ENERGY DENSITY FUNCTIONS FOR PROTEIN STRUCTURES

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Summary

In this paper, we adopt the calculus of variations to study the structure of protein with an energy functional $\mathcal{F}(\kappa, \tau, \kappa', \tau')$ dependent on the curvature, torsion and their derivatives with respect to the arc length of the protein backbone. Minimising this energy among smooth normal variations yields two Euler–Lagrange equations, which can be reduced to a single equation. This equation is identically satisfied for the special case when the free-energy density satisfies a certain linear condition on the partial derivatives. In the case when the energy depends only on the curvature and torsion, it can be shown that this condition is satisfied if the free-energy density is a homogeneous function of degree one. Another simple special solution for this case is shown to coincide with an energy density linear in curvature, which has been examined in detail by previous authors. The Euler–Lagrange equations are illustrated with reference to certain simple special cases of the energy density function, and a family of conical helices is examined in some detail.

1. Introduction

The folding of proteins presents one of the most challenging research problems in molecular physics, biochemistry and biology. Difficulties in modelling this problem arise for several reasons, including the complicated molecular structure of proteins and their interactions with other molecules (such as molecular chaperones) and their environment. As misfolding of proteins has been established as the major cause of many illnesses, such as Alzheimer's, mad cow and Creutzfeldt–Jacob diseases (**1**, **2**), understanding the basic mechanisms of folding could lead to new approaches for preventing such diseases. Experimental, theoretical and computational studies of protein structure are all currently very active research areas. Various models have been proposed, including lattice models, statistical mechanical models, random energy models and molecular dynamics simulations. For details of these and other models, see (**3** to **11**) and the references contained therein. Although widely different techniques are employed, all these researchers and others (**12**, **13**) agree that proteins fold into minimum-energy structures. In order to minimise the energy, here we use the approach of the classical calculus of variations and we extend the work of Feoli *et al.* (**14**), who assume that the energy density depends only on the curvature of the protein backbone. In particular, for helical proteins, they examine an energy density function that is linear in curvature, namely $\mathcal{F}(\kappa) = A + B\kappa$, where κ denotes the curvature and A and B denote arbitrary constants. The study of Feoli *et al.* (**14**)

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may be appropriate for the secondary structures α-helix that admit a near-perfect helical shape or the tertiary structures that comprise all the α-helix classes. However, in general, the tertiary or native structures of proteins are of a much more complicated configuration. In order to generalise the basic idea used in (**14**) for more complicated protein structures, the present paper considers those energy density functions that are dependent on the curvature κ, the torsion τ and the derivatives of the curvature and torsion, κ' and τ', of the protein backbone curve. It should be noted that the curvature and torsion encode all geometric information about a curve in three-dimensional (3D) space, up to rotations and translations. While the curvature dependence of the energy is the most significant, in many situations the torsion of the protein backbone may also play an important role. We comment here that particular energy density functions involving both curvature and torsion that are related to elasticity theory, and the ensuing Euler–Lagrange equations, are examined from a purely mathematical perspective in (**15** to **18**), for example.

Further, we note that the study of Feoli *et al.* (**14**) has been extended by Zhang *et al.* (**19**), who consider energy density functions depending on the curvature, torsion and the derivative of the curvature for polymer chains. However, the resulting Euler–Lagrange equations (see (2.31) and (2.32) in (**19**)) are incorrect. Here, we give the correct Euler–Lagrange equations by extending the analysis to the case when $\mathcal{F} = \mathcal{F}(\kappa, \tau, \kappa', \tau')$ and by further simplifying these equations we show that they can be reduced to a single equation (see (2.7) below). This equation constitutes the critical identification of the formal underlying mathematical structure of the two complicated Euler–Lagrange equations. No such identification is given by Zhang *et al.* (**19**) for the corresponding equations.

In this paper, we model the protein backbone or polymer chain as a smooth curve C in Euclidean 3D space. Let $\mathbf{r}(s) = (x(s), y(s), z(s))$ denote the position vector of points on C, where $s \in [a, b]$ is a parameter. In general, the curvature and torsion of C are given respectively by

$$\kappa = \frac{|\mathbf{r}' \times \mathbf{r}''|}{|\mathbf{r}'|^3}, \quad \tau = \frac{\det(\mathbf{r}', \mathbf{r}'', \mathbf{r}''')}{|\mathbf{r}' \times \mathbf{r}''|^2}. \tag{1.1}$$

Here and throughout this paper, we use primes to denote differentiation with respect to the parameter s.

We denote a moving orthonormal frame along the curve C by $\{\mathbf{T}(s), \mathbf{N}(s), \mathbf{B}(s)\}$, where $\mathbf{T}$, $\mathbf{N}$ and $\mathbf{B}$ are, respectively, the unit tangent, normal and binormal vectors at position $\mathbf{r}(s)$. If s denotes the arc length of the protein curve, then the parametrisation is of unit speed, that is, $|\mathbf{r}'(s)| \equiv 1$, and we have the usual 3D Frenet formulae relating derivatives of the moving frame vectors, namely

$$\mathbf{T}' = \kappa\mathbf{N}, \quad \mathbf{N}' = -\kappa\mathbf{T} + \tau\mathbf{B}, \quad \mathbf{B}' = -\tau\mathbf{N}. \tag{1.2}$$

The above formulae for κ and τ obviously simplify in the case of the unit-speed parametrisation. However, in computing variations, we will require the above general formulation. For more details of the above equations, see (**20**) or (**21**).

