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Kissinger method applied to the crystallization of glass-forming liquids: Regimes revealed by ultra-fast-heating calorimetry

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ABSTRACT

Numerical simulation of DSC traces is used to study the validity and limitations of the Kissinger method for determining the temperature dependence of the crystal-growth rate on continuous heating of glasses from the glass transition to the melting temperature. A particular interest is to use the wide range of heating rates accessible with ultra-fast DSC to study systems such as the chalcogenide $Ge_2Sb_2Te_5$ for which fast crystallization is of practical interest in phase-change memory. Kissinger plots are found to show three regimes: (i) at low heating rates the plot is straight, (ii) at medium heating rates the plot is curved as expected from the liquid fragility, and (iii) at the highest heating rates the crystallization rate is thermodynamically limited, and the plot has curvature of the opposite sign. The relative importance of these regimes is identified for different glass-forming systems, considered in terms of the liquid fragility and the reduced glass-transition temperature. The extraction of quantitative information on fundamental crystallization kinetics from Kissinger plots is discussed.

1. Introduction

There is much current interest in ultra-fast differential scanning calorimetry (DSC) [1], also known as chip, flash, thin-film sensor calorimetry, or differential fast scanning calorimetry. This technique, based on a thin-film geometry with very low sample masses (less than 100 ng), greatly extends the capabilities of conventional DSC through access to higher heating rates (up to $\sim 10^6\,\mathrm{K\,s^{-1}}$ [2]) and high sensitivity. The present work is on the application of ultra-fast DSC to study the crystallization of glasses. Conventional DSC has been widely applied, notably to study the crystallization of polymeric and metallic glasses, and work has begun to explore the possibilities of using ultra-fast DSC. For example, the technique has been applied to analyze 'cold crystallization' in glassy polymers [3,4]. Our focus is on the the well known Kissinger method [5] for determining activation energy (Section 2); preliminary uses of this method with ultra-fast DSC have been reported for polymeric [6] and chalcogenide [7,8] systems.

Crystallization can be securely analyzed only if the microstructures at different stages of the reaction are characterized [9]. For example, it is necessary to determine if there is a single crystallization reaction or superposed reactions, if the crystallization occurs uniformly through the sample, what is the shape of the growing crystallites and how their population varies through the crystallization reaction. However, if the basic nature of the crystallization is known (for example by microscopical observation), then DSC can be very convenient for characterizing the crystallization kinetics, and ultra-fast DSC is attractive in extending the capabilities of the method. For fundamental studies of crystallization kinetics, isothermal anneals are attractive. They are limited, unfortunately, to a narrow temperature range: if the anneal temperature is too high, the crystallization starts during the heating up to the isothermal hold; if the anneal temperature is too low, the signal is weak and difficult to distinguish accurately from the DSC baseline. There has therefore been interest in crystallization studies on continuous heating (temperature increasing linearly with time). Crystallization peak shapes are then more difficult to analyze than under isothermal conditions.

While peak shapes can be fitted, the Kissinger method simplifies matters by considering only the peak temperatures T_p (i.e. the temperatures at which the crystallization rate is maximum), and specifically how these shift to higher values at

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higher heating rate Φ. The nature of the shift gives the activation energy for the crystallization process Q, through:

$$\ln\left(\frac{\Phi}{T_p{}^2}\right) = -\frac{Q}{RT_p} + \text{const.} \quad (1),$$

where R is the gas constant. In conventional DSC, the range of heating rates used in applying the Kissinger method is typically two orders of magnitude at most, and the plot of $\ln(Q/RT_p{}^2)$ vs. $(1/T_p)$ is typically a straight line giving a single activation energy. With the greater range of Φ possible with ultra-fast DSC, more complicated behaviour can be expected. Indeed, work on crystallization of the phase-change chalcogenide glass $Ge_2Sb_2Te_5$ (GST) has shown that, over a range of >6 orders of magnitude in Φ (combining data from different techniques including ultra-fast DSC), the Kissinger plot can be markedly curved [7]. In the present work, we build on these results to analyze the origins of the curvature and the extra information that can be obtained from the Kissinger analysis.

The rate of crystal growth as a function of temperature shows a maximum, the rate being limited at low temperature by sluggish kinetics, and at high temperature by lack of thermodynamic driving force. The study by Orava et al. [7] showed that the high heating rates obtainable with ultra-fast DSC enable information to be obtained on the crystal growth at high temperatures close to the growth-rate maximum. This is of technological relevance in the development of phase-change random access memory for which the rate of write/erase operations is limited by the rate of crystallization [7].

