Dimensional vs dimensionless model

I will denote all unscaled variables with a hat over top of them,and all scaled variables without (i.e. $\hat{R}$ has units, R does not).

In its most general form, the unscaled model is

$$\begin{aligned}
\hat{E}(\hat{R},\hat{L};\hat{\psi}(\hat{r}),\hat{\rho}_\delta(\hat{z})) &= \frac{2\pi}{\pi\hat{R}^2\hat{L}}\int_0^{\hat{L}} d\hat{z}\int_0^{\hat{R}}\hat{r}d\hat{r}\left[\frac{1}{2}\hat{K}_{22}\left(\hat{\psi}'+\frac{\sin 2\hat{\psi}}{2\hat{r}}-\hat{q}\right)^2+\frac{1}{2}\hat{K}_{33}\frac{\sin^4\hat{\psi}}{\hat{r}^2}\right]\\
&+\frac{\hat{\Lambda}}{2}\frac{2\pi}{\pi\hat{R}^2\hat{L}}\int_0^{\hat{L}} d\hat{z}\int_0^{\hat{R}}\hat{r}d\hat{r}\hat{\rho}_\delta\left(\frac{4\pi^2}{\hat{d}_0^2\cos^2\hat{\psi}}+\frac{\partial^2}{\partial\hat{z}^2}\right)^2\hat{\rho}_\delta\\
&+\hat{\omega}\frac{\pi\hat{R}^2}{\pi\hat{R}^2\hat{L}}\int_0^{\hat{L}} d\hat{z}\hat{\rho}_\delta^2\left(\hat{\rho}_\delta^2-\hat{\chi}^2\right)-\frac{(\hat{K}_{22}+\hat{k}_{24})}{\hat{R}^2}\sin\hat{\psi}(\hat{R})+\frac{2\hat{\gamma}}{\hat{R}}\\
&=\frac{2}{\hat{R}^2}\int_0^{\hat{R}}\hat{r}d\hat{r}\left[\frac{1}{2}\hat{K}_{22}\left(\hat{\psi}'+\frac{\sin 2\hat{\psi}}{2\hat{r}}-\hat{q}\right)^2+\frac{1}{2}\hat{K}_{33}\frac{\sin^4\hat{\psi}}{\hat{r}^2}\right]\\
&+\frac{\hat{\Lambda}\hat{\chi}^2}{\hat{R}^2\hat{L}}\int_0^{\hat{L}} d\hat{z}\int_0^{\hat{R}}\hat{r}d\hat{r}\left(\frac{\hat{\rho}_\delta}{\hat{\chi}}\right)\left(\frac{4\pi^2}{\hat{d}_0^2\cos^2\hat{\psi}}+\frac{\partial^2}{\partial\hat{z}^2}\right)^2\left(\frac{\hat{\rho}_\delta}{\hat{\chi}}\right)\\
&+\frac{\hat{\omega}\hat{\chi}^4}{\hat{L}}\int_0^{\hat{L}} d\hat{z}\left(\frac{\hat{\rho}_\delta}{\hat{\chi}}\right)^2\left[\left(\frac{\hat{\rho}_\delta}{\hat{\chi}}\right)^2-1\right]-\frac{(\hat{K}_{22}+\hat{k}_{24})}{\hat{R}^2}\sin\hat{\psi}(\hat{R})+\frac{2\hat{\gamma}}{\hat{R}}
\end{aligned}\tag{1}$$

where I have ignored any surface contributions from the ends of the fibril, and $\hat{L}$ is some multiple of the periodic structure along the $\hat{z}$ axis. I have assumed that $\hat{\chi}^2>0$, as the density amplitude term (pre-factor $\hat{\omega}$) would be positive definite if not, meaning no density modulations would occur. The units of $\hat{\Lambda}$ are $\mathrm{pN}\cdot\mu\mathrm{m}^8$, the units of $\hat{\omega}$ are $\mathrm{pN}\cdot\mu\mathrm{m}^{10}$, and the units of $\hat{\chi}^2$ are $\mu\mathrm{m}^{-6}$. If I divide both side of eqn 1 by $\hat{K}_{22}\hat{q}^2$, I can make the system dimensionless and reduce to the form

