization process can be related to the Avrami parameter as

$$\chi^{(1)} = \alpha_o f_{\text{cry}} + \alpha_d (1 - f_{\text{cry}}) = \alpha_o + (\alpha_d - \alpha_o) \exp(-kt^n), \quad (3)$$

$$n_2 = [1 + \alpha_o + (\alpha_d - \alpha_o) \exp(-kt^n)]^{1/2}. \quad (4)$$

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 α_d , $(\alpha_d - \alpha_o)$, 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 $n = 0.963 \pm 0.053$, while the nine measurements from 103.5 to 107.5 K (n values from 1.955 ± 0.002 to 2.265 ± 0.006) give $n = 2.110 \pm 0.120$. 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.^{15,16} Remarkably, this abrupt change is coincident with methanol's T_g of 103 K.¹

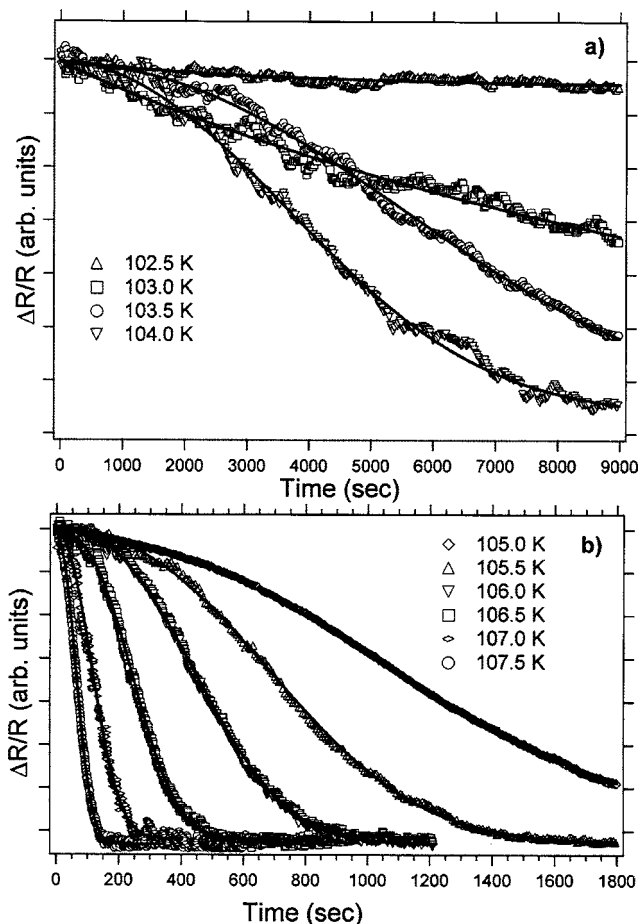


FIG. 2. Differential reflectivity as a function of time during isothermal crystallization at temperatures between (a) 102.5–104 K and (b) 105–107.5 K. The solid lines show the fittings to the Avrami crystallization model. The y-scale intensities in (b) have been normalized to the same initial and final values to aid viewing.

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 $k = k_0 \exp(-E_a/RT)$ and changes with n in units of $(\text{sec})^{1/n}$, Fig. 3 is plotted as $\ln(k^{1/n})$ vs $1/T$. This plot should give a straight line with the slope as activation

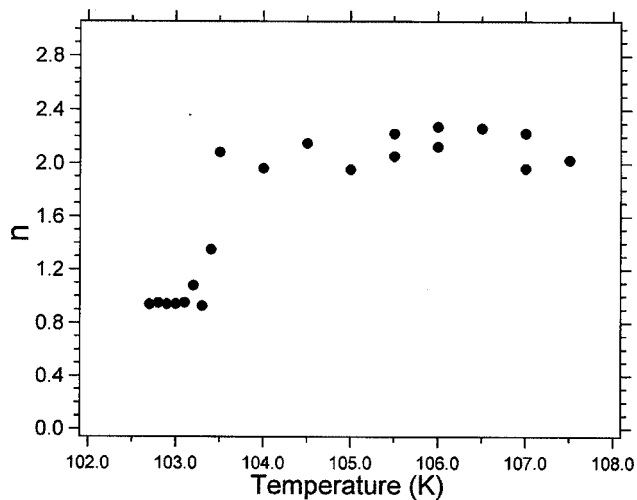


FIG. 3. A plot of the Avrami parameter n as a function of crystallization temperature.

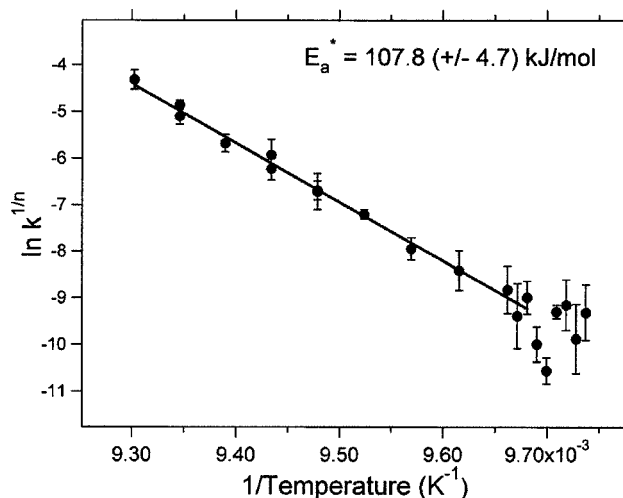


FIG. 4. The Arrhenius plot ($\ln k^{1/n}$ vs $1/T$) of the crystallization rate constants. The solid line shows the linear fitting to the points at $T > 103.4$ K.

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 $E_a^* = 107.8 (\pm 4.7)$ kJ/mol, the activation energy for crystallization in the supercooled liquid phase. 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.^{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 \rightarrow 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 \rightarrow C and A \rightarrow 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 nuclei¹⁶). This condition corresponds to a rapid nucleation rate¹⁶ 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(\pm 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(\pm 4.7) kJ/mol.

This work is supported by a grant from the Air Force Office of Scientific Research. The equipment for this research was supported by a grant from the National Science Foundation, MRSEC program, No. DMR00-79909.

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