We consider a variation to the curve by setting

$$\tilde{\mathbf{r}}(s) = \mathbf{r}(s) + \varepsilon_1\psi_1(s)\mathbf{T}(s) + \varepsilon_2\psi_2(s)\mathbf{N}(s) + \varepsilon_3\psi_3(s)\mathbf{B}(s),$$

where ε_1, ε_2 and ε_3 are small parameters and ψ_1, ψ_2 and ψ_3 are arbitrary smooth functions which we assume to have compact support within (a, b), that is, both they and all their derivatives vanish smoothly at the end points of the curve. One may then easily compute the corresponding variation of various quantities associated with the curve including velocity, curvature, torsion and so on. We are interested in energy functionals defined for our space curves by

$$E[\mathbf{r}] := \int_C \mathcal{F}(\kappa, \tau, \kappa', \tau')d\mathcal{L} = \int_a^b \mathcal{F}(\kappa(s), \tau(s), \kappa'(s), \tau'(s))|\mathbf{r}'(s)|ds,$$

where the energy density $\mathcal{F}$ is a suitably differentiable function depending on curvature κ, torsion τ and their derivatives with respect to the arc length, κ' and τ', of the curve. Under the variation to the curve, defined above, we find the Euler–Lagrange equations corresponding to extremising E by setting

$$\frac{\partial}{\partial \varepsilon_i} E[\tilde{\mathbf{r}}]\bigg|_{\varepsilon_1=\varepsilon_2=\varepsilon_3=0} = 0, \quad \text{for each } i = 1, 2, 3. \tag{1.3}$$

In section , we present the Euler–Lagrange equations resulting from (1.3) for the free-energy density depending on the curvature, torsion and the derivatives of both the curvature and the torsion. The detailed mathematical derivations of these equations are provided in Appendices A and B. We again note that the case of $\mathcal{F}$ depending only upon the curvature has been previously examined in Feoli *et al.* (**14**) and the case of $\mathcal{F}$ depending on the curvature, torsion and the derivative of the curvature has also been previously considered by Zhang *et al.* (**19**). Again, we comment that the two Euler–Lagrange equations shown in (**19**) are incorrect. Further, we show that the Euler–Lagrange equations derived here dramatically simplify when expressed in terms of the 'generalised' Legendre transform

$$w(\kappa, \tau, \kappa', \tau') = \kappa \left\{ \frac{\partial \mathcal{F}}{\partial \kappa} - \frac{d}{ds}\left(\frac{\partial \mathcal{F}}{\partial \kappa'}\right) \right\} + \tau \left\{ \frac{\partial \mathcal{F}}{\partial \tau} - \frac{d}{ds}\left(\frac{\partial \mathcal{F}}{\partial \tau'}\right) \right\} + \kappa' \frac{\partial \mathcal{F}}{\partial \kappa'} + \tau' \frac{\partial \mathcal{F}}{\partial \tau'} - \mathcal{F}, \tag{1.4}$$

and indeed, we deduce a single equation for $w(\kappa, \tau, \kappa', \tau')$ (see (2.7) or (2.8) below). From this single equation, it is clear that $w \equiv 0$ and $w \equiv$ constant (assumed non-zero) constitute two special cases. As shown in section 3, when the free-energy density depends only on the curvature and torsion, it can be shown that the case $w \equiv 0$ gives rise to $\mathcal{F}$ being a homogenous function of degree one, namely $\mathcal{F}(\kappa, \tau) = \kappa f(\tau/\kappa)$ for any f, while $w \equiv$ constant can be shown to collapse on the previously mentioned case $\mathcal{F}(\kappa, \tau) = A + B\kappa$, where A and B denote constants. In section 4, we examine certain special cases of the energy densities, including a particular homogeneous function of degree one, and in section 5, we examine a family of conical helices that admit simple expressions for the curvature and torsion and for which we investigate implications of the resulting Euler–Lagrange equations. We note that the conical helix protein structures can be seen in GvpA protein that forms the ribbed gas vesicles in many aquatic bacteria (see, for example, (**22**, **23**, **24**)). In section 6, conclusions are presented, and finally in Appendix C, an alternative derivation to that described by Feoli *et al.* (**14**) is presented for solving the Euler–Lagrange equations when the energy function depends only on the curvature.

2. Euler–Lagrange equations

As shown in Appendices A and B, we find that the variation in the tangential direction $(\partial/\partial\varepsilon_1)$ $E[\tilde{\mathbf{r}}]|_{\tilde{\varepsilon}=0}$ does not result in any information for determining $\mathcal{F}(\kappa, \tau, \kappa', \tau')$. Geometrically, tangential variation corresponds to reparametrising the curve and such variations do not change the energy.

