Supporting Information

Facilitation of Nucleation of Polymorphic Solids Due to the Presence of Multiple Metastable Phases: Effects of Non-Classical Surface Tension

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I. Kinetics of phase transformation

The rate equation for an intermediate metastable phase, MS,i can be written as

$$\begin{aligned} \frac{\partial}{\partial t} P_{MS,i}(r, t) = & -k_{MS,i \rightarrow MS,i+1} P_{MS,i}(r, t) - k_{MS,i \rightarrow MS,i-1} P_{MS,i}(r, t) + k_{MS,i-1 \rightarrow MS,i} P_{MS,i-1}(r, t) \\ & + k_{MS,i+1 \rightarrow MS,i} P_{MS,i+1}(r, t) - k_{Pr} P_{MS,i}(r, t) \end{aligned} \quad (S1)$$

The population of a particular metastable phase, MS,i depends on the radius of that phase, r. k_{Pr} is the rate of precipitation of MS,i state. This behaves like a Heaviside step function

$$k_{Pr} = k(1 - \Theta(R - r)) \quad (S2)$$

Here R is the critical nucleus size. If the radius of a particular phase, r becomes greater than R, then only k_{Pr} is nonzero and nucleation and growth of that particular metastable phase become possible.

II. Analytical Expression of Surface tension

a. Model I

In Model I(Figure 1(a)), we assume the grand free energy density of the free energy surfaces of melt (M), stable solid phase (SS) and metastable phases (MS1, MS2, MS3) have the following forms:

$$\begin{aligned}\Delta\omega_M &= \frac{1}{2}\lambda_M(\rho - \rho_M)^2 \\ \Delta\omega_{MSi} &= \frac{1}{2}\lambda_{MSi}(\rho - \rho_{MSi})^2 + E_0; \quad i = 1, 2, 3 \\ \Delta\omega_{SS} &= \frac{1}{2}\lambda_{SS}(\rho - \rho_{SS})^2\end{aligned}\tag{S3}$$

Here λ_M , λ_{MSi} and λ_{SS} are the curvatures of the free energy surfaces of different phases. If we assume them to be equal, the total surface tension between melt and SS can be written as

$$\begin{aligned}\gamma &= \gamma_1 + \gamma_2 + \gamma_3 + \gamma_4 + \gamma_5 + \gamma_6 + \gamma_7 + \gamma_8 \\ &= 2\sqrt{\kappa} \left[\begin{aligned} &\sqrt{\frac{\lambda}{2}} \int_{\rho_M}^{\rho_1} (\rho - \rho_M) d\rho + \int_{\rho_1}^{\rho_{MS1}} \left[\frac{\lambda}{2} (\rho - \rho_{MS1})^2 + E_0 \right]^{1/2} d\rho + \int_{\rho_{MS1}}^{\rho_2} \left[\frac{\lambda}{2} (\rho - \rho_{MS1})^2 + E_0 \right]^{1/2} d\rho \\ &+ \int_{\rho_2}^{\rho_{MS2}} \left[\frac{\lambda}{2} (\rho - \rho_{MS2})^2 + E_0 \right]^{1/2} d\rho + \int_{\rho_{MS2}}^{\rho_3} \left[\frac{\lambda}{2} (\rho - \rho_{MS2})^2 + E_0 \right]^{1/2} d\rho + \int_{\rho_3}^{\rho_{MS3}} \left[\frac{\lambda}{2} (\rho - \rho_{MS3})^2 + E_0 \right]^{1/2} d\rho \\ &+ \int_{\rho_{MS3}}^{\rho_4} \left[\frac{\lambda}{2} (\rho - \rho_{MS3})^2 + E_0 \right]^{1/2} d\rho + \sqrt{\frac{\lambda}{2}} \int_{\rho_4}^{\rho_{SS}} (\rho - \rho_{SS}) d\rho \end{aligned} \right]\end{aligned}\tag{S4}$$

The first and last terms (γ_1 and γ_8), with $E_0=0$, leads to a simple solution

$$\begin{aligned}
\gamma_1 &= \frac{\sqrt{2\lambda\kappa}}{2}(\rho_1 - \rho_M)^2 \\
\gamma_8 &= \frac{\sqrt{2\lambda\kappa}}{2}(\rho_4 - \rho_{SS})^2
\end{aligned} \tag{S5}$$

However, for the other terms it leads to the solution

$$\begin{aligned}
\gamma_i &= 2\sqrt{\kappa} \int_{\rho_i}^{\rho_{MSi}} \left[\frac{\lambda}{2}(\rho - \rho_{MSi})^2 + E_0 \right]^{1/2} d\rho \\
&= \sqrt{\frac{2\kappa}{\lambda}} E_0 \left[-\sqrt{1 + \frac{\lambda}{2E_0}(\rho_i - \rho_{MSi})^2} \left(\sqrt{\frac{\lambda}{2E_0}}(\rho_i - \rho_{MSi}) \right) \right. \\
&\quad \left. - \arcsin h \left(\sqrt{\frac{\lambda}{2E_0}}(\rho_i - \rho_{MSi}) \right) \right]
\end{aligned} \tag{S6}$$

b. Model II

For Model II(Figure 1(b)), the free energy minima of MS phases are not equal and the grand free energy density of all the phases can be considered by the following forms:

$$\begin{aligned}
\Delta\omega_M &= \frac{1}{2}\lambda_M(\rho - \rho_M)^2 \\
\Delta\omega_{MS1/MS3} &= \frac{1}{2}\lambda_{MS1/MS3}(\rho - \rho_{MS1/MS3})^2 + \frac{E_0}{2} \\
\Delta\omega_{MS2} &= \frac{1}{2}\lambda_{MS2}(\rho - \rho_{MS2})^2 + E_0 \\
\Delta\omega_{SS} &= \frac{1}{2}\lambda_{SS}(\rho - \rho_{SS})^2
\end{aligned} \tag{S7}$$