In the present work we also explore the regime in which Φ is so high that crystallization occurs mainly at temperatures above the maximum in the crystal growth rate. This leads directly to effective bypassing of crystallization on heating from the glass into the equilibrium liquid state. This possibility was first suggested for a metallic glass by Kui and Turnbull [10] and subsequent studies have shown that the critical heating rate to avoid crystallization is significantly higher (by nearly two orders of magnitude) than the rate to avoid crystallization on cooling (i.e. the critical cooling rate for glass formation) [11]. Avoidance of crystallization on heating is of technological relevance in rapid thermoplastic forming of metallic glasses [12] and has also been investigated for polymers [13].

There are thus a number of areas of practical relevance for studies of crystallization at high heating rates. The phenomena discussed may be observable for some glass-forming systems with conventional DSC, but the much wider range of heating rates accessible with ultra-fast DSC greatly extends the range of materials that can usefully be studied. To explore the usefulness of the Kissinger method over a wide range of heating rate, we perform computer modeling of crystallization rate for a kinetic model in which a fixed number density of crystallites (presumed spherical, of radius r) grow at a rate ($U = \mathrm{d}r/\mathrm{d}t$) that is dependent only on temperature (and not on time t, on r, or on fraction crystallized). This model, though simple, does fit the observed behaviour of, for example, marginal metallic glass-formers, for which eutectic crystallization occurs from a fixed number density of pre-existing (quenched-in) nuclei [14]. The model allows conclusions to be drawn on the validity and usefulness of the Kissinger method in the case of isokinetic crystallization, in which the reaction takes the same course at every temperature with only the timescale being different.

2. The Kissinger method

The Kissinger method has been very widely studied and remains of interest in current work, for example on analyses of complex reaction sequences [15]. In the present work we consider only the analysis of a single reaction. Eq. (1) was originally derived for first-order chemical reactions, but there has been extensive work (for example by Henderson [16]) analyzing its validity when applied to solid-state transformations following Johnson–Mehl–Avrami kinetics, in which the fraction transformed, x, varies with time according to:

$$x = 1 - \exp\left[-(Kt)^n\right] \quad (2),$$

where K is a temperature-dependent kinetic coefficient and n is the Avrami exponent. The transformation gives an exothermic peak in the DSC trace, and as shown by Henderson [16], the value of x at the peak temperature T_p is invariant with a usual value of 0.63(2). The invariance of this value for different Φ validates the use of T_p values in Eq. (1) to derive the activation energy. The validity of the method has also been tested by numerical simulation of DSC peaks (their shape and shifts with Φ): Greer [14] and Kelton [17] found that the Q used as an input for calculation was accurately recovered from the Kissinger method applied to the shifts in the simulated DSC peaks. Importantly, Henderson [16] also suggested that the Kissinger method remains valid when K (Eq. (2)) does not have an Arrhenius temperature dependence. This is examined further in the present work.

The crystallization of a glass (devitrification) occurs by nucleation and growth. As discussed, for example by Kelton [17] for crystallization of $Li_2O{\cdot}2SiO_2$ glass, the Kissinger method predominantly gives the local activation energy (i.e. the activation energy at temperatures close to T_p) for crystal growth. In most cases of continuous heating, crystal nucleation largely precedes growth. The rate of crystallization is affected by number density of nucleation centres (N per unit volume), but N often saturates on heating, determined by the number density of heterogeneities, and thereby is insensitive to the heating rate. Even when the nucleation fully overlaps with growth, the temperature dependence of crystal growth is predominant. Taking the example of steady-state nucleation at a rate I^s and 3-dimensional linear growth at a rate U, then $K = (\pi I U^3/3)^{1/4}$. Where both I^s and U show Arrhenius temperature dependences, with activation energies of Q_I and Q_U respectively, the overall activation energy (as given by the Kissinger analysis) is $Q = (3/4)Q_U + (1/4)Q_I$. In the present work the kinetic model (Section 3), by taking a fixed number density of nucleation sites, focuses only on the temperature dependence of the growth rate.

A practical concern in applying the Kissinger method is with the temperature lag in the calorimeter, such that the temperatures indicated are higher than true sample temperatures. The lag is proportional to the heating rate and increases linearly with the thermal mass of the sample. Using uncorrected temperatures, the measured activation energy is significantly lower than the correct value, by an amount depending on the calorimeter and sample, but typically by ~15% for conventional DSC [14]. Fortunately, correction for the lag is straightforward by standard methods. In the present work, the calculations (Section 3) assume ideal DSC performance: no thermal lag, no temperature gradients within the sample, no limit on heating (cooling) rate or on maximum attainable temperature. The intention is not to model a particular DSC system, but rather to explore the potential and limits of the Kissinger method when applied over a very wide range of Φ as enabled by ultra-fast DSC.

3. The kinetic model

The present study is based entirely on numerical simulation of DSC peaks and does not involve any experimental measurements. The modeling follows the methods used in earlier work [7,14,17], in which linear heating was approximated as a series of short