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Notes

Effect of Specimen Thickness on Crystallization Rate

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In the lore of crystallization studies, there is the general experience that overall crystallization rates measured on bulk specimens (e.g., via DSC or X-ray diffraction) are higher than those measured from thin films (e.g., via small-angle light scattering or by IR). This problem has been addressed in the recent past by detailed modeling of the nucleation, growth, and truncation of spherulites present within the film.[1−3] The present note addresses the same problem by a different route, modifying the Avrami equation by expunging the effects of spherulites which would have existed beyong the surface of the film. In the following, we provide a conceptual picture of the present approach and offer a simple geometrical analysis of the behavior.

The situation can be understood in the context of Figure 1. The space of Figure 1 is to be understood as that of an unbounded molten mass undergoing spherulitic crystallization. Here spherulitic nuclei are taken to be generated randomly in space. In time, the nucleation may occur instantaneously (the classical heterogenous case), at a constant rate (the classical homogeneous case), or at any intermediate condition. The homogeneous case is depicted in Figure 1. In Figure 1 any neighboring spherulite can grow into space that would otherwise be available to any other spherulite. The Avrami analysis[4,5] then addresses this overlap problem and produces a realistic kinetic equation.

Now consider what would occur in a thin molten film. In Figure 1 the space between the dashed lines represents a thin film. Only spherulites which have nucleated within the film (spherulites A and B in the figure) can contribute to its growth. Any spherulite whose center lies outside the film (such as C−F) cannot contribute. On the other hand, spherulites such as C−F will contribute in a bulk specimen and are counted in the Avrami analysis. Because such spherulites do not contribute to crystallization of the thin film, the overall crystallization rate of the film must be lower than that of the bulk. This much is conceptually obvious.

Algebraically, the problem can be treated in the following way. In the Avrami formalism,[1,2] for a bulk of infinite extent, the relationship between the mass fraction transformed *X(t)* and the clock time *t* is

$$X(t) = 1 - \exp\left[-\left(\frac{\rho_s}{\rho}\right)\int_0^t N(t)v(t,\tau)\,d\tau\right] \qquad (1)$$

where ρ_s is the spherulite mass density, ρ is the mass density of the melt, $N(\tau)$ is the nucleation rate (per unit volume), and $v(t,\tau)$ is the volume at time t of a spherulite nucleated at time τ. For the case of a thin film, the spherulitic volume which would have been contributed by out-of-film centers must be subtracted. Thus $v(t,\tau)$ is truncated to a value

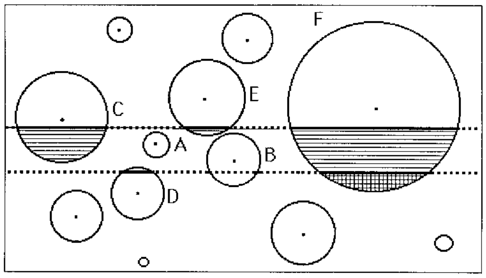

Figure 1. Schematic illustration of homogeneous nucleation in a large system. The dotted line shows the surfaces of a mooted thin film. Spherulites A and B have nucleated within the thin film volume; others have not. Horizontally hatched volumes would be included in an unmodified Avrami analysis. For the doubly hatched volume, see the text and Figure 2.

$$v^*(t,\tau) = v(t,\tau) - \Delta V(t,\tau) \qquad (2)$$

where $\Delta V(t,\tau)$ is the mean in-film contribution of out-of-film spherulites. Equation 1 now becomes

$$X(t) = 1 - \exp\left[-\left(\frac{\rho_s}{\rho}\right)\int_0^t N(t)v^*(t,\tau)\,d\tau\right] \qquad (3)$$

Consider the special case in which the nucleation is perfectly homogeneous; that is, nucleation occurs at a constant rate throughout the untransformed volume. Here, $N(\tau)$ becomes N_0, a constant. In this case, (3) becomes

$$X(t) = 1 - \exp\left\{-\left[\frac{\rho_s}{\rho}N_0\int_0^t v^*(t,\tau)\,d\tau\right]\right\} \qquad (4)$$

In a boundless system, a spherulite nucleated at time τ grows to the volume $v(t-\tau)$ by time t according to

$$v(t-\tau) = \left(\frac{4}{3}\right)\pi[R(t-\tau)]^3 = \left(\frac{4}{3}\right)\pi g^3(t-\tau)^3 \qquad (5)$$

where $R(t-\tau)$ is the instantaneous radius of the spherulite and g is the linear growth rate. Substituting (2) and (5) into (4), we have

$$X(t) = 1 - \exp\left\{-\left(\frac{\rho_s}{\rho}\right)N_0\left[\left(\frac{\pi g^3}{3}\right)t^4 - \int_0^t \Delta V(t,\tau)\,d\tau\right]\right\} \qquad (6)$$