Total surface energy can be obtained using Eq. (S4), (S5) and (S6).

III. Relation between $\gamma_{M/SS}$ and $\gamma_{M/SS}^w$

If Let us consider the curvatures of two surfaces are equal, then the crossing point of two

surfaces can be defined as $\rho_1 = \frac{\rho_M + \rho_{SS}}{2} = \rho_M + \frac{\Delta\rho}{2}$

where, we define density difference, $\Delta\rho = \rho_{SS} - \rho_M$

The total surface tension between melt(M) and SS phase can be written as

$$\begin{aligned}\gamma_{M/SS} &= \gamma_1 + \gamma_2 = 2\sqrt{\kappa} \left[\sqrt{\frac{\lambda}{2}} \int_{\rho_M}^{\rho_1} (\rho - \rho_M) d\rho + \sqrt{\frac{\lambda}{2}} \int_{\rho_1}^{\rho_{SS}} (\rho - \rho_{SS}) d\rho \right] \\ &= 2 \times \frac{1}{2} \frac{\sqrt{2\kappa\lambda}}{4} (\Delta\rho)^2 = \frac{\sqrt{2\kappa\lambda}}{4} (\Delta\rho)^2 = \frac{\sqrt{2\kappa\lambda}}{4} (\rho_{SS} - \rho_M)^2\end{aligned}\tag{S8}$$

Now, for 2 metastable states in between melt and solid phases,

$$\begin{aligned}\Delta\rho &= \frac{\rho_{SS} - \rho_M}{2+1} \\ \rho_i &= \rho_M + i\Delta\rho; \quad i = 1 \text{ for MS1, } i = 2 \text{ for MS2} \\ \rho_1 &= \rho_M + \frac{\Delta\rho}{2} \\ \rho_2 &= \rho_M + \frac{3}{2}\Delta\rho \\ \rho_3 &= \rho_M + \frac{5}{2}\Delta\rho\end{aligned}\tag{S9}$$

The total surface energy can be written as a sum of six terms:

$$\begin{aligned}
\gamma &= \gamma_1 + \gamma_2 + \gamma_3 + \gamma_4 + \gamma_5 + \gamma_6 \\
&= \sqrt{2\kappa\lambda} \left[\int_{\rho_M}^{\rho_1} (\rho - \rho_M) d\rho + \int_{\rho_1}^{\rho_{MS1}} (\rho_{MS1} - \rho) d\rho + \int_{\rho_{MS1}}^{\rho_2} (\rho - \rho_{MS1}) d\rho \right. \\
&\quad \left. + \int_{\rho_2}^{\rho_{MS2}} (\rho_{MS2} - \rho) d\rho + \int_{\rho_{MS2}}^{\rho_3} (\rho - \rho_{MS2}) d\rho + \int_{\rho_3}^{\rho_{SS}} (\rho_{SS} - \rho) d\rho \right] \\
&= \frac{1}{2} \sqrt{2\kappa\lambda} \left[(\rho_1 - \rho_M)^2 + (\rho_{MS1} - \rho_1)^2 + (\rho_2 - \rho_{MS1})^2 + (\rho_{MS2} - \rho_2)^2 + (\rho_3 - \rho_{MS2})^2 + (\rho_{SS} - \rho_3)^2 \right] \\
&= 6 \times \frac{1}{2} \sqrt{2\kappa\lambda} \left(\frac{\Delta\rho}{2} \right)^2
\end{aligned} \tag{S10}$$

Now, if we use the expression of $\Delta\rho$ from Eq.(S9), we get

$$\begin{aligned}
\gamma_{M/SS}^w &= \frac{1}{2} \sqrt{2\kappa\lambda} \frac{(\rho_{SS} - \rho_M)^2}{4} \times \frac{6}{(3)^2} \\
&= \frac{1}{2} \sqrt{2\kappa\lambda} \frac{(\rho_{SS} - \rho_M)^2}{4} \times \frac{(2N+2)}{(N+1)^2}; \text{ here } N = 2 \text{ for MS1 and MS2} \\
&= \sqrt{2\kappa\lambda} \frac{(\rho_{SS} - \rho_M)^2}{4} \times \frac{1}{(N+1)} \\
&= \frac{\gamma_{M/SS}}{N+1}
\end{aligned} \tag{S11}$$

IV. Fractional dependence of surface tension on number of metastable phases (N)

Figure S1: The scaling parameter, α as a function of the ratio of the curvatures at different energy values (E_0). We have shown the results of model I as a solid line and that of model II as dotted line.