$$\begin{aligned}
E(R,L;\psi(r),\rho_\delta(z)) &= \frac{2}{R^2}\int_0^R rdr\left[\frac{1}{2}\left(\psi'+\frac{\sin 2\psi}{2r}-1\right)^2+\frac{1}{2}K_{33}\frac{\sin^4\psi}{r^2}\right]\\
&+\frac{\Lambda}{R^2L}\int_0^L dz\int_0^R rdr\rho_\delta\left(\frac{4\pi^2}{d_0^2\cos^2\psi}+\frac{\partial^2}{\partial z^2}\right)^2\rho_\delta\\
&+\frac{\omega}{L}\int_0^L dz\rho_\delta^2\left(\rho_\delta^2-1\right)-\frac{(1+k_{24})}{R^2}\sin\psi(R)+\frac{2\gamma}{R}.
\end{aligned}\tag{2}$$

In general, the liquid crystal elastic constants $\hat{K}_{ii}$, $\hat{q}=\hat{k}_2/\hat{K}_{22}$, and $\hat{k}_{24}$ depend on the density

of the system [**?**]. Therefore, any density modulations $\hat{\rho}_\delta$ from some reference density $\hat{\rho}_0$ must be small. For systems with periodicity in only a single axis, it is reasonable to take a single mode approximation to the density modulations of the form

$$\hat{\rho}_\delta = \delta \cos(\hat{\eta}\hat{z}), \quad \hat{\delta} \ll \hat{\rho}_0. \tag{3}$$

For collagen fibrils, $\hat{\delta} \sim 0.1\hat{\rho}_0$. Inserting the eqn 3 in dimensionless form into eqn 2 and noting that the period of this structure will be $L = 2\pi/\eta$, I get

$$\begin{aligned}
E(R,\eta,\delta;\psi(r)) &= \frac{2}{R^2}\int_0^R rdr\left[\frac{1}{2}\left(\psi' + \frac{\sin 2\psi}{2r} - 1\right)^2 + \frac{1}{2}K_{33}\frac{\sin^4\psi}{r^2}\right] \\
&\quad + \frac{\Lambda}{R^2\frac{2\pi}{\eta}}\int_0^{\frac{2\pi}{\eta}} dz \int_0^R rdr\delta^2\cos^2(\eta z)\left(\frac{4\pi^2}{d_0^2\cos^2\psi} - \eta^2\right)^2 \\
&\quad + \frac{\omega}{\frac{2\pi}{\eta}}\int_0^{\frac{2\pi}{\eta}} dz\delta^2\cos^2(\eta z)\left(\delta^2\cos^2(\eta z) - 1\right) - \frac{(1+k_{24})}{R^2}\sin\psi(R) + \frac{2\gamma}{R} \\
&= \frac{2}{R^2}\int_0^R rdr\left[\frac{1}{2}\left(\psi' + \frac{\sin 2\psi}{2r} - 1\right)^2 + \frac{1}{2}K_{33}\frac{\sin^4\psi}{r^2}\right] \\
&\quad + \frac{\Lambda\delta^2}{2R^2}\int_0^R rdr\left(\frac{4\pi^2}{d_0^2\cos^2\psi} - \eta^2\right)^2 \\
&\quad + \frac{\omega\delta^2}{2}\left(\frac{3}{4}\delta^2 - 1\right) - \frac{(1+k_{24})}{R^2}\sin\psi(R) + \frac{2\gamma}{R}.
\end{aligned} \tag{4}$$

The following is a list of the redefined, dimensionless quantites:

$$E = \frac{\hat{E}}{\hat{K}_{22}\hat{q}^2}, \tag{5}$$

$$R = \hat{R}\hat{q}, \tag{6}$$

$$r = \hat{r}\hat{q}, \tag{7}$$

$$\psi(r) = \hat{\psi}(\hat{r}), \tag{8}$$

$$K_{33} = \frac{\hat{K}_{33}}{\hat{K}_{22}}, \tag{9}$$

$$L = \hat{L}\hat{q}, \tag{10}$$

$$\Lambda = \frac{\hat{\Lambda}\hat{\chi}^2\hat{q}^2}{\hat{K}_{22}}, \tag{11}$$

$$\rho_\delta = \frac{\hat{\rho}_\delta}{\hat{\chi}}, \tag{12}$$

$$\delta = \frac{\hat{\delta}}{\hat{\chi}}, \tag{13}$$

$$\eta = \frac{\hat{\eta}}{\hat{q}}, \tag{14}$$

$$d_0 = \hat{d}_0\hat{q}, \tag{15}$$

$$\omega = \frac{\hat{\omega}\hat{\chi}^4}{\hat{K}_{22}\hat{q}^2}, \tag{16}$$

$$\gamma = \frac{\hat{\gamma}}{\hat{K}_{22}\hat{q}}. \tag{17}$$

Approximating coefficients

Approximating $\hat{\chi}$

To begin with, I will determine the value of $\hat{\chi}$ with two assumptions:

1. The standard d-band model holds, where gap regions have 4/5 the density of filled regions and so $\hat{\delta} = 0.1\hat{\rho}_0$.

