[pex37] Lateral growth of polymer lamellae

Consider a polymer chain modelled as a chain of cubes with side a assembling into stems of length l and undergoing lateral lamellar growth at a temperature $T = T_m(\infty) - \Delta T$ below the bulk melting temperature $T_m(\infty)$.
(a) If L_m is the latent heat of melting per unit volume and σ_f the interfacial energy per unit area, reason that

$$\Delta g = -L_m l a^2 \frac{\Delta T}{T_m(\infty)} + 2a^2\sigma_f \tag{1}$$

is the change in free energy when a stem of length l is added to a preexisting lamella. Note that $L_m/T_m(\infty)$ can be interpreted as the configurational entropy per unit volume lost in the process. Then show that spontaneous growth at given ΔT only takes place if $l > l_c = 2\sigma_f T_m(\infty)/L_m\Delta T$ or $T < T_m(l) = T_m(\infty)[1 - 2\sigma_f/L_m l]$.
(b) If the melt → crystal and crystal → melt transition rates can be written in the form $u_{mc} = \tau^{-1}e^{-\epsilon_{mc}/k_BT}$ and $u_{cm} = \tau^{-1}e^{-\epsilon_{cm}/k_BT}$, respectively, where τ is a convenient reference time scale, and the energy barrierers are $\epsilon_{mc} = T|\Delta S|$ and $\epsilon_{cm} = T|\Delta S| - \Delta g$, respectively, and if we assume that the entropy change is simply proportional to the length of the stem, $|\Delta S|/k_B = l/l_0$, then we can write the velocity of lateral lamellar growth as $v(l) = (u_{mc} - u_{cm})a$. Show if we also assume that $|\Delta g|/k_BT \ll 1$ we obtain

$$v(l) = v_0 e^{-l/l_0}\left[\frac{l}{l_c} - 1\right], \quad v_0 = \frac{2\sigma_f a^3}{\tau k_B T}. \tag{2}$$

Plot v/v_0 versus l/l_0 for a scenario with $l_0/l_c = 2$. Identify the stem length l^* for which lamellar growth is fastest and determine the maximum growth velocity v^*/v_0 for that scenario. Connect that point in the curve by a horizontal and a vertical dashed line to the axes.
(c) Use the Vogel-Fulcher relaxation time, $\tau = \tau_0 \exp(B/(T - T_0))$ from [pln14] to evaluate (2) at $l = l^*$ and bring it into the form shown in [pln55].

[adapted from Jones 2002]

Solution: