

Viewpoint Paper

Triple lines in nucleation

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Abstract—Triple lines are created when a new phase is nucleated at an interface. Such heterogeneous nucleation is inevitably affected by the tension of the triple lines. Triple lines can also act as sites for nucleation. Experimental examples and analyses of nucleation involving triple lines are reviewed.

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1. Introduction

Along a triple line, three boundaries meet. When all are interphase boundaries, then three phases meet. It is useful to include the possibility of grain boundaries within a phase. Thus two interphase boundaries and a grain boundary can meet at a triple line between two phases, or three grain boundaries can meet at a triple line within a single phase. In homogeneous nucleation, triple lines do not arise, but they are present and potentially important for heterogeneous nucleation on planar defects (surfaces and interfaces, Section 2) and linear defects (triple lines themselves, Section 3). More details can be found in Ref. [1].

2. Nucleation on interfaces and the influence of line tension

For nucleation at an interface, a classical description of the work of formation of an embryo of the new phase includes not only the free energies associated with the volume transformed and with the interfaces between the various phases, but also the energy of the new triple line that bounds the embryo. A special case is nucleation on the surface of an inert, non-deformable planar substrate: we consider a phase β nucleating out of α in contact with a nucleant solid N. Interfacial energies (taken to be isotropic) can be defined between each pair of phases, $\sigma_{\alpha\beta}$, $\sigma_{\alpha N}$ and $\sigma_{\beta N}$. When the inequality

$$\sigma_{\alpha\beta} \geq |\sigma_{\alpha N} - \sigma_{\beta N}|, \quad (1)$$

is satisfied, both α and β phases can simultaneously contact N. A planar α – β interface would meet the surface of N at the contact angle ϕ_∞ given by Young's equation

$$\sigma_{\alpha\beta} \cos \phi_\infty = \sigma_{\alpha N} - \sigma_{\beta N}, \quad (2)$$

derived by balancing interface tensions resolved parallel to the substrate surface (Fig. 1a). The new phase takes the form of a spherical cap (Fig. 1b).

That a triple line must itself have an excess energy was originally noted by Gibbs [2], but this line tension has often been ignored. For a spherical cap of lateral radius R , the line tension Γ alters the mechanical equilibrium, as analysed by Gretz [3,4]; the contact angle ϕ is:

$$\sigma_{\alpha\beta} \cos \phi = \sigma_{\alpha N} - \sigma_{\beta N} - \frac{\Gamma}{R}. \quad (3)$$

From Eq. (2),

$$\cos \phi = \cos \phi_\infty - \frac{\Gamma}{\sigma_{\alpha\beta} R}, \quad (4)$$

showing that $\phi \rightarrow \phi_\infty$ as $R \rightarrow \infty$. Measurements of the contact angle of liquid caps, for example by interferometry [5], show that the effect of line tension is measurable for small R . The variation of ϕ with R is as expected (Fig. 2a), and, using Eq. (4), values of Γ are obtained (Fig. 2b). When Γ is positive, it increases ϕ , impeding the spreading of the spherical cap, i.e. (for liquid caps co-existing with vapour on the substrate) impeding the wetting of the surface. At small sizes, Γ may force detachment of the cap from the surface, even for a phase that would wet the surface macroscopically [6,7].

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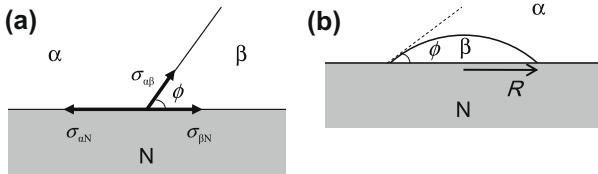


Figure 1. (a) At the junction of a planar α - β interface with a planar substrate surface, the contact angle ϕ is determined by the Young equation (Eq. (2)). (b) The more stable phase, β , forms a spherical cap of lateral radius R .

When Eq. (1) is satisfied, the spherical cap (Fig. 1b) is stable; this is partial wetting. Otherwise, a mechanical balance (Eq. (2)) cannot be established, and there is complete wetting of the substrate by either the α or the β phase. For example, if $\sigma_{\alpha N} > (\sigma_{\alpha\beta} + \sigma_{\beta N})$ when α and β co-exist, then a layer of β always separates α and N . In the case of the α and β phases forming a spinodal system, both $\sigma_{\alpha\beta}$ and $(\sigma_{\alpha N} - \sigma_{\beta N})$ tend to zero on heating towards the critical temperature where the phases merge. But, as $\sigma_{\alpha\beta}$ tends more strongly to zero [8], there should be a transition from partial to complete wetting at a critical temperature T_w (used to normalize the temperature scale in Fig. 2b). This wetting transition and related surface transitions are normally first-order [9,10].

