## Last time
### Growth with moving interfaces—Stefan conditions

### Solidification of Pure Substances

### Diffusional Growth during Precipitation

### Solidification with and without Undercooling

### Shape Stability of moving interfaces; constitutional undercooling

## 3.21 Spring 2002: Lecture 34

# Johnson-Mehl-Avrami: Evolution of Transformation Fraction

Consider the growth stage for the case where a parent phase will undergo a compete transformation to a new equilibrium phase. The amount of new equilibrium phase will depend on time, growth rate and the number of nuclei.

For simplicity, suppose that all the nuclei grow as spheres with constant velocity, $v$, and are nucleated at some different time $\tau$.

The nucleus which nucleated at some time $\tau$ will have a volume at time $t$:

$$V(t,\tau) = \frac{4\pi}{3}R^3 = \frac{4\pi}{3}v^3(t-\tau)^3 \tag{34-1}$$

*If the nuclei do not interfere (collide during growth)*, then the total volume of transformed material is the sum of all the nuclei which have created at times $\tau$

$$V_{total}(t) = \int_0^t \frac{4\pi}{3}v^3(V_{total}\dot{N})(t-\tau)^3 d\tau = \tag{34-2}$$

The volume fraction, $f$, of transformed material is:

$$f = \frac{\pi}{3}\dot{N}v^3t^4 \tag{34-3}$$

*If the nuclei do interfere with each other* (a condition which would apply at either high density of nucleation sites or long times), then the above equation must be modified to account for volumes of particles which are multiply counted. If the particles are nucleated independently, then the volume fraction is given by the *Avrami* equation:

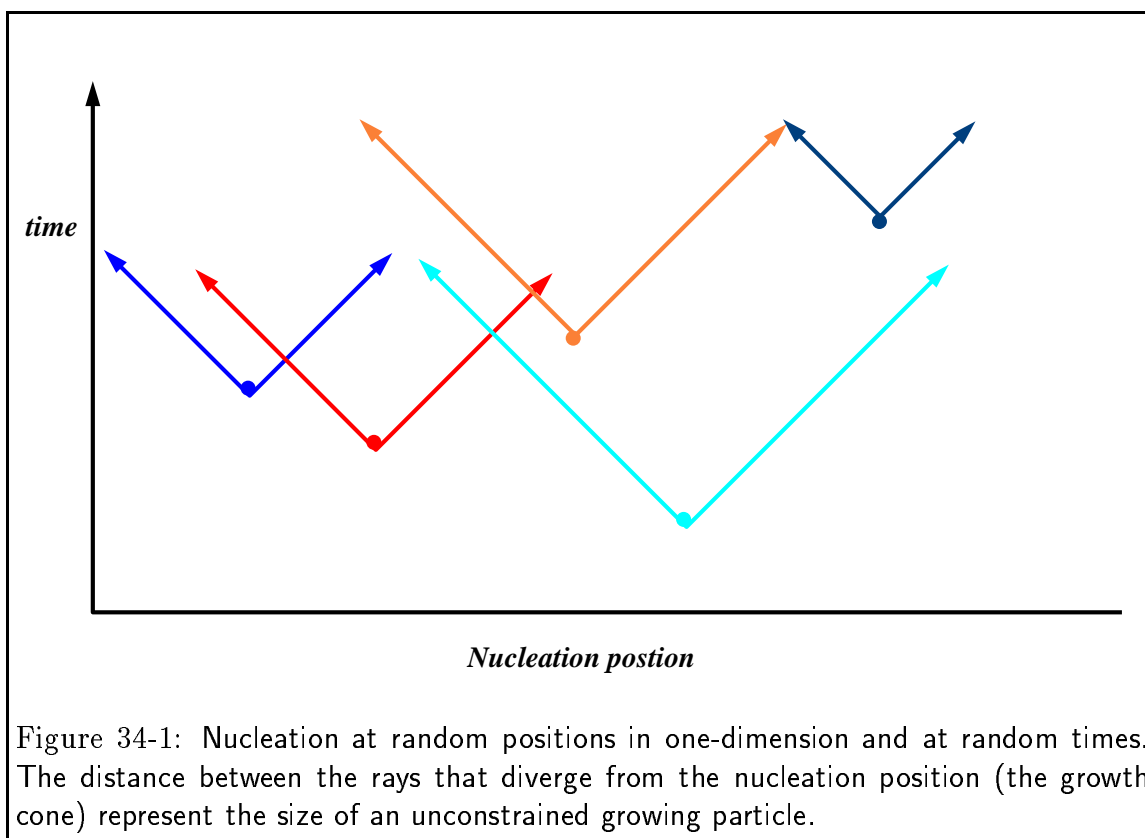$$f = 1 - \exp\left(-\frac{\pi}{3}\dot{N}v^3t^4\right) \tag{34-4}$$