The variations $(\partial/\partial\varepsilon_2)E[\tilde{\mathbf{r}}]|_{\tilde{\varepsilon}=0}$ and $(\partial/\partial\varepsilon_3)E[\tilde{\mathbf{r}}]|_{\tilde{\varepsilon}=0}$ in the normal and the binormal directions give rise to

$$\frac{d^2}{ds^2}\left[\frac{\partial\mathcal{F}}{\partial\kappa}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\kappa'}\right)\right]+\frac{2\tau}{\kappa}\frac{d^2}{ds^2}\left[\frac{\partial\mathcal{F}}{\partial\tau}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\tau'}\right)\right]$$
$$+\left(\frac{\tau'}{\kappa}-\frac{2\kappa'\tau}{\kappa^2}\right)\frac{d}{ds}\left[\frac{\partial\mathcal{F}}{\partial\tau}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\tau'}\right)\right]+(\kappa^2-\tau^2)\left[\frac{\partial\mathcal{F}}{\partial\kappa}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\kappa'}\right)\right]$$
$$+2\kappa\tau\left[\frac{\partial\mathcal{F}}{\partial\tau}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\tau'}\right)\right]+\kappa\left(\kappa'\frac{\partial\mathcal{F}}{\partial\kappa'}+\tau'\frac{\partial\mathcal{F}}{\partial\tau'}-\mathcal{F}\right)=0 \tag{2.1}$$

and

$$-\frac{1}{\kappa}\frac{d^3}{ds^3}\left[\frac{\partial\mathcal{F}}{\partial\tau}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\tau'}\right)\right]+\frac{2\kappa'}{\kappa^2}\frac{d^2}{ds^2}\left[\frac{\partial\mathcal{F}}{\partial\tau}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\tau'}\right)\right]$$
$$+2\tau\frac{d}{ds}\left[\frac{\partial\mathcal{F}}{\partial\kappa}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\kappa'}\right)\right]+\left(\frac{\tau^2}{\kappa}+\frac{\kappa''}{\kappa^2}-\frac{2\kappa'^2}{\kappa^3}-\kappa\right)\frac{d}{ds}\left[\frac{\partial\mathcal{F}}{\partial\tau}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\tau'}\right)\right]$$
$$+\tau'\left[\frac{\partial\mathcal{F}}{\partial\kappa}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\kappa'}\right)\right]-\kappa'\left[\frac{\partial\mathcal{F}}{\partial\tau}-\frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\tau'}\right)\right]=0, \tag{2.2}$$

respectively. We refer the reader to Appendices A and B for details of the derivation of (2.1) and (2.2) and the alternative boundary conditions. We recognise in particular the structure of the square-bracketed terms in (2.1) and (2.2) and expect a similar pattern if higher derivatives of κ and τ are included in the energy. We note that a general pure mathematical formulation of these equations involving exterior differential systems exists in the literature (**25**, pp. 50–56, **26**) but does not include any explicit equations such as (2.1) and (2.2) derived here. Starostin and van der Heijden (**27**) use the general approach to determine the Möbius strip. The Möbius strip is also studied by Hangan (**15**) and Hangan and Murea (**28**), who adopt the specific Sadowsky's functional $\mathcal{F}=\kappa^2(1+\tau^2/\kappa^2)^2$ and derive the two Euler–Lagrange equations that are entirely consistent with our results.

For the case when the energy function depends only on the curvature κ, namely $\mathcal{F}(\kappa(s))$, the Euler–Lagrange equations (2.1) and (2.2) reduce to

$$\frac{d^2}{ds^2}\left(\frac{d\mathcal{F}(\kappa)}{d\kappa}\right)+(\kappa^2-\tau^2)\frac{d\mathcal{F}(\kappa)}{d\kappa}-\kappa\mathcal{F}(\kappa)=0, \tag{2.3}$$

$$\tau'\frac{d\mathcal{F}(\kappa)}{d\kappa}-2\frac{d}{ds}\left[\tau\frac{d\mathcal{F}(\kappa)}{d\kappa}\right]=0, \tag{2.4}$$

respectively. Equations (2.3) and (2.4) are precisely those derived by Feoli *et al.* (**14**). We note that in the context of modelling a relativistic particle with maximal acceleration, Nesterenko *et al.* (**29**) also derive precisely (2.4); however, in their context, the first Euler–Lagrange equation is slightly different and is given by

$$\frac{d^2}{ds^2}\left(\frac{d\mathcal{F}(\kappa)}{d\kappa}\right)-(\kappa^2+\tau^2)\frac{d\mathcal{F}(\kappa)}{d\kappa}+\kappa\mathcal{F}(\kappa)=0.$$

In Appendix C, we show that the integration of (2.3) and (2.4) can be effected in general terms for any given $\mathcal{F}(\kappa)$. The same result can also be found in Feoli *et al.* (**14**), but the procedure given in Appendix C is far more direct and formal. We note that for a curve in two dimensions, where the free-energy function depends only on the curvature, the Euler–Lagrange equation is given by Giaquintoa and Hildebrandt (**21**).