The origins of Γ are complex and have been well reviewed [5,11]. When the α - β interface of the spherical cap approaches the substrate, it is distorted over a length scale comparable to the interface width. Locally the interface curvature can change sign. The line tension, a measure of the energy of the cap not accounted for by volume and interfacial terms, is very dependent on the order of the wetting transition and on the range of intermolecular forces. A typical magnitude of Γ is 10^{-12} to 10^{-10} N [12]; it is temperature-dependent and can change sign (Fig. 2b). Typically for $T \ll T_w$, Γ is negative. For $T \leq T_w$, Γ is positive and it diverges as T_w is approached; nucleation becomes difficult and metastable surface states can be long-lived [13–15]. The line tension can be curvature-dependent, and the consequences of this have been explored [13,16].

We next consider how line tension affects the energy of formation of a spherical-cap nucleus (Fig. 1b). We

consider a condensed system, with original and new phases (α and β) having the same composition, with the same number of molecules per unit volume (avoiding any effects of strain), the Gibbs free energy changing by Δg per unit volume on transformation from α to β . Ignoring line tension, the spherical cap has a contact angle ϕ_∞ set by the interfacial energies (Eq. (2)), and the work of forming an embryo is:

$$W(r) = \left(\frac{4\pi}{3} r^3 \Delta g + 4\pi r^2 \sigma_{\alpha\beta} \right) f(\phi_\infty), \quad (5)$$

where r is the radius of curvature of the α - β interface. This work is that for homogeneous nucleation, multiplied by:

$$f(\phi_\infty) = (2 - 3 \cos \phi_\infty + \cos^3 \phi_\infty) / 4, \quad (6)$$

scaling with the volume of the embryo. Setting $dW/dr = 0$, the critical radius is identical to that for homogeneous nucleation:

$$r^* = - \frac{2\sigma_{\alpha\beta}}{\Delta g}. \quad (7)$$

The work of forming the critical heterogeneous nucleus,

$$W_{\text{het}}^* = W_{\text{hom}}^* f(\phi_\infty) \quad (8)$$

relates to that for the homogeneous case W_{hom}^* by the same $f(\phi_\infty)$, which varies from 0 for $\phi_\infty = 0$ to 1 for $\phi_\infty = \pi$. The presence of a nucleant substrate can thus strongly favour nucleation, especially at low contact angles.

When the line tension Γ is included in the analysis, the contact angle ϕ is given by Eq. (3), and the work of cap formation is:

$$W(r) = \left(\frac{4\pi}{3} r^3 \Delta g + 4\pi r^2 \sigma_{\alpha\beta} \right) f(\phi) + \pi(r \sin \phi) \Gamma. \quad (9)$$

This is similar to Eq. (5), but ϕ is not only different in value from ϕ_∞ ; it also depends on $r \sin \phi$ ($\equiv R$ in Eq. (4)). Because ϕ varies with r , differentiation of $W(r)$ with respect to r is not straightforward. Nevertheless, the critical condition can be found because Eq. (7) still applies for the α - β interface in unstable equilibrium at the critical condition. With r^* determined from Eq. (7) and with a known Γ , Eq. (4) yields a value for ϕ^* , the contact

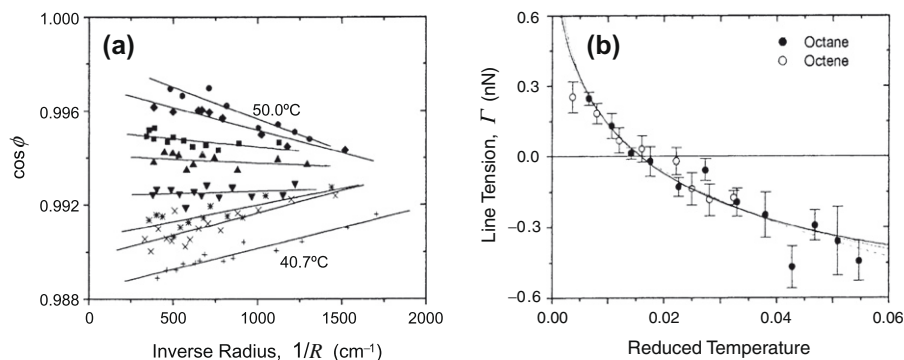


Figure 2. (a) Contact angle ϕ as a function of R ($\cos \phi$ vs. $1/R$) for spherical-cap droplets of 1-octene on coated silicon at temperatures between the values shown. (b) From data as in (a), the line tension Γ for 1-octene and *n*-octane droplets is obtained as a function of reduced temperature $(T_w - T)/T_w$, where T_w is the critical temperature for wetting [5].