In general, depending on whether all the nuclei appear at one time, or the dimensionality of growth, the general equation for volume transformed looks like:

$$f = 1 - \exp\left(-Kt^n\right) \tag{34-5}$$

This equation summarizes transformation kinetics and is called generally, *Johnson-Mehl-Avrami* kinetics. In any case, $f \to 1$ as $t \to \infty$.

## Cahn's Time-Cone Analysis of JMA Kinetics The method is first described
for the one-dimension case: nucleation and growth on a wire. Extensions to higher dimensional nucleation domains is straightforward.

The first step is to add a time axis to the nucleation domain as follows:



Figure 34-1: Nucleation at random positions in one-dimension and at random times. The distance between the rays that diverge from the nucleation position (the growth cone) represent the size of an unconstrained growing particle.

The small circles in the figure represent random nucleation positions and times. The lines which emanate from the nucleation positions indicate the growth fronts for the particles as a function of time as if the particles do not interact—these are called *growth time-cones*. If the growth rates are constant, the growth cones are truly circular conical shapes. At later

times, some regions are covered by one or more growth cones. Since a particlar region cannot transform twice, it is incorrect to count the overlapping area more than once.

The actual fraction of transformed material can be determined by turning the problem upside-down. Consider an arbitrary test point at some time $t$, that point will *not* have been transformed if and only there is no nucleation event which can influence that point. The nucleation events which can influence that point lie within a *cone of influence* which extends backwards in time from that point:
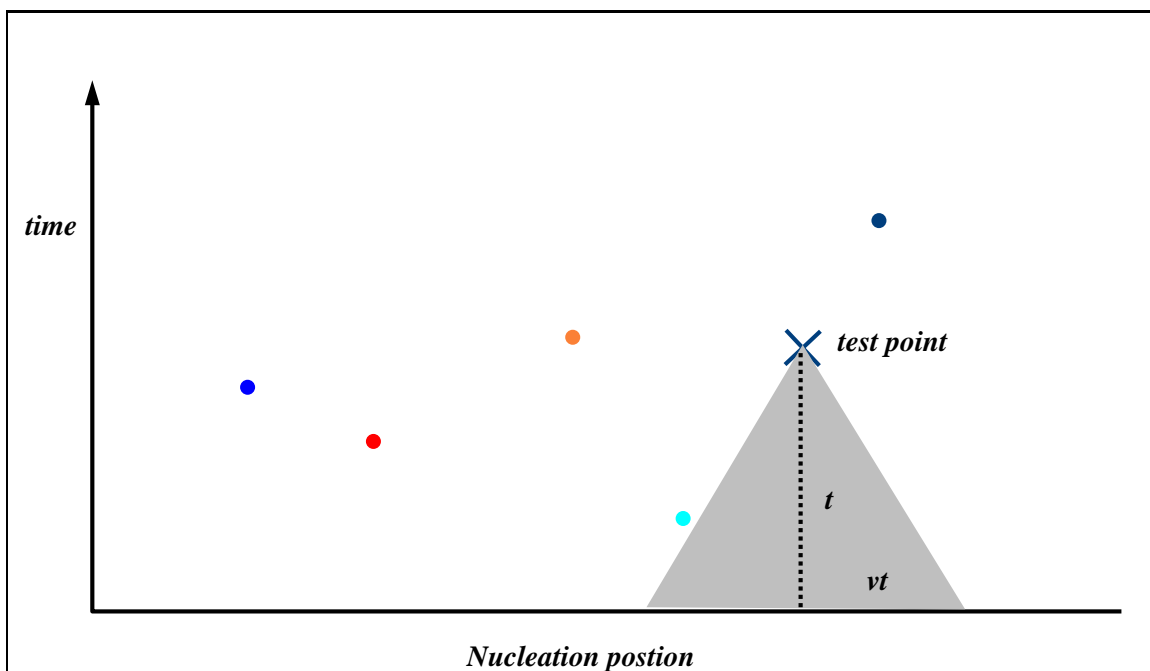


