

# An Analysis of Transients in Primary Nucleation

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## Synopsis

An analysis is presented of the equations governing time dependent primary nucleation in polymer crystallization. Solution of the one-dimensional diffusion equation for the transient formation of embryos consisting of either chain folded or bundlelike nuclei, near the critical point, leads to a simple expression for estimating the transient time constant. Numerical estimates demonstrate that transient processes are unimportant in solution crystallization and potentially important in melt crystallization unless heterogeneities are present.

## INTRODUCTION

Primary nucleation in polymer crystallization has been extensively analyzed on the basis of expressions derived from the classical kinetic theory for small molecules (e.g., Ref. 1). The number distribution of embryos  $N(\nu, l)dl$ , whether bundles of  $\nu$  chains of crystalline segment length  $l$ ,<sup>2</sup> or single chains with  $\nu$  crystalline segments of length  $l$ ,<sup>3</sup> in the size range  $l$  to  $l + dl$ , is expressed by the equilibrium Boltzmann distribution for the temperature  $T$ ,

$$N(\nu, l)dl = A_0 \exp[-\Delta G(\nu, l)/kT]dl \quad (1)$$

where  $\Delta G(\nu, l)$  is the free energy of forming the embryo, either spontaneously or on a heterogeneity, and  $k$  is the Boltzmann constant. The preexponential term,  $A_0$ , is proportional to the number density of molecules in the system  $n_0$ .<sup>3</sup> Equation (1) in combination with the steady state analysis developed by Turnbull and Fisher<sup>4</sup> leads directly to the familiar steady state expression for the formation of critical-sized stable nuclei  $\dot{N}$ ,<sup>3</sup>

$$\dot{N} = n_0(kT/h) \exp[-(\Delta F^* + \Delta G^*)/kT] \quad (2)$$

where  $\Delta G^*$  and  $\Delta F^*$  are respectively the free energy of forming the stable, 3-dimensional nucleus and the activation energy associated with the jump process at the nucleus interface.

Though eq. (2) has been applied in nearly every published analysis of polymer nucleation, little or no discussion is given of the basis for neglecting transients other than cursory comments to the effect that they should be negligible or that trends in the transformation data are fully consistent with the assumption of steady state nucleation.<sup>5</sup> In light of estimates of nucleation transients for low molecular weight systems,<sup>6</sup> it seems reasonable to expect polymer nucleation to also be a steady state process; on the other hand, simple methods for estimating this effect have not been discussed. Ziabicki<sup>7</sup> has developed a generalized theory of nucleation kinetics from which calculations of the time lag indicate the possibility of very large transients in athermal nucleation from solution. In this paper a more simplified analysis, based on formulations of the 1-dimensional

kinetic equation from earlier treatments of transient nucleation in low molecular weight systems,<sup>6,8</sup> is presented to arrive at a simple expression for estimating the transient time constant for polymer solutions and melts. Such analysis shows that transient processes are unimportant in solution crystallization but potentially important in melt crystallization unless heterogeneities are present.

### TRANSIENT EMBRYO DISTRIBUTION

Using the nomenclature of Lauritzen and Hoffman,<sup>3</sup> the transient formation rate of embryos  $i(l, \nu, t)dl$  with  $\nu$  elements in the range  $l$  to  $l + dl$  can be written for large  $\nu$  as a type of diffusive flux,<sup>8</sup>

$$i(l, \nu, t)dl = -D dl \left[ \left( \frac{\partial \eta}{\partial \nu} \right) + \frac{\eta}{kT} \left( \frac{\partial \Delta G}{\partial \nu} \right) \right] \quad (3)$$

in which  $\eta dl$  is the number concentration of embryos and  $D$  is a diffusion coefficient given in this case by

$$D = kT/h \exp \left( \frac{-\Delta F^*}{kT} \right) \exp \left[ \frac{-(\partial \Delta G / \partial \nu)}{2kT} \right]$$

The steady state form of eq. (3) for  $i(l)dl$  constant can be derived by straightforward application of the scheme developed by Zeldovich,<sup>6,8</sup> which for the region near  $\nu_c$ , where  $(\partial \Delta G / \partial \nu)_{\nu_c} = 0$  and  $\Delta G = \Delta G_c$ , gives the same expression as derived by Lauritzen and Hoffman,<sup>3</sup>

$$i(l)dl = A_0 Z \frac{kT}{h} \exp \left( \frac{-\Delta F^*}{kT} \right) \exp \left( \frac{-\Delta G_c}{kT} \right) dl \quad (4)$$

This shows the nucleation rate near the critical region ( $\nu = \nu_c$ ) to be the product of the equilibrium Boltzmann distribution of such critical embryos with their diffusion coefficient and the nonequilibrium Zeldovich factor,

$$Z = \left[ \frac{1}{2\pi kT} \left( \frac{-\partial^2 \Delta G}{\partial \nu^2} \right)_{\nu_c} \right]^{1/2}$$

