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LETTER TO THE EDITOR

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Abstract. We show that the timescale, τ_g, for rapid growth onset following the nucleation stage, should in general be non-monotonic as a function of quench depth. This behaviour is controlled by the corresponding non-monotonic variation of the critical germ size.

Classical nucleation theory [1, 2] works well for shallow quenches, when supersaturation (or undercooling) is weak compared with barrier height again nucleation, ΔE_c. It leads first to the static quantities, ΔE_c and R_c (the critical germ radius):

$$R_c = 2\gamma/\Delta f \qquad \Delta E_c = \tfrac{16}{3} \pi \gamma^3 [1/(\Delta f)^2] \tag{1}$$

where γ is the interfacial energy, f the free-energy density (including the chemical potential term whenever the order parameter φ is conserved, as e.g. in precipitation). Δf is the free-energy imbalance between metastable and stable phases. In general, Δf is simply proportional to undercooling ΔT and to $\Delta \varphi$, the order-parameter shift from coexistence.

The full energy includes a stiffness term, $\tfrac{1}{2}\lambda|\nabla\varphi|^2$, which controls the kinetics (equation (3) below) and the nucleation rate

$$J \sim \lambda \sqrt{T/\gamma} \exp(-\Delta E_c/T) \sim \tau_n^{-1}. \tag{2}$$

The nucleation time τ_n decreases exponentially with quench depth for shallow quenches due to the decrease of barrier height (1). At deeper quenches, τ_n increases due to the combined effect of $\sqrt{T}\exp(-\Delta E_c/T)$ and $\lambda(T)$. (The intrinsic kinetics slow down at low temperatures, see e.g. [1]). Hence the celebrated 'C shape' of τ_n plotted horizontally against temperature in a so-called time–temperature transformation (TTT) diagram.

That later-stage timescales *should* be C-shaped too, while not following the same quantitative laws, has perhaps not been correspondingly appreciated. A recent numerical 'experiment' [3] identifies a time τ_g for 'catastrophic growth' of crystalline nuclei in quenched liquids. For a broad set of initial conditions, τ_g is much larger than τ_n and shows a non-monotonic dependence on quench depth, first decreasing but then increasing again as quenching proceeds further.

We show here that such a behaviour—definite, but as yet only qualitative—is consistent with the standard Becker–Döring theory [2]. We shall stress the quantitative

effects of order–parameter conservation. This notion has been fully discussed by Nozières [4]. (In facet growth from the melt, for instance, φ is not conserved since the liquid acts as an external reservoir.)

To put our point as simply as possible, we shall assume that (i) viable nuclei grow slowly enough for the inequality $\tau_n \ll \tau_g$ to be enforced; in other words, the two processes, nucleation and growth, do not interfere much and (ii) problems associated with release of latent heat (recalescence) can be ignored within the limits of the model.

Once formed, a nucleus with radius $R > R_c$ grows according to

$$\dot{R} \sim \lambda(R - R_c) \qquad \text{or} \qquad \dot{R} = c(1 - R_c/R) \tag{3}$$

for a conserved or non-conserved φ, respectively. In these expressions, the negative terms represent the slowing-down effect of the capillary force. The rates λ and c are given by the standard theory [2]. In the first case (φ conserved), the growth is exponential ('catastrophic'), with characteristic time

$$\tau_g = R_c^2/D_s \Delta \varphi \sim \lambda^{-1} \tag{4}$$

where D_s is a self-diffusion coefficient and $\Delta \varphi$ is a measure of supersaturation. (This is in fact the relevant case for the work in [3], with D_s replaced by a thermal diffusivity.)

For a non-conserved order parameter, the growth is asymptotically linear, after a typical time

$$\tau_g \sim R_c/c = \gamma R_c/D \Delta f \tag{5}$$

where D is an interface, or 'wall', diffusivity. Strictly speaking, (4) and (5) imply weak undercooling. The following points are to be noted.

(i) The kinetics are controlled by a bulk (D_s), or interface (D), transport coefficient, depending on whether φ is or is not conserved.

(ii) In either case, the variation of τ_g with quench depth will be controlled, in general, by that of the critical radius R_c—which is known to be C-shaped. Close to the coexistence curve ($\varphi \simeq \varphi_{cx}$), R_c^{-1} is of course proportional to the level of undercooling, whereas R_c^{-1} varies as the square root of the distance to the spinodal for $\varphi \simeq \varphi_{sp}$ [5] (see comment below).

(iii) The activation energy ΔE_c—the variation of which with supersaturation dominated the behaviour of τ_n (2)—has now dropped out from both (4) and (5) for τ_g. Growth time-scales are 'barrier free' and the only residual T-dependence, besides $R_c(T)$ and the undercooling itself, is associated with dissipation (D_s or D).

One should not ignore the latter at low temperatures. (D_s, for example, vanishes at the spinodal line and in [3] the observed slowing down is traced back to this effect). But, even so a characteristic time for growth, τ_g, is obtained which is C-shaped as a function of quench depth whether the order parameter is or is not conserved

$$\begin{aligned} \tau_g &\sim (\Delta T)_{cx}^{-3}, (\Delta T)_{sp}^{-1} \qquad (\varphi \text{ conserved}) \\ \tau_g &\sim (\Delta T)_{cx}^{-2}, (\Delta T)_{sp}^{-1/2} \qquad (\varphi \text{ not conserved}) \end{aligned} \tag{6}$$

where ΔT denotes the distance to the coexistence or spinodal curves. The exponents in (6) result from (4) and (5), respectively. It may be recalled that $R_c^{-1} \sim (\Delta T)_{cx}$ whereas $R_c^{-1} \sim (\Delta T)_{sp}^{1/2}$.

As one goes toward the spinodal line, the barrier height ΔE_c decreases of course, while the critical radius R_c increases. But, as Cahn and Hilliard have shown in their

seminal work [5], the order-parameter profile varies smoothly on the scale of the full cluster size. Clearly then, the standard model—based as it is on sharp profile and modest supersaturation—cannot be applied in quantitative detail in the SP region.

Nevertheless, the *trend* (equation (6)) of the growth time τ_g, as a function of super-saturation or undercooling, should stay valid over a wide range of quench depths as long as the concept of metastability, which governs nucleation, remains meaningful, i.e. provided the barrier height remains larger than thermal fluctuations, $\Delta E_c > k_B T$. Indeed, far enough away from the critical point, this condition is enforced down to the close vicinity of the spinodal [4].

To summarise, we expect a non-monotonic variation with quench depth, not only of the nucleation time τ_n, but of the growth time τ_g as well. The latter is smoother ('barrier free', see (iii) above) and is controlled by the variation of R_c with undercooling, itself non-monotonic.

Quantitative experiments, or simulations, with selected characteristics (φ conserved or not, distance to the critical point), would help assess the operative range of this simple model.

References

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