Figure 34-2: The test point also has a set of diverging rays—called the time cone. If there is any nucleation event inside the time cone, then the test point must have transformed.

It is reasonable to assume that the nucleation events are random in time—in this case, Poisson statistics apply. In Poisson statistics, the probability of exactly $n$ events occurring in a volume $V$ is given by:
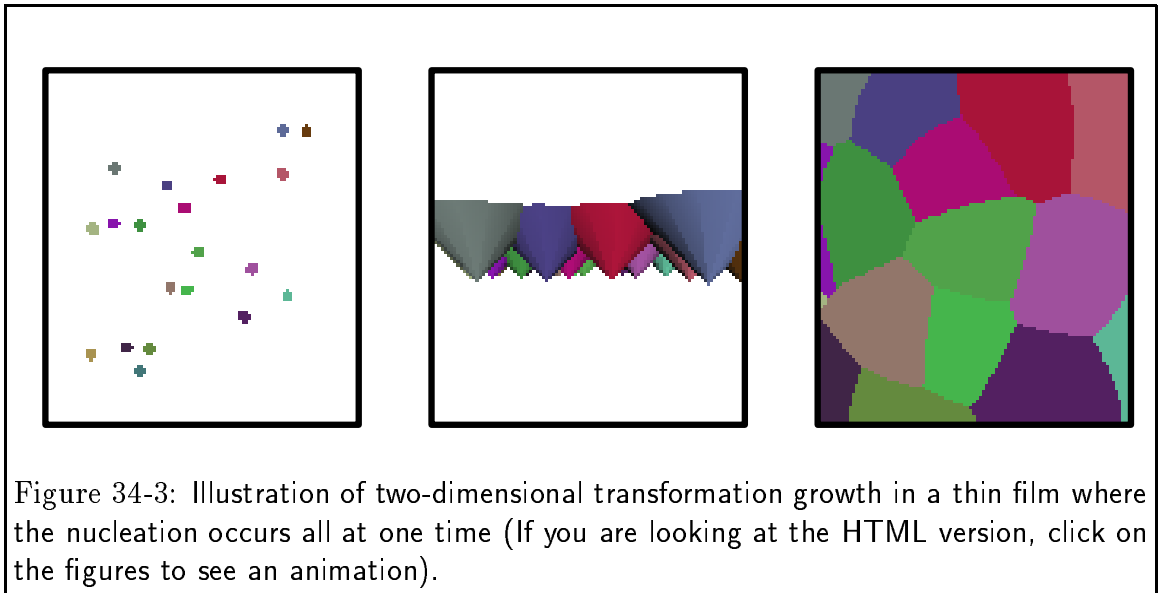
$$P_n(V) = \frac{\langle N \rangle^n}{n!} \exp{-\langle N \rangle} = \frac{(\lambda V)^n}{n!} \exp{-\lambda V} \qquad (34\text{-}6)$$

where $\langle N \rangle$ is the mean number events and $\lambda$ is the average density of events.