Integration of eq. (4) gives  $\int_N [\text{eq. (2)}].^3$  The unsteady embryo distribution for large  $\nu$  satisfies the equation for 1-dimensional diffusion in a force field,<sup>6,8</sup>

$$\frac{\partial \eta}{\partial t} = \frac{\partial}{\partial \nu} \left[ D \left( \frac{\partial \eta}{\partial \nu} + \frac{\eta}{kT} \frac{\partial \Delta G}{\partial \nu} \right) \right] \quad (5)$$

An analytic solution to eq. (5) for short times has been given<sup>9</sup> but of greater interest is the region near  $\nu = \nu_c$  where one can take

$$\frac{\partial \Delta G}{\partial \nu} \approx 0 \quad \text{and} \quad \left( \frac{\partial^2 \Delta G}{\partial \nu^2} \approx \frac{\partial^2 \Delta G}{\partial \nu^2} \right)_{\nu_c}$$

In consequence, eq. (5) reduces to

$$\frac{\partial \eta}{\partial t} = D \frac{\partial^2 \eta}{\partial \nu^2} - 2\pi D Z^2 \eta \quad (6)$$

which is the equation for diffusion with simultaneous first-order reaction for which analytic solutions are available.<sup>10</sup> The initial and boundary conditions consistent with the steady state treatment for homogeneous nucleation<sup>3</sup> are

$$\eta(\nu, 0) = 0 \quad (7a)$$

$$\eta(0,t) = A_0 \quad (7b)$$

$$\eta(\infty,t) = 0 \quad (7c)$$

The solution to eq. (6) can be written as

$$\frac{\eta_\infty - \eta(t)}{\eta_\infty} = \frac{2}{\sqrt{\pi}} \exp(\nu\sqrt{2\pi Z^2}) \int_0^{\nu/2\sqrt{Dt}} \exp\left(-\beta^2 - \frac{\pi Z^2 \nu^2}{2\beta^2}\right) d\beta \quad (8)$$

where  $\eta_\infty$  is the steady state solution,  $A_0 \exp(-\nu\sqrt{2\pi Z^2})$ . An example of eq. (8) for the concentration buildup of the 3-dimensional critical nucleus ( $\nu^* = c^2\sigma_s^2/a(\Delta f)^2$ ,<sup>3</sup> where  $a$  is the molecular cross section,  $c$  a geometric constant =  $2\sqrt{\pi}$ ,  $\sigma_s$  the side surface energy, and  $\Delta f$  the free energy of crystallization) is shown in Figure 1 for various crystallization temperatures of polyethylene in xylene. Inspection shows the time constant to be on the order of  $10^{-9}$  s to  $10^{-10}$  s and therefore fully negligible. A simple means of estimating this from eq. (8) is possible since the steady state occurs for upper limits of the integral on the order of two. Thus the time constant for the critical nucleus,  $\tau^*$ , is roughly,

$$\tau^* \sim \frac{\nu^{*2}}{16D} \sim \frac{c^4\sigma_s^4 h \exp(\Delta F^*/kT)}{16a^2 kT(\Delta f)^4} \quad (9)$$

Likewise, from eqs. (8) and (3),

$$\frac{i(l)dl - i(\nu,l,t)dl}{i(l)dl} = \frac{\exp(\nu\sqrt{2\pi Z^2})}{\sqrt{2\pi}Z} \times \left[ 2\pi Z^2 \nu \int_0^{\nu/2\sqrt{Dt}} \exp\left(-\beta^2 - \frac{\pi^2 Z^2 \nu^2}{2\beta^2}\right) \frac{d\beta}{\beta^2} \frac{-\exp(-\nu^2/4Dt - 2\pi DZ^2 t)}{\sqrt{Dt}} \right] \quad (10)$$

where  $i(l)dl$  is given by eq. (4). Equation (10) has essentially the same transient time constant as given in eq. (9). This expression is, however, not readily integrable to give a form for comparison to eq. (2). The approximate treatment developed by Wakeshima<sup>11</sup> leads instead to

$$i(l,\nu_c,t) = i(l)[1 - \exp(-t/\tau')] \quad (11)$$

where the time constant  $\tau'$  is given by

$$\tau' = 1/4\pi Z^2 D \quad (12)$$

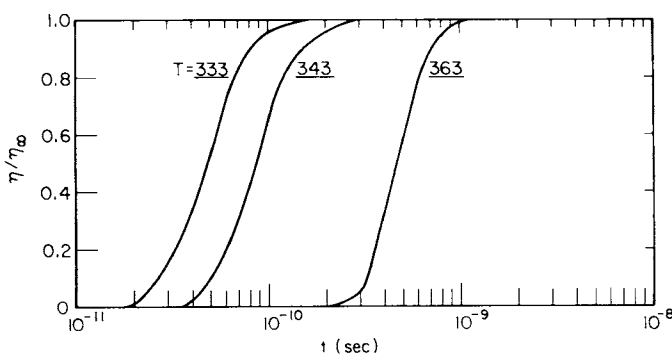


Fig. 1. Dimensionless transient embryo concentration for critical nuclei forming homogeneously vs. time for several different crystallization temperatures. Parameters are typical for polyethylene in xylene.<sup>12</sup>