Next, we introduce the transformations $h = p - P'$ and $k = q - Q'$, where $p = \partial\mathcal{F}/\partial\kappa$, $q = \partial\mathcal{F}/\partial\tau$, $P = \partial\mathcal{F}/\partial\kappa'$ and $Q = \partial\mathcal{F}/\partial\tau'$. Upon substituting h and k into (2.1) and (2.2), we obtain

$$h'' + \frac{2\tau}{\kappa}k'' + \left[\frac{\tau'}{\kappa} - \frac{2\kappa'\tau}{\kappa^2}\right]k' + [\kappa^2 - \tau^2]h + 2\kappa\tau k + \kappa(\kappa' P + \tau' Q - \mathcal{F}) = 0,$$

$$-\frac{1}{\kappa}k''' + \frac{2\kappa'}{\kappa^2}k'' + 2\tau h' + \left[\frac{\tau^2}{\kappa} + \frac{\kappa''}{\kappa^2} - \frac{2\kappa'^2}{\kappa^3} - \kappa\right]k' + \tau' h - \kappa' k = 0,$$

for which further simplification gives

$$(\kappa^{-1}[\kappa h + \tau k + \kappa' P + \tau' Q - \mathcal{F}]')' + \tau(k'/\kappa)' + \kappa(\kappa h + \tau k + \kappa' P + \tau' Q - \mathcal{F}) + \tau(\kappa k - \tau h) = 0,$$

$$(k'/\kappa)'' + (\kappa k - \tau h)' - (\tau/\kappa)(\kappa h + \tau k + \kappa' P + \tau' Q - \mathcal{F})' = 0.$$

By introducing $\upsilon = \kappa k - \tau h$ and $w = \kappa h + \tau k + \kappa' P + \tau' Q - \mathcal{F}$, we obtain

$$\frac{1}{\tau}\left(\frac{w'}{\kappa}\right)' + \frac{\kappa}{\tau}w + \left(\frac{k'}{\kappa}\right)' + \upsilon = 0, \tag{2.5}$$

$$\left[\left(\frac{k'}{\kappa}\right)' + \upsilon\right]' = \frac{\tau}{\kappa}w'. \tag{2.6}$$

Thus, by substituting (2.6) into (2.5), we deduce

$$\left[\frac{1}{\tau}\left(\frac{w'}{\kappa}\right)' + \frac{\kappa}{\tau}w\right]' + \frac{\tau}{\kappa}w' = 0 \tag{2.7}$$

as the basic equation for determining the curvature κ and the torsion τ. We note that upon introducing $\xi = \tau/\kappa$ and a new parameter λ such that $d\lambda = \kappa ds$, (2.7) can be written as

$$\frac{d}{d\lambda}\left[\frac{1}{\xi}\left(\frac{d^2w}{d\lambda^2} + w\right)\right] + \xi\frac{dw}{d\lambda} = 0. \tag{2.8}$$

We note here that (2.7) or (2.8) is satisfied identically when $w = 0$, giving rise to

$$\mathcal{F} = \kappa\left\{\frac{\partial\mathcal{F}}{\partial\kappa} - \frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\kappa'}\right)\right\} + \tau\left\{\frac{\partial\mathcal{F}}{\partial\tau} - \frac{d}{ds}\left(\frac{\partial\mathcal{F}}{\partial\tau'}\right)\right\} + \kappa'\frac{\partial\mathcal{F}}{\partial\kappa'} + \tau'\frac{\partial\mathcal{F}}{\partial\tau'}.$$

3. Energy density functions depending only on curvature and torsion

For the remainder of this paper, we deal with the case when the free-energy density depends only on the curvature and torsion, namely $\mathcal{F} = \mathcal{F}(\kappa, \tau)$. For this case, it can be seen that (2.7) or (2.8) is satisfied identically if $w = 0$ or in the other words if $\mathcal{F}(\kappa, \tau)$ is a homogeneous function of degree one, namely

$$\mathcal{F}(\kappa, \tau) = \kappa \frac{\partial \mathcal{F}(\kappa, \tau)}{\partial \kappa} + \tau \frac{\partial \mathcal{F}(\kappa, \tau)}{\partial \tau},$$

for which the function $\mathcal{F}(\kappa, \tau)$ is given by $\mathcal{F}(\kappa, \tau) = \kappa f(\tau/\kappa)$ for an arbitrary function f. In this special case $\mathcal{F}(\kappa, \tau) = \kappa f(\xi)$, where $\xi = \tau/\kappa$, we have $p = f - \xi f_\xi$ and $q = f_\xi$, noting that $f_\xi = df(\xi)/d\xi$. Thus, we may obtain

$$v = \kappa\{(1 + \xi^2) f_\xi - \xi f\}. \tag{3.1}$$

With $w = 0$, we find from (2.5) that $(q'/\kappa)' = -v$, and by combining this with (3.1), we deduce

$$(q'/\kappa)' = -\kappa\{(1 + \xi^2) f_\xi - \xi f\}, \tag{3.2}$$

which from $q = f_\xi$ we may rewrite (3.2) as

$$(f_\xi'/\kappa)' = -\kappa\{(1 + \xi^2) f_\xi - \xi f\}. \tag{3.3}$$

Further, by introducing a parameter λ, where $d\lambda = \kappa ds$, we find that (3.2) reduces to