2. As the d-banding strength increases, our model is consistent with the standard d-band model, i.e. the dimensional version of $\delta(\omega \to \infty) = \sqrt{2/3}$ is always $0.1\hat{\rho}_0$.

Taking a hexagonal packing of collagen molecules within the fibril with intermolecular spacings of 1.53 nm (cross section) and $\sim$ 35 nm (axial), the primitive unit cell of a fibril has lattice vectors $\boldsymbol{a} = 1.53\,\text{nm}\,\hat{\boldsymbol{x}}$, $\boldsymbol{b} = 1.53\,\text{nm}(0.5\,\hat{\boldsymbol{x}} + 0.866\,\hat{\boldsymbol{y}})$, and $\boldsymbol{c} \sim 330\,\text{nm}\,\hat{\boldsymbol{z}}$, giving a molecular number density $\hat{\rho}_0 \sim 1.67 \times 10^6\,\mu\text{m}^{-3}$, and so $\hat{\delta} \sim 1.67 \times 10^5\,\mu\text{m}^{-3}$ using assumption 1. above. By assumption 2, this implies

$$\hat{\chi} = \sqrt{\frac{3}{2}}\hat{\delta} \sim 2 \times 10^5\,\mu\text{m}^{-3}. \tag{18}$$

Approximating ω

In approximating ω, we can utilize experimental work [**?**] which measures the Gibbs free energy of type I collagen molecules polymerizing into fibrils as $13\,\text{kcal}\,\text{mol}^{-1} \sim 2 \times 10^5\,\text{pN}\,\mu\text{m}^{-2}$. If we assume that most of this energy comes from formation of the d-band, then we can take this value as an estimate for $\hat{\omega}\hat{\chi}^4$. From there, the approximation relies on the estimates of $\hat{K}_{22}$ and $\hat{q}$, which have been estimated in our previous work [**?**]. If we choose $\hat{K}_{22} = 6\,\text{pN}$ and $\hat{q} = 10\,\mu\text{m}^{-1}$, our estimate of ω is

$$\omega = \frac{2 \times 10^5\,\text{pN}\,\mu\text{m}^{-2}}{6\,\text{pN}\,(10\,\mu\text{m}^{-1})^2} \sim 300. \tag{19}$$

Approximating Λ

In order to approximate Λ, we can look at how our model will respond to a small strain on the periodic spacing (i.e. the d-band), a method that has been applied in determining the bulk modulus of contribution in phase field crystal models [**?**]. If I define $\eta_{eq} = 2\pi/d_{eq}$, with d_{eq} being the equilibrium d-band spacing, then expanding our free energy in terms of the applied strain $u = (d - d_{eq})/d_{eq}$ will provide a dimensionless bulk modulus, $K = 1/2\partial^2 E/\partial u^2$, from the definition

$$E(u; R_{eq}, \eta_{eq}, \delta_{eq}) = E(0; R_{eq}, \eta_{eq}, \delta_{eq}) + \frac{1}{2}\left.\frac{\partial^2 E}{\partial u^2}\right|_{u=0} u^2 + \mathcal{O}(u^3). \tag{20}$$