In particular, the probability that *no* event occurs is $P_0(V) = \exp - \langle N \rangle$; so the probability that *at least one* event occurs is $1 - \exp - \langle N \rangle$. For the case illustrated in the figure above, one needs to calculate the fraction of points which are influenced by at least one event:

$$f = 1 - \exp[-(\text{events in influence cone})] = 1 - \exp(-\dot{N}vt^2) \qquad (34\text{-}7)$$

For larger dimensionality nucleation domains, the calculation is quite similar:



Figure 34-3: Illustration of two-dimensional transformation growth in a thin film where the nucleation occurs all at one time (If you are looking at the HTML version, click on the figures to see an animation).

The final frame shows the cones from below (looking in direction of increasing time). Since the growth velocity is constant, the resulting microstructure after full impingement is a Voronoi tessellation.

### Example of Time-Cone: Edge Effects

Consider transformation kinetics in one dimension, such as recrystallization in a narrow wire. For a finite wire of length $L$, you might expect that probability that a region will have transformed will depend on the proximity to the end of the wire. Investigate the end effects

on transformation kinetics on a finite length of wire $0 < x < L$, with constant transformation growth rate $\dot{R}$ (length/time) and a constant, uniform, nucleation rate $J$ (number/(length time)). Calculate the probability that a point $x$ will have transformed at time $t$.

This problem is ideally suited for the 'time-cone' method: for each point on the wire, there an 'area' in 'length-time' in which if *any* nucleation occurs, then $x$ will have transformed.



Figure 34-4: Illustration of time cone method for recrystallization on a finite wire.
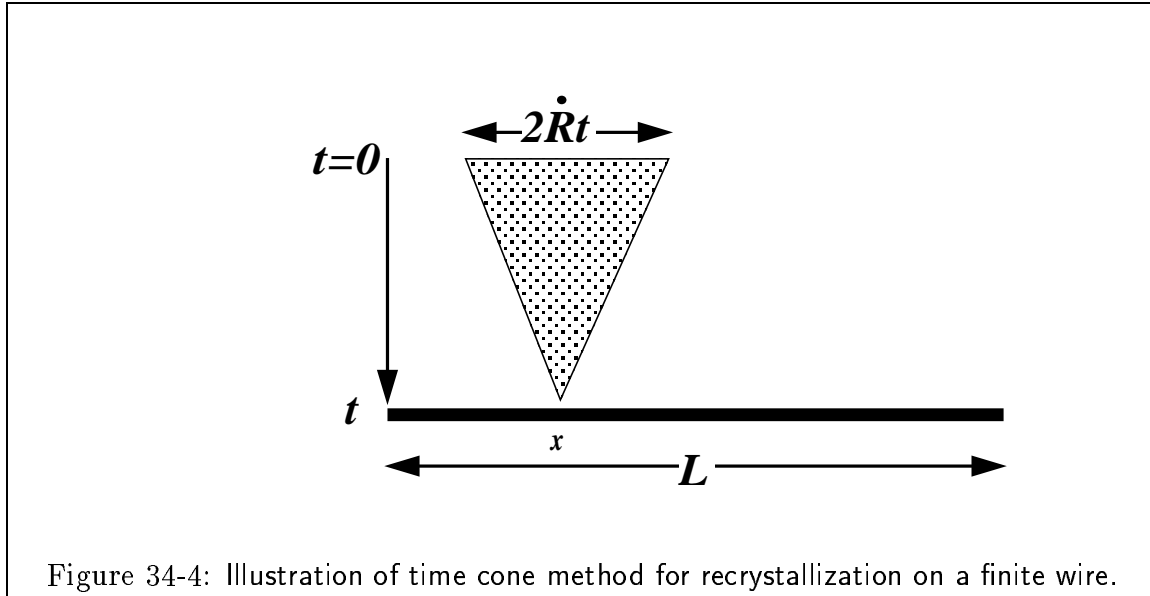
If the nucleation events are independent, then Poisson statistics apply (it may be useful to look in an elementary statistics book) and the key to the solution will be to find the probability that *no* nucleation event occurs in the time-cone for a point $x$.