$$\frac{d^2 q}{d\lambda^2} = -\{(1 + \xi^2) f_\xi - \xi f\}. \tag{3.4}$$

Now, we introduce a Legendre transformation $\rho = \xi f_\xi - f$, where $d\rho = \xi dq$ and $q = f_\xi$. As a result, (3.4) becomes

$$\frac{d^2 q}{d\lambda^2} = -q - \xi\rho. \tag{3.5}$$

By multiplying both sides of (3.5) with $dq/d\lambda$ and using $\xi = d\rho/dq$, (3.5) may be readily integrated to give

$$\left(\frac{dq}{d\lambda}\right)^2 + \rho^2 + q^2 = C_1, \tag{3.6}$$

where C_1 denotes an arbitrary constant. Equation (3.6) can be traced back to the original variables as

$$f_\xi'^2 + \kappa^2\{(1 + \xi^2) f_\xi^2 - 2\xi f f_\xi + f^2\} = C_1\kappa^2, \tag{3.7}$$

remembering that $f_\xi' = df_\xi/ds$.

Finally, in this section, we note from (2.8) that there is also a special case of $w = C$, where C is an arbitrary constant. This case corresponds to $\mathcal{F}(\kappa, \tau) = -C + \kappa f(\xi)$, where $\xi = \tau/\kappa$, and reduces to

$$\frac{d}{d\lambda}\left(\frac{C}{\xi}\right) = 0,$$

for which we may obtain $\tau = \kappa C_1$, where C_1 denotes an arbitrary constant. Accordingly, in this case (for $C \neq 0$), the free-energy density becomes

$$\mathcal{F}(\kappa, \tau) = -C + \kappa f(C_1), \tag{3.8}$$

and therefore coincides with the case of a free-energy density that is linear in curvature and examined in some detail by Feoli *et al.* (**14**). Note, however, that no such simple situation applies when the constant C is zero, that is, when $\mathcal{F}(\kappa, \tau)$ is a homogeneous function of degree one. We observe that for $w = C$, we have from (2.5)

$$\frac{C}{C_1} + \left(\frac{q'}{\kappa}\right)' + \upsilon = 0,$$

which is entirely consistent with (2.6). But from (3.8), we have formally $q \equiv 0$ and $\upsilon = -\tau f(C_1)$ so that $\tau = C/[C_1 f(C_1)]$ which is a constant and corresponds to the case of circular helices studied by Feoli *et al.* (**14**).

In section 4, we give some simple illustrative examples.

4. Some simple special cases

For $\mathcal{F}(\kappa, \tau)$ completely general and $\kappa(s)$ and $\tau(s)$ as yet unspecified, the Euler–Lagrange equations (2.5) and (2.6) (or (2.7)) still constitute a formidable system for further analysis, and progress can only be made either by an examination of a specific simple form of the energy density or by assuming a prescribed curve for the protein, so that precise forms of the curvature and torsion may be deduced from (1.1). In this section, we examine some simple forms for $\mathcal{F}(\kappa, \tau)$ and in section 5, we consider a family of conical helices.

4.1 $\mathcal{F}(\kappa, \tau) = \alpha + \beta\kappa + \gamma\tau$

A simple candidate for an energy with a torsion dependence is a density that is linear in both curvature and torsion, namely $\mathcal{F}(\kappa, \tau) = \alpha + \beta\kappa + \gamma\tau$, where α, β and γ denote arbitrary constants. In this case, the Euler–Lagrange equations (2.1) and (2.2) reduce to

$$-\alpha\kappa + \gamma\kappa\tau - \tau^2\beta = 0, \quad \beta\tau' - \gamma\kappa' = 0,$$

which are easily solved to give

$$\kappa = \frac{-C_0^2\beta}{\alpha + C_0\gamma}, \quad \tau = \frac{\alpha C_0}{\alpha + C_0\gamma}.$$

The corresponding curves are circular helices and these are the only solutions for this particular energy density. Note in particular the different behaviours of the curvature and torsion with respect to the parameters α, β and γ. Such a three-parameter model may be useful in practice for adjusting circular helix shapes in practical protein models.

4.2 $\mathcal{F}(\kappa, \tau) = \sqrt{\kappa^2 + \tau^2}$

In the special case of both $\upsilon = w = 0$, we have that $\mathcal{F}(\kappa, \tau)$ is a homogeneous function of degree one, which is given by $\mathcal{F}(\kappa, \tau) = \kappa f(\xi)$, where $\xi = \tau/\kappa$, and that

$$\kappa\frac{\partial\mathcal{F}(\kappa, \tau)}{\partial\tau} = \tau\frac{\partial\mathcal{F}(\kappa, \tau)}{\partial\kappa}. \tag{4.1}$$

By substituting $\mathcal{F}(\kappa, \tau)$ into (4.1), we obtain an ordinary differential equation $(1 + \xi^2) f_\xi = \xi f$, which can be integrated to give $f = \sqrt{1 + \xi^2}$ or $\mathcal{F}(\kappa, \tau) = \sqrt{\kappa^2 + \tau^2}$.