angle at the critical condition. With a positive Γ , at low enough r^* there is a regime in which Eq. (4) has no solution. This corresponds to the condition, noted above, where the line tension prevents the formation of a cap and causes detachment of the β phase from the substrate. Outside this regime, Eq. (4) has two solutions but the smaller value applies to the critical nucleus [17]. Taking this value, the work of formation of the critical nucleus W_{het}^* is [3]:

$$W_{\text{het}}^* = W_{\text{hom}}^* f(\phi^*) - \frac{2\pi \sin \phi^* \sigma_{\alpha\beta} \Gamma}{\Delta g} \quad (10)$$

As noted earlier, Γ may be positive or negative. In the latter case, Eq. (4) always has a solution. In the limit of small r^* there would be barrierless formation of small caps on the substrate, even for positive values of the free energy change Δg . As Γ is negative only well below the temperature of the wetting transition, this barrierless regime is probably in the unphysical limit of r^* less than the molecular radius. For large r^* , independent of the sign of Γ , the values of contact angle and W_{het}^* converge on those that would apply in the absence of any line tension. The line tension thus dramatically affects the temperature dependence of nucleation behaviour.

Figure 3 shows measured critical supersaturations for nucleation of zinc condensation onto glass over a broad range of substrate temperature [17]. The data cannot be matched taking $\Gamma = 0$ and a fixed contact angle. On the other hand, a positive Γ ($\sim 4.2 \times 10^{-11} \text{ J m}^{-1}$, decreasing slightly with temperature) gives an excellent fit. This illustrates the general point that self-consistent application of classical theory to heterogeneous nucleation on a substrate must include the line tension. If the line tension is ignored, a breakdown of classical theory as r^* is reduced can appear sooner than is fundamentally justified, as explored next.

The classical theory of nucleation is expected to fail at small values of r^* when the width of the naturally diffuse interface between the original and new phases is comparable to r^* itself. Diffuse interfaces can be treated using density-functional modelling, and this has been applied to nucleation on a planar non-deformable substrate by Talanquer and Oxtoby [18]. Modelling a van der Waals

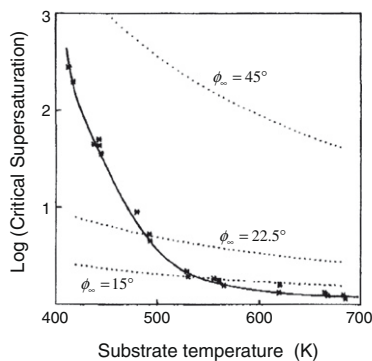


Figure 3. The critical supersaturation for the condensation of zinc vapour onto glass as a function of the substrate temperature. The data cannot be matched for any contact angle ϕ_{∞} neglecting line tension (dashed lines). When line tension is included, a good fit is obtained (solid line) [17].

fluid, with parameters for water, they compared the predictions of classical theory with and without line tension, and density-functional theory. Figure 4 shows the ratio of predicted nucleation rates for temperatures far from the liquid–vapour critical temperature T_c . For homogeneous nucleation at moderate driving force (supersaturation), the classical theory gives good predictions (i.e. close to the results of the density-functional theory); it slightly overestimates the nucleation rate, a problem that gets worse as the temperature is raised towards T_c . This is seen in Figure 4 at large values of contact angle. As ϕ is decreased (by adjusting the interaction with the substrate) to less than 90° , the tendency to overestimate the nucleation rate becomes extreme for the classical theory neglecting line tension. When line tension is included, however, the theory continues to match the density-functional predictions until $\phi < 40^\circ$.

We now give brief consideration to cases other than that of a spherical cap on a planar non-deforming substrate. We note first that the spherical cap cannot provide a good description of the embryo shape if the contact angle is small, for around the edge a substantial fraction of the cap is, unphysically, less than one atomic diameter in height. For such cases, lying beyond our present scope, a pill-box shape is typically assumed. If the substrate is deformable, as when the phase is formed on the interface between two fluids [19,20], a lenticular shape is expected. A similar shape may be found for nucleation on a disordered high-angle grain boundary in α phase. If the new phase β forms with no special orientation relationship with either grain, the two α – β interfaces then have similar energies $\sigma_{\alpha\beta}$, leading to a symmetrical embryo. In general, however, nucleation on a crystal–crystal interface has many possibilities for the embryo shape, depending on whether or not the interphase interfaces are coherent or incoherent, faceted or non-faceted. The line tension must always play a role in determining the embryo shape and its work of formation, but analyses have not considered this.

