Modelling d-banding with phase-field-crystal

I would like to couple d-banding of fibrils into the current free energy picture of the system. One way to do this is to use a phase-field-crystal model approach [**?**], in which the periodic density modulations are described by an additional term in the free energy functional. To start with, I consider the free energy functional F of a cylinder with a radius R, length L, and some internal structure given by a director field $\boldsymbol{n}(\boldsymbol{r})$ and a density $\rho(\boldsymbol{r})$, which is surrounded by a fluid. I'll suppose that the surface tension γ between the cylinder and the fluid depends on whether it is measured on the cylinder's side (with area $2\pi RL$ and $\gamma = \gamma_s$), or on one of the two (flat) tops of the fibril (each with area πR^2 and $\gamma = \gamma_t$). The total free energy is then

$$F(R, L) = \int_0^R \int_0^L \int_0^{2\pi} f(\boldsymbol{r}, \boldsymbol{n}(\boldsymbol{r}), \rho(\boldsymbol{r})) r dr dz d\phi + 2\pi RL\gamma_s + 2\pi R^2 \gamma_t. \tag{1}$$

The equilibrium configuration is determined by minimization of eqn 1 with respect to R, L, $\boldsymbol{n}(\boldsymbol{r})$, and $\rho(\boldsymbol{r})$.

To make this problem tractable, there are several assumptions that must I'm going to apply. The first assumption is that the director field follows a double-twist, so $\boldsymbol{n}$ is reduced to a single twist field $\psi(r)$ which is dependent only on the radius. With no consideration of density fluctuations, this reduces the free energy f to the familiar Frank free energy of a double-twisted liquid crystal,

$$\begin{aligned} f_{dt} =& \frac{1}{2} K_{22} q^2 - K_{22} q \left(\psi' + \frac{\sin 2\psi}{2r} \right) + \frac{1}{2} K_{22} \left(\psi' \frac{\sin 2\psi}{2r} \right)^2 + \frac{1}{2} K_{33} \frac{\sin^4 \psi}{r^2} \\ & - \frac{1}{2} \left(K_{22} + k_{24} \right) \frac{1}{r} \frac{d \sin^2 \psi}{dr}. \end{aligned} \tag{2}$$

The elastic constants k_i and K_j, as well as the inverse cholesteric pitch q, in eqn 2 are dependent on the density of the liquid crystal [**?**], and so density fluctuations may couple into the frank free energy. For this work, I will only allow for density fluctuations along the z axis of the cylinder to mimic the d-banding of fibrils. Without considering the coupling of density to eqn 2, two additional terms from the phase-field-crystal literature can be introduced into the free energy of the form

$$f_{pfc} = \frac{b}{2} \Delta\rho(z) \left[\lambda_0^2 + \frac{\partial^2}{\partial z^2} \right]^2 \Delta\rho(z). \tag{3}$$

$$f_a = c \Delta\rho(z)^2 \left(\Delta\rho(z)^2 - \chi^2 \right) \tag{4}$$

Here, λ_0^{-1} is the length of the d-band period preferred from the molecular interactions (which we ignore the details of). $\Delta\rho(z)$ are the local density fluctuations, and $\chi^2 > 0$ encourages non-zero density fluctuations. For collagen fibrils, we make the hypothesis that the d-band couples with the twist angle by the geometrical construction

$$\lambda_0 = \frac{2\pi}{d_0 \cos\psi(r)}, \tag{5}$$

where $d_0 = 67\,\mathrm{nm}$ is the d-band spacing for a fibril with no twist. This assumption is known as the "projective coupling hypothesis".

To build a tractable form of the free energy, I assume that the elastic constants are independent of the density variations, and assume $\Delta\rho(z) = \delta\cos(\eta z)$. Combining the three parts (eqns 2, 3 and 4) into a single free energy, the free energy per volume of fibril is

$$\begin{aligned}
E \equiv & \frac{F}{\pi R^2 L} \\
= & \frac{2}{R^2}\int_0^R r dr \left[-K_{22} q \left(\psi' + \frac{\sin 2\psi(r)}{2r}\right) + \frac{1}{2}K_{22}\left(\psi' + \frac{\sin 2\psi(r)}{2r}\right)^2 + \frac{1}{2}K_{33}\frac{\sin^4\psi(r)}{r^2}\right] \\
& - (K_{22}+k_{24})\frac{\sin^2\psi(R)}{R^2} + \frac{b\delta^2}{2R^2}\left(1 + \frac{\sin(2\eta L)}{2\eta L}\right)\int_0^R r dr \left(\left[\frac{2\pi}{d_0\cos\psi(r)}\right]^2 - \eta^2\right)^2 \\
& + \frac{c\delta^2}{2}\left(\frac{3}{4}\delta^2 - \chi^2 + \frac{\sin(2\eta L)}{2\eta L}\left(\delta^2 - \chi^2\right) + \delta^2\frac{\sin(4\eta L)}{16\eta L}\right) + \frac{2\gamma_{\mathrm{side}}}{R} + \frac{2\gamma_{\mathrm{top}}}{L}
\end{aligned} \tag{6}$$

Minimization of this free energy corresponds to a $\psi(r)$, R, L, and k which simultaneously satisfy the constraints

$$\frac{\delta E}{\delta\psi} = 0, \tag{7}$$

$$\frac{\partial E}{\partial R} = 0, \tag{8}$$

$$\frac{\partial E}{\partial L} = 0, \tag{9}$$

$$\frac{\partial E}{\partial k} = 0. \tag{10}$$

This is numerically difficult. My best idea so far is to use simulated annealing or gradient descent to determine R, L, and k.