Upon substituting $f = \sqrt{1+\xi^2}$ into (3.3) or (3.7), we find that this equation reduces to $f'_\xi = C\kappa$, where C is an arbitrary constant. Thus, we deduce an equation for determining κ and τ, namely

$$\frac{d}{ds}\left(\frac{\tau}{\sqrt{\kappa^2+\tau^2}}\right) = C\kappa, \tag{4.2}$$

and this is the sole consequence of the Euler–Lagrange equations when $\mathcal{F}(\kappa,\tau) = \sqrt{\kappa^2+\tau^2}$.

4.3 $\mathcal{F}(\kappa,\tau) = g(\kappa)f(\tau)$

Here, we look at the two special cases when $\mathcal{F}(\kappa,\tau) = \kappa f(\tau)$ and $\mathcal{F}(\kappa,\tau) = \tau g(\kappa)$. Thus, we have $w = \kappa\tau f_\tau$ and $w = \kappa\tau g_\kappa$, respectively. For $\mathcal{F}(\kappa,\tau) = \kappa f(\tau)$, we find that (2.1) and (2.2) become, respectively,

$$2\tau\tau'^2 f_{\tau\tau\tau} + \left[2\tau'^2 + \frac{2\tau}{\kappa}\kappa'\tau' + 2\tau\tau''\right] f_{\tau\tau} + \left[\tau'' + \frac{2\tau}{\kappa}\kappa'' + \frac{\tau'\kappa'}{\kappa} - \frac{2\kappa'^2\tau}{\kappa^2} + 2\tau\kappa^2\right] f_\tau - \tau^2 f = 0,$$

$$\tau'^3 f_{\tau\tau\tau\tau} + \left[\frac{\kappa'\tau'^2}{\kappa} + 3\tau\tau''\right] f_{\tau\tau\tau} + \left[\tau''' + (\kappa^2-\tau^2)\tau' - \frac{2\kappa'^2\tau'}{\kappa^2} + \frac{\kappa'\tau'' + 2\kappa''\tau'}{\kappa}\right] f_{\tau\tau}$$
$$+ \left[2\kappa\kappa' - 2\tau\tau' + \frac{2\kappa'^3}{\kappa^3} - \frac{3\kappa'\kappa''}{\kappa^2} + \frac{\kappa''' - \kappa'\tau^2}{\kappa}\right] f_\tau - \tau' f = 0.$$

Similarly, for $\mathcal{F}(\kappa,\tau) = \tau g(\kappa)$, (2.1) and (2.2) reduce to

$$\tau\kappa'^2 g_{\kappa\kappa\kappa} + \left[2\tau'\kappa' + \tau\kappa'' + \frac{2\tau}{\kappa}\kappa'^2\right] g_{\kappa\kappa} + \left[\tau'' + \frac{2\tau}{\kappa}\kappa'' + \frac{\tau'\kappa'}{\kappa} - \frac{2\tau\kappa'^2}{\kappa^2} + \kappa^2\tau - \tau^3\right] g_\kappa$$
$$+\tau\kappa g = 0,$$

$$-\kappa'^3 g_{\kappa\kappa\kappa} + \left[2\tau^2\kappa\kappa' - 3\kappa'\kappa'' + \frac{2\kappa'^3}{\kappa}\right] g_{\kappa\kappa} + \left[3\kappa\tau\tau' - \kappa''' + (\tau^2-\kappa^2)\kappa' - \frac{2\kappa'^3}{\kappa^2} + \frac{3\kappa'\kappa''}{\kappa}\right] g_\kappa$$
$$-\kappa\kappa' g = 0.$$

Clearly, without assuming a particular family of curves, further analytical progress in general terms is difficult.

4.4 $\mathcal{F}(\kappa,\tau) = \mathcal{F}(\tau)$

In this case, we have $p = \partial\mathcal{F}/\partial\kappa = 0$ and as such we find that (2.5) gives rise to

$$\frac{2\tau}{\kappa}q'' + \left(\frac{\tau'}{\kappa} - \frac{2\kappa'\tau}{\kappa^2}\right) q' + 2\kappa\tau q - \kappa\mathcal{F} = 0, \tag{4.3}$$

noting that $q = \partial\mathcal{F}/\partial\tau$. Equation (4.3) can be rewritten as

$$\left(\frac{\sqrt{\tau}}{\kappa}q'\right)' + \kappa\tau\frac{d}{d\tau}\left(\frac{\mathcal{F}}{\sqrt{\tau}}\right) = 0. \tag{4.4}$$