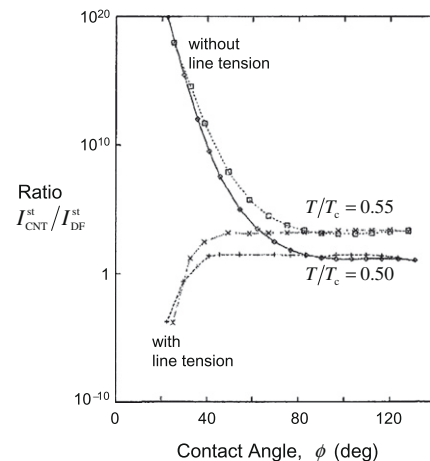


Figure 4. Nucleation rates on a substrate calculated for condensation of a van der Waals fluid based on parameters for water [18]. The steady-state rate $I_{\text{CNT}}^{\text{st}}$ predicted by classical theory with and without line tension is compared with the predictions, $I_{\text{DF}}^{\text{st}}$, of a density-functional-theory calculation for two reduced temperatures.

Line tension effects have been considered in some detail for liquid condensation from a vapour, but have been universally ignored for condensed systems (crystallization from a liquid, precipitation and interfacial reactions in solids). In the former case, the contact angle is measurable (Fig. 2a). In the latter case, such direct characterization is mostly not possible, and in addition the analyses are complicated by factors such as anisotropic interfacial energies. And the line tension itself could in principle be anisotropic.

3. Nucleation on triple lines

Line defects in the form of dislocations are favourable sites for heterogeneous nucleation in crystalline solids [1,21]. Their catalytic action is usually analysed in terms of their line energy, associated with elastic distortions. Triple lines are also nucleation sites, but in contrast their line energy (line tension, Γ) is rarely considered and other factors are the focus of attention. Considering triple lines where three grain boundaries meet, the treatment of Cahn [22], takes the new phase nucleating on this grain edge to have an incoherent interface with each of the surrounding grains. The precipitate embryo is bounded by three surfaces of uniform curvature. The critical work of nucleation can be derived with appropriate geometrical factors that are functions of the contact angle ϕ [22]. For $0 < \phi < \pi$, the work of forming a heterogeneous nucleus is less than that for the homogeneous case, an important contribution to the reduction coming from the energy of the eliminated grain-boundary area. Though not included, the line and point energies of grain edges and corners must play a role.

For incoherent interfaces, it is interesting to analyse how effective grain edges are as nucleation sites, compared to grain faces and corners. For a given contact angle, the work of formation of the critical nucleus decreases in the order: homogeneous nucleation, heterogeneous nucleation on a boundary, on an edge and at a corner. There are, however, large differences in the numbers of molecules that can participate in the nucleation. For homogeneous nucleation all the molecules can participate, and the pre-factor N_V is their number per unit volume. In a polycrystalline material with average grain diameter d and grain-boundary width δ , the number of participating molecules per unit volume is approximately $N_V(\delta/d)$ for nucleation on grain faces, $N_V(\delta/d)^2$ at grain edges and $N_V(\delta/d)^3$ at grain corners. For different conditions, Cahn calculated the dominant nucleation type. For small driving forces the most favourable sites – corners – dominate the transformation. As the driving force is increased, the grain size increased or $\sigma_{\alpha\alpha}/\sigma_{\alpha\beta}$ decreased, however, other, less favourable sites dominate and, in the limit, homogeneous nucleation dominates.

A simpler geometry arises at the planar interface between two reacting phases. Interest in the nucleation of the product phase at such interfaces has been stimulated in particular by reactions in thin films and multilayers. The nucleation of such reactions can be on randomly distributed sites. But in some cases triple lines at grain boundaries in one of the reactant phases (Fig. 5, inset)

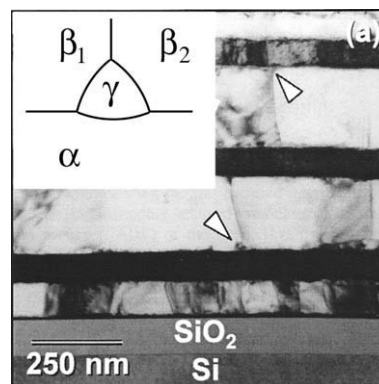


Figure 5. Transmission electron micrograph [23] of a cross-section of a multilayer of Al (thicker) and Nb (thinner) layers. Arrows indicate where Al_3Nb nucleates at the Al–Nb interfaces and grows along grain boundaries in the Al layers (inset).

are preferred sites for nucleation of the product phase. The example in Figure 5 shows the formation of Al_3Nb at the interfaces in multilayers of polycrystalline aluminium and polycrystalline niobium [23]. The density of nucleation sites for the product phase increases with decreasing grain size in the polycrystalline reactants.