For the opposite limiting case—all nuclei forming at once at time $t = 0$—the corresponding expression would be

$$X(t) = 1 - \exp\left\{-\left(\frac{\rho_s}{\rho}\right)N'\left[\left(\frac{4\pi g^3}{3}\right)t^3 - \int_0^t \Delta V(t)\,d\tau\right]\right\} \qquad (7)$$

where N' is the number of nucleating centers per unit volume.

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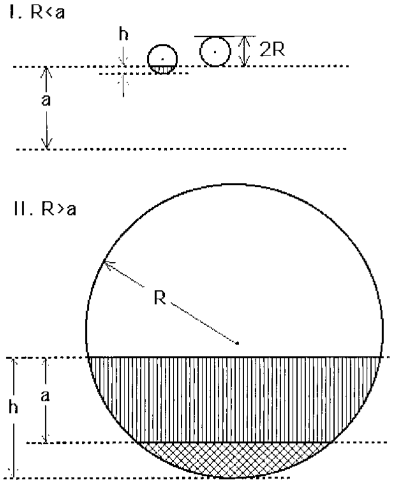

Figure 2. Illustration of volumes to be excluded for the cases (I) $R \leq a$ and (II) $R > a$. Here R is the spherulite radius, a is the film thickness, and h is the height of a spherical cap. In both cases, the vertically hatched volume is to be excluded from the kinetic analysis, but the doubly hatched volume must be retained for case II.

The volume Δv_1 to be excluded for one virtual spherulite nucleated outside the film volume depends on whether or not the radius of the spherulite exceeds the thickness a of the film, as illustrated in Figure 2. If $R \leq a$ (top portion of Figure 2), then a spherical cap is excluded. If $R > a$ (bottom portion of Figure 2), then only the vertically hatched two-based sector of the cap is excluded. The applicable expression for Δv_1 when $R \leq a$ is

$$R < a: \qquad \Delta v_1 = \left(\frac{\pi h^2}{3}\right)(3R - h) \tag{8}$$

where h is the height of the cap. The average value $\langle \Delta v_1 \rangle$ is

$$\langle \Delta v_1 \rangle = \frac{\left(\frac{\pi}{3}\right) \int_0^R h^2 (3R - h)\, \mathrm{d}h}{R} \tag{9}$$

and the relative contribution ΔV to the transformed volume is

$$\langle \Delta V \rangle = \frac{2R}{a} \frac{\left(\frac{\pi}{3}\right) \int_0^R h^2 (3R - h)\, \mathrm{d}h}{R} = \frac{\pi}{2a} R^4 \tag{10}$$

In (10) the factor $2R/a$ represents the relative volume contribution within the film from spherulites whose centers lie outside the film. Substituting $g(t - \tau)$ for R, we have

$$\Delta V = \frac{\pi g^4}{2a} (t - \tau)^4 \tag{11}$$

For $R > a$, the volume $\Delta V'$ of the spherical cap which lies beyond the film must be subtracted from ΔV. An analysis similar to (8)–(11) gives

$R > a$:

$$\Delta V' = \frac{2\pi}{3a} \left\{ g(t - \tau)\, [g(t - \tau) - a]^3 - \frac{[g(t - \tau) - a]^4}{4} \right\} \tag{12}$$

Substituting ΔV or $\Delta V - \Delta V'$ in (6) or (7) and integrating, one now has an expression for the rate of transformation of a thin film.

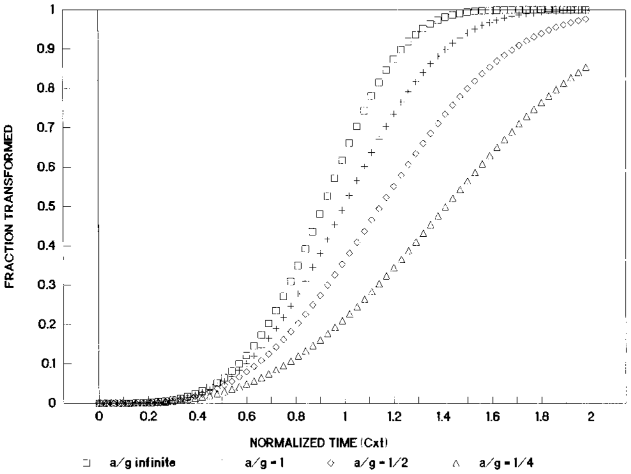

Figure 3. Computed kinetics of transformation for the case of homogeneous nucleation within a film of thickness a. The curves represent $a/g = \infty$, 1, $^1/_2$, and $^1/_4$.