Treating  $\tau'$  as independent of  $l$  (i.e., at  $l = l^*$ ,<sup>3</sup>  $\tau' = \tau'^*$ ) enables direct integration of eq. (11) to yield

$$\overset{\circ}{N}(t) = \overset{\circ}{N} [1 - \exp(-t/\tau'^*)] \quad (13)$$

However, numerical values of  $\tau'^*$  are generally lower than those predicted by eq. (9) by about 1 order of magnitude. Thus, the more exact form [eq. (9)] is preferred.

For the case of melt crystallization,  $\Delta F^*/kT$  is generally replaced by the approximation<sup>12</sup>  $U^*/R(T - T_\infty)$  and for systems quenched rapidly to low crystallization temperatures, using the more accurate approximation for  $\Delta f$ ,<sup>12</sup>  $\tau^*$  can become quite large. Typically,<sup>12</sup>  $U^* \sim 1500$  cal/mol,  $T_\infty \sim 250^\circ\text{K}$ , and, taking  $T \sim 300^\circ\text{K}$ , the exponential factor in eq. (9) can easily exceed the value for solution growth by factors of  $10^8$  or more, thus yielding time constants approaching measurable values. On the other hand, abundant evidence is available<sup>1</sup> to indicate that melt crystallization is heterogeneous, in which case initial condition (7a) should be replaced by some initial distribution  $\eta'$  which results from heterogeneities, self-seeding, or athermal mechanisms. In consequence, the solution to eq. (6) becomes

$$\frac{\eta}{\eta_\infty} = 1 - \frac{2(A_0 - \eta')}{\eta_\infty \sqrt{\pi}} \int_0^{v/2\sqrt{Dt}} \exp\left(-\beta^2 \frac{\pi Z^2 v^2}{2\beta^2}\right) d\beta \quad (14)$$

which retains the same time constant; however, the effect of  $\eta'$  is to reduce the effect of the transient term on  $\eta$ . A result also shown by the integral formulation for the time lag was developed elsewhere.<sup>13</sup>

To summarize, a simple time constant expression for nucleation transients can be derived from considerations of the classical nucleation equations applied to the critical nucleus formation rate. Numerical estimates indicate that transients in solution nucleation, even under extreme conditions of rapid cooling or stress induced nucleation,<sup>14</sup> should always be negligible. For the case of melt nucleation, the lack of observation of transient kinetics is consistent with the generally accepted description of the nucleation process as heterogeneous. Conclusions regarding transients in chain-folded secondary nucleation have also been considered<sup>15</sup> and lend further credence to the overall treatment of crystallization data in terms of steady state nucleation and growth models.

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## References

1. B. Wunderlich, *Macromolecular Physics*, Academic, New York, 1976, Vol. 2.
2. L. Mandelkern, *Crystallization of Polymers*, McGraw-Hill, New York, 1963.
3. J. I. Lauritzen and J. D. Hoffman, *J. Res. Natl. Bur. Std.*, **64A**, 73 (1960).
4. D. Turnbull and J. C. Fisher, *J. Chem. Phys.*, **17**, 71 (1949).
5. R. L. Cormia, F. P. Price, and D. Turnbull, *J. Chem. Phys.*, **37**, 1333 (1962).
6. J. Feder, K. C. Russell, J. Lothe, and G. M. Pound, *Advan. Phys.*, **15**, 111 (1966).
7. A. Ziabicki, *J. Chem. Phys.*, **48**, 4368, 4374 (1968).
8. J. Frenkel, *Kinetic Theory of Liquids*, Oxford University Press, London, 1946.
9. A. Kantrowitz, *J. Chem. Phys.*, **19**, 1097 (1951).
10. J. Crank, *The Mathematics of Diffusion*, Oxford University Press, London, 1957.
11. H. Wakeshima, *J. Phys. Soc. Jpn.*, **10**, 374 (1955).
12. J. D. Hoffman, G. T. Davis, and J. I. Lauritzen, in *Treatise on Solid State Chemistry*, N. B. Hannay, Ed., Plenum, New York, 1976, Vol. 3, Chap. 7.

13. H. L. Frisch, *J. Chem. Phys.*, **27**, 90 (1957).
14. A. Ziabicki, *Fundamentals of Fiber Formation*, Wiley, New York, 1976, Chap. 1.
15. J. J. Point, *Disc. Faraday Soc.*, **68**, 168 (1979).

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