For the simple special case of $\mathcal{F}(\tau) = \sqrt{\tau}$, we obtain from (4.4) that

$$\frac{\sqrt{\tau}}{\kappa} q' = -\frac{C_1}{4}, \tag{4.5}$$

where C_1 denotes an arbitrary constant. Since $q = 1/(2\sqrt{\tau})$ and $q' = -\tau'/(4\tau^{3/2})$, from (4.5) we have $\tau' = C_1 \kappa \tau$. We note that for $p = 0$, (2.6) reduces to

$$\left(\frac{q'}{\kappa}\right)'' + (\kappa q)' - \frac{\tau^2}{\kappa} q' = 0,$$

which upon substituting our expressions for q and q' and simplifying, we may arrive at

$$\left(\frac{C_1^2}{4} + 1\right)\left(\frac{\kappa}{\sqrt{\tau}}\right)' + \frac{C_1}{2}\tau^{3/2} = 0,$$

which can be further simplified as $(\alpha^2 + 1)(\kappa' - \alpha\kappa^2) + \alpha\tau^2 = 0$, where $\alpha = C_1/2$, and from which we may deduce $\kappa' = \alpha(\kappa^2 - \beta\tau^2)$, where $\beta = 1/(1 + \alpha^2)$. Thus, we require to solve

$$\tau' = 2\alpha\kappa\tau, \quad \kappa' = \alpha(\kappa^2 - \beta\tau^2).$$

By division, we have

$$\frac{d\tau}{d\kappa} = \frac{2\kappa\tau}{\kappa^2 - \beta\tau^2}. \tag{4.6}$$

By introducing $V = \tau/\kappa$ or $\tau = \kappa V$, we may integrate this equation to deduce $V = C_2\kappa(1 + \beta V^2)$, where C_2 denotes a further arbitrary constant, and this gives rise to an explicit relation between κ and τ as $\tau = C_2(\kappa^2 + \beta\tau^2)$.

5. Family of conical helices

In the context of protein folding, helical-shaped curves tend to arise most often (**13**). The circular helix given by

$$x(t) = a\cos t, \quad y(t) = a\sin t, \quad z(t) = bt,$$

for constants a and b, gives rise to constant curvature and torsion, and has been studied in detail by Feoli *et al.* (**14**) within the present context. However, there are many different forms of helices that might also be of considerable interest for protein folding, including elliptical, spherical and conical (**30**). Here as a simple illustrative example, we consider a particular conical helix given by the parametric equations

$$x(t) = \alpha t\cos(\beta\log t), \quad y(t) = \alpha t\sin(\beta\log t), \quad z(t) = \gamma t, \tag{5.1}$$

for certain constants α, β and γ. In a cylindrical polar coordinate system (r, θ, z), this curve is given by

$$r(t) = \alpha t, \quad \theta(t) = \beta\log t, \quad z(t) = \gamma t, \tag{5.2}$$

and therefore, the curve represents a helix on the the surface of the cone $r = (\alpha/\gamma)z$ (see Fig. 1). We comment that the conical helix given above has not previously appeared in the literature, and

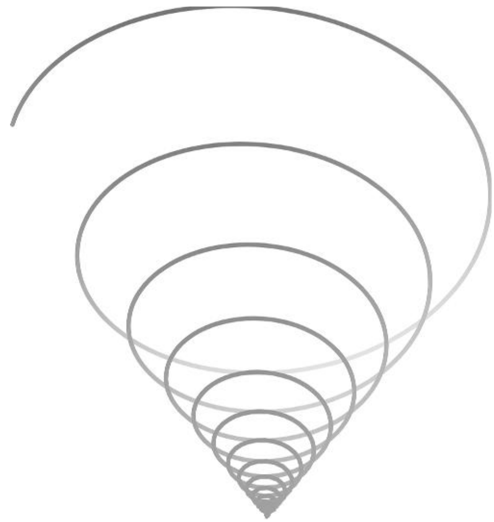

Fig. 1 Conical helix

the logarithm is purposely chosen so that the arc-length parameter s is simply the parameter t which is rescaled by a constant. Further, we note that the presence of conical helix protein structures in the form of ribbed end caps of gas vesicle proteins in aquatic bacteria is mentioned in (**22**, **23**, **24**).

From (1.1) and (5.1), we find that the curvature and torsion are given, respectively, by

$$\kappa(s) = \kappa_0/s, \quad \tau(s) = \tau_0/s, \tag{5.3}$$

where κ_0 and τ_0 are constants defined by

$$\kappa_0 = \alpha\beta(1+\beta^2)^{1/2}/\delta, \quad \tau_0 = \gamma\beta/\delta, \tag{5.4}$$

and δ is a new constant defined by $\delta = [\alpha^2(1+\beta^2)+\gamma^2]^{1/2}$ which is such that the arc length s is related to the parameter t in (5.1) by the equation $s = \delta t$ (namely $ds = \delta dt$). We observe that both $\kappa(s)$ and $\tau(s)$ are singular at $s = 0$ and that from (5.3) it is clear that

$$\xi = \tau(s)/\kappa(s) = \xi_0, \tag{5.5}$$

where $\xi_0 = \tau_0/\kappa_0$ is a constant, and we now examine the implications of the Euler–Lagrange equations in the case when (5.3) and (5.5) are assumed to hold.

First suppose that $\mathcal{F}(\kappa, \tau)$ is homogeneous of degree one, then from both (3.2) and (3.7), since df_ξ/ds is zero, we conclude that $f(\xi) = C_1^{1/2}(1+\xi^2)^{1/2}$; see section 4.2.