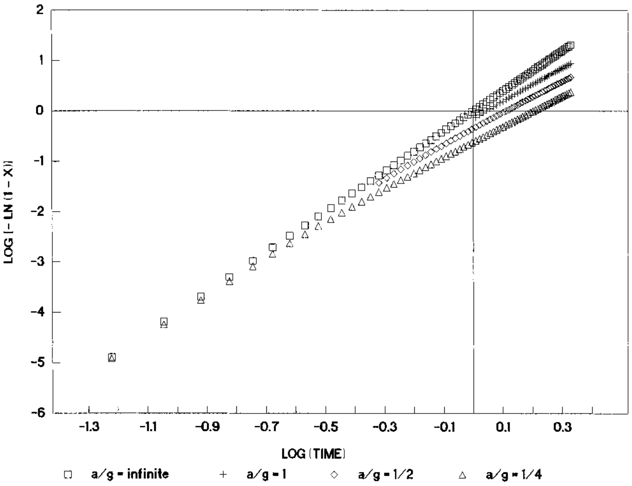

Figure 4. Avrami plots for the case of homogeneous nucleation within a film of thickness a. The curves represent $a/g = \infty$, 1, $^1/_2$, and $^1/_4$.

For illustration, the substitution has been carried out for the case of a homogeneously nucleated system:

$$gt \leq a: \qquad X(t) = 1 - \exp\left\{-Ct^4\left[1 - 0.3\left(\frac{g}{a}\right)t\right]\right\} \tag{13a}$$

$$gt > a: \qquad X(t) = 1 - \exp\left\{-C\left\{\left[t^4 - 0.3\left(\frac{g}{a}\right)t^5\right] - t\frac{\left(t - \frac{a}{g}\right)^4}{\frac{2a}{g}} + \frac{\left[t - \left(\frac{a}{g}\right)\right]^5}{\frac{5a}{g}}\right\}\right\} \tag{13b}$$

where

$$C = \frac{\pi \rho_s N_0 g^3}{3\rho}$$

In an Avrami plot—log{−ln[1 − $X(t)$]} vs log(t)—C acts as a shift parameter along the log(t) axis.

It is noted that the ratio a/g uniquely determines the deviation from the kinetics of transformation of an infinite system. As a/g becomes very large, the kinetics approach those of the ideal system. This condition relates to very thick systems, as expected, but also to slowly crystallizing material (g small). This latter case relates to the condition in which the growth velocity is so slow that the degree of transformation is never large and no appreciable spherulite overlap or encroachment is expected. As a/g becomes small, the correction to the classical kinetics becomes large. This is the condition for very thin systems or cases in which virtual spherulites from outside the system encroach rapidly.

In Figure 3 are plotted the kinetics of homogeneously nucleated transformation for several values of film thickness. Here the degree of transformation $X(t)$ is plotted against t for the cases in which the a/g ratio is infinite, 1, $^1/_2$, and $^1/_4$ s. In (13a,b) the constant C is effectively a time-scaling factor and has been set to unity for the computations. We see in Figure 3 the strong effect of the ratio of film thickness to growth velocity (a/g) on the transformation kinetics.

In Figure 4 is shown the same information as in Figure 3, but plotted in the Avrami format. The slope of the ideal material (a/g infinite) gives the expected Avrami coefficient of 4.0. The Avrami coefficient at later times is lower, the lowest slope shown, for $a/g = {}^1/_4$ s, being 3.15. This demonstrates that thin specimens exhibit anomalously low values of the Avrami coefficient and that values inferred from thin film specimens should be treated with circumspection.

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References and Notes

(1) Stein, R. S.; Powers, J. *J. Polym. Sci.* **1962**, *56*, S9.
(2) Escleine, J. M.; Monasse, B.; Wey, E.; Haudin, J. M. *Colloid Polym. Sci.* **1984**, *262*, 366.
(3) Billon, N.; Escleine, J. M.; Haudin, J. M. *Colloid Polym. Sci.* **1989**, *267*, 668.
(4) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103; **1940**, *8*, 212; **1941**, *9*, 177.
(5) Johnson, W. A.; Mehl, R. F. *Trans. AIME* **1939**, *A16*, 135.

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