While such nucleation effects can be qualitatively explained, detailed analysis is complicated by the evolution of the grain structures themselves during annealing. Grain growth and recrystallization in the original phases, and in the product phase, give complex kinetics and can lead to distinct final grain structures, including equiaxed grain structures in which the initial layering is completely destroyed [23].

In interfacial reactions in thin films, competitive growth often dominates in phase selection [24,25]. However, the selection of a metastable product phase cannot be analysed in this way, and depends on preventing the nucleation of the equilibrium product phases. This has been examined in detail for the solid-state amorphization reaction (SSAR), in which the product phase is amorphous [26,27]. SSAR has been found at the interfaces between many combinations of metals, but we focus only on the most studied: Ni/Zr. When deposited under normal conditions, thin films of nickel or zirconium are polycrystalline, and some amorphous phase is already present at the interfaces between the two metals in the as-deposited state [28]. The SSAR is then not limited by nucleation of the amorphous phase and the reaction proceeds rapidly at 300 °C. In contrast, when polycrystalline Ni is deposited onto single-crystal Zr, there is no interfacial reaction of any kind at 300 °C [29]. Similarly, there is no reaction at 300 °C between polycrystalline Ni and a recrystallized Zr foil, polycrystalline but with only low-energy grain boundaries [30]. Thus, there is clear evidence that high-energy grain boundaries in Zr are required for nucleation of the amorphous phase. Grain boundaries in Ni are not required: SSAR occurs readily at interfaces between single-crystal Ni and polycrystalline Zr [30,31]. This asymmetry in the nucleation of SSAR is expected since Ni is a fast, interstitial diffuser in Zr, while Zr (having twice the atomic volume of Ni) is a slow diffuser in Ni [32]. Finally, we note that the observed barrier to the

formation of the amorphous phase is indeed for nucleation, not growth. SSAR proceeds readily in contact with single-crystal zirconium, provided the initial interface has some amorphous phase nucleated at it by ion-beam mixing [29] or by initial deposition of an amorphous layer [33].

The importance of grain boundaries (in one of the original phases) has been noted for interfacial reactions. The preference for nucleation on grain boundaries can be analysed in terms of the energetic benefit of removal of part of the grain-boundary area. Also, a grain boundary is a fast path (short circuit) for atomic diffusion. Nucleation, and subsequent growth, may be favoured because a grain boundary facilitates the partitioning of solute necessary for the transformation. For nucleation of amorphous Ni–Zr at grain boundaries in Zr, this is unlikely to be significant as there is fast interstitial transport of Ni through the Zr grains. Short-circuit diffusion, while it may sometimes play a role, has also been discounted for other types of interfacial reaction. For example, in conventional aluminium alloys intermetallic particles dispersed in the α -Al matrix may be induced by annealing to transform in situ from one phase to another. The transformation of a given particle nucleates where its surface meets a matrix grain boundary. Detailed study of model systems [34] shows that grain boundaries remain preferred sites even when the composition is no different from the surrounding grains. Instead, grain boundaries may be preferred nucleation sites because plastic flow at boundaries can occur more easily than within a grain [34,35], accommodating shear and volume changes on nucleation, and reducing the contribution of elastic strain energy to the work of formation of the critical nucleus. This may be a key reason why triple lines are favoured sites.

4. Conclusions

Embryos forming on a nucleant substrate are bounded by a triple line, and the line tension affects the energy of their formation. Though extensively analysed for condensation of a liquid from a vapour, the effects of line tension have been ignored for other cases, such as crystallization from a liquid. The other cases are more difficult to characterize experimentally, and further studies may rely heavily on computer modelling, in particular accounting for diffuse interphase interfaces. Triple lines of various kinds within crystalline solids can act as preferred sites for nucleation. Reasons for their potency (line tension, facilitated solute transport and stress relaxation) can be identified, but remain poorly analysed.

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