Poisson statistics apply when events are random and mutually independent, which is assumed to be the case both in time and along the wire.[38] Therefore, the problem depends only on the area of the time cone illustrated for the three distinct cases for $0 < x < L/2$.



*Case I*        *Case II*        *Case III*

Figure 34-5: Illustration of the three possible cases.
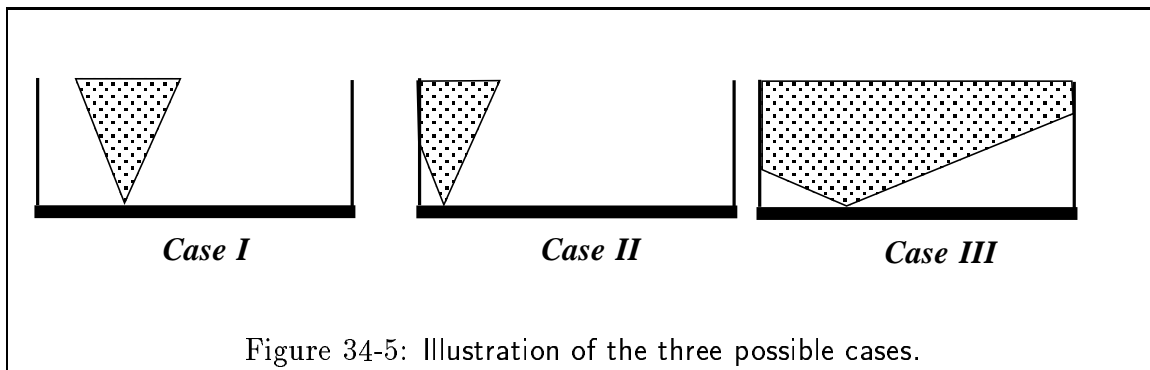
1. **Very short times or effectively infinite $L$** There is no interference from the boundaries. The condition for this case is $x > vt$. The area of the time cone is $A_I = \dot{N}t \times t =$

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[38]It may seem like the probability of a nucleation event must depend on the previous events since the available fraction of untransformed wire (for the occurrence of a nucleation event) is a decreasing function of time. However, such considerations will not affect our result since any nucleation event which would have occurred inside a time cone (representing the transformed region of a previous event) will have its time cone lying completely inside the former. Since we are looking the probability of untransformed wire, such 'ghost' nucleation events cannot change our results.

$vt^2$. The probability that a point $x$ will have transformed is independent of $x$ when $vt < x < L/2$:

$$P = 1 - \exp(-\dot{N}vt^2)$$

2. **Near the end of a finite wire** There is interference from only the boundary at $x = 0$ The condition for this case is $L > vt$ and $x < vt$ (or in a slightly different form, $x < vt$ and $x < L - vt$). The area of the time cone, $A_{II}$, is $A_I$ minus the area where $x < 0$.

$$A_{II} = A_I - \frac{vt - x}{2}\frac{vt - x}{v} = \frac{v^2t^2 + 2vtx - x^2}{2v}$$

so that: $P(n \geq 1, A_{II}) = 1 - \exp(-\dot{N}A_{II})$ or

$$P(n \geq 1, A_{II}) = 1 - (1 - P(n \geq 1, A_I))\exp(\dot{N}\frac{(vt - x)^2}{2v})$$

3. **Very short wire or long times** There is interference from both boundaries. The condition for this case is $L < vt$ (or, $x < vt$ and $x < L - vt$). The area of the time cone, $A_{III}$, is $A_II$ minus the area where $x > L$.

$$A_{III} = A_II - \frac{vt - (L - x)}{2}\frac{vt - (L - x)}{v} = \frac{2(Lvt + Lx) - (L^2 + 2x^2)}{2v}$$

so that: $P(n \geq 1, A_{III}) = 1 - \exp(-\dot{N}A_{III})$