Note that unless the twist field $\psi(r) = 0$ everywhere, $d_{eq} \neq d_0$. In general, $d_{eq} \leq d_0$, as $|\cos\psi(r)| \leq 1$ is constrained by the boundary condition at fibril center, $\psi(0) = 0$, meaning $|\psi(r)| \leq \pi/2$, else

the free energy diverges. Inserting $\eta_{eq}/(1+u)$ into eqn 4,

$$\begin{aligned} E(u; R_{eq}, \eta_{eq}, \delta_{eq}) = \frac{2}{R_{eq}^2}\int_0^{R_{eq}} rdr \left[\frac{1}{2}\left(\psi' + \frac{\sin 2\psi}{2r} - 1\right)^2 + \frac{1}{2}K_{33}\frac{\sin^4\psi}{r^2}\right] \\ + \frac{\Lambda\delta_{eq}^2}{2R_{eq}^2}\int_0^{R_{eq}} rdr \left(\frac{4\pi^2}{d_0^2\cos^2\psi} - \frac{\eta_{eq}^2}{(1+u)^2}\right)^2 \\ + \frac{\omega\delta_{eq}^2}{2}\left(\frac{3}{4}\delta_{eq}^2 - 1\right) - \frac{(1+k_{24})}{R_{eq}^2}\sin\psi(R_{eq}) + \frac{2\gamma}{R_{eq}}. \end{aligned} \tag{21}$$

Evaluating the second order partial derivative at $u = 0$ I find

$$\begin{aligned} K = \frac{1}{2}\left.\frac{\partial^2 E}{\partial u^2}\right|_{u=0} &= \Lambda\delta_{eq}^2\left[\frac{5}{2}\frac{\eta_{eq}^4}{(1+(0))^6} - \frac{3}{2}\frac{d_{eq}^2}{d_0^2}\frac{\eta_{eq}^4}{(1+(0))^4}\frac{2}{R_{eq}^2}\int_0^{R_{eq}} rdr\frac{1}{\cos^2\psi(r)}\right] \\ &= \frac{1}{2}\Lambda\delta_{eq}^2\eta_{eq}^4\left[5 - 3\left(\frac{d_{eq}}{d_0}\right)^2\frac{2}{R_{eq}^2}\int_0^{R_{eq}} rdr\frac{1}{\cos^2\psi(r)}\right] \\ &\sim \Lambda\delta_{eq}^2\eta_{eq}^4, \end{aligned} \tag{22}$$

where I have assumed that the last term is fairly close to 3, which is reasonable for small twist $\psi(r)$. In dimensional units, this bulk modulus becomes

$$\hat{K} = \frac{16\pi^4\hat{\Lambda}\hat{\delta}_{eq}^2}{\hat{d}_{eq}^4}. \tag{23}$$

To approximate the bulk modulus, there are two options. The first is to gauge an approximation from the relationship between hydrostatic pressure and molecular spacing (cite paper Laurent mentioned). The second is to assume that any distribution of d-banding observed in fibrils through e.g. diffraction measurements arise from a thermodynamic distribution with Boltzmann factor $\exp(-\hat{\beta}\Delta E)$, where ΔE is the energy difference between the equilibrium d-band configuration and a configuration with a slight strain. In the latter case, the distribution of fibrils can be fit with a probability distribution function of the form

$$P(u) = P_0\exp\left(\frac{-\beta\hat{K}u^2}{\hat{\rho}_0}\right). \tag{24}$$

Using the full-width half-max (FWHM), *sigma* of a d-band distribution, the modulus $\hat{K}$ can be

determined by

$$\hat{K} = \frac{4 \ln 2 \hat{\rho}_0}{\hat{\beta} \sigma^2} \tag{25}$$

at a given inverse temperature $\hat{\beta}$ and density $\hat{\rho}_0 = 1.67 \times 10^6 \, /\mu\text{m}^{-3}$. Using results from (cite paper with width of 0.13 nm) where $\sigma = 0.13\,\text{nm}/67\,\text{nm} = 1.94 \times 10^{-3}$, the resulting modulus is $\hat{K} = 5.2 \times 10^9\,\text{pN}\,\mu\text{m}^{-2} = 5.2\,\text{GPa}$, which is within a reasonable range of values for a collagen fibril.

Using this value in eqn 23, I get $\hat{\Lambda} = 2.4 \times 10^{-9}\,\text{pN}\mu\text{m}^8$, and so from eqn 11,

$$\Lambda = \frac{2.4 \times 10^{-9}\,\text{pN}\mu\text{m}^8 (2 \times 10^5\,\mu\text{m}^{-3})^2 (10\,\mu\text{m}^{-1})^2}{6\,\text{pN}} \sim 1500 \tag{26}$$

(using the same values of $\hat{q} = 10\,\mu\text{m}^{-1}$ and $\hat{K}_{22} = 6\,\text{pN}$ as I used above in the ω calculation).

References