Next, suppose $\mathcal{F}(\kappa, \tau)$ is unrestricted, then in the event $\xi = \xi_0$, a constant, (2.8) becomes

$$\frac{d^3w}{d\lambda^3} + (1+\xi_0^2)\frac{dw}{d\lambda} = 0,$$

which on integration yields

$$w(\lambda) = -w_0 - w_1 \sin[(1+\xi_0^2)^{1/2}\lambda] - w_2 \cos[(1+\xi_0^2)^{1/2}\lambda],$$

where w_0, w_1 and w_2 denote three arbitrary constants, which in the present context could be functions of $\xi = \xi_0$. Now, from (5.3) and the relation $d\lambda = \kappa(s)ds$, we may deduce $\lambda = \kappa_0 \log s$ and from (5.4) we find that $\kappa_0(1+\xi_0^2)^{1/2} = \beta$, and therefore from the definition (1.4) of $w(\kappa, \tau)$, we may deduce

$$\mathcal{F} - \left(\kappa \frac{\partial \mathcal{F}}{\partial \kappa} + \tau \frac{\partial \mathcal{F}}{\partial \tau}\right) = w_0 + w_1 \sin(\beta \log s) + w_2 \cos(\beta \log s). \tag{5.6}$$

However, on noting the relations (5.3), we have

$$\frac{d}{ds}\mathcal{F}(\kappa(s), \tau(s)) = -\left(\frac{\kappa_0}{s^2}\frac{\partial \mathcal{F}}{\partial \kappa} + \frac{\tau_0}{s^2}\frac{\partial \mathcal{F}}{\partial \tau}\right) = -\frac{1}{s}\left(\kappa \frac{\partial \mathcal{F}}{\partial \kappa} + \tau \frac{\partial \mathcal{F}}{\partial \tau}\right),$$

and (5.6) becomes simply

$$\frac{d}{ds}(s\mathcal{F}) = w_0 + w_1 \sin(\beta \log s) + w_2 \cos(\beta \log s),$$

which may be readily integrated to yield

$$\mathcal{F}(\kappa(s), \tau(s)) = w_0 + \frac{(w_1 + \beta w_2)}{(1+\beta^2)} \sin(\beta \log s) + \frac{(w_2 - \beta w_1)}{(1+\beta^2)} \cos(\beta \log s) + \frac{w_3}{s}, \tag{5.7}$$

where w_3 denotes an additional constant, which could also be a function of $\xi = \xi_0$. Thus, we might conclude that the conical helix (5.1) applies for any energy density function $\mathcal{F}(\kappa, \tau)$ which has the general form

$$\mathcal{F}(\kappa, \tau) = f_0(\xi) + f_1(\xi)\sin(\beta \log \kappa) + f_2(\xi)\cos(\beta \log \kappa) + \kappa f_3(\xi), \tag{5.8}$$

where $f_i(\xi)$ $(i = 0, 1, 2, 3)$ denote functions of $\xi = \tau/\kappa$ only, and are suitably redefined from (5.7). We note that essentially the same result arises if we formally replace s by τ instead of κ since $\log \tau = \log(\tau/\kappa) + \log \kappa$ and on expanding the trigonometric functions, the terms arising from $\log \xi$ can be absorbed into a redefinition of the four functions $f_i(\xi)$ $(i = 0, 1, 2, 3)$. We also observe that the previously mentioned homogeneous function of degree one is embodied in the final term of (5.8), noting that the specific form $f_3(\xi) = C_1^{1/2}(1+\xi^2)^{1/2}$ arises as a consequence of (3.2) and the integral (3.7), while the general form (5.8) is merely a consequence of (2.8).

6. Conclusions

In this paper, we have extended the model of Feoli *et al.* (**14**) for the problem of determining protein structures by including curvature, torsion and their derivatives with respect to the arc-length parameter in the free-energy density function $\mathcal{F}$. Even though the case $\mathcal{F} = \mathcal{F}(\kappa, \tau, \kappa')$ has been previously studied by Zhang *et al.* (**19**), their two resultant Euler–Lagrange equations are incorrect (see (2.31) and (2.32) in (**19**)). The correct equations are given by (B.13) and (B.17) in this paper, which, as shown in section 2, can be further simplified to (2.1) and (2.2), respectively. We have shown that the equations obtained simplify to those given in Feoli *et al.* (**14**) for the case when $\mathcal{F}$ is a function of curvature only. Further, we have shown that the two Euler–Lagrange equations can be dramatically simplified to a single equation (see (2.7)) when expressed in terms of a 'generalised' Legendre transform w of $\mathcal{F}$ (see (1.4)). This equation has the solutions $w \equiv 0$ and $w \equiv$ constant in the case when $\tau/\kappa =$ constant. In the case that $\mathcal{F}$ depends only on the curvature and torsion, the first

$w = 0$ arises when $\mathcal{F}(\kappa, \tau)$ is a homogeneous function of degree one, namely $\mathcal{F}(\kappa, \tau) = \kappa f(\tau/\kappa)$, and for any $f(\tau/\kappa)$ by introducing a new parameter λ such that $d\lambda = \kappa ds$, we may reduce the Euler–Lagrange equations to a single first-order relation (see (3.7)). The question is, to what extent do the homogeneous functions of degree one arise in any experimental determinations of the free-energy density? To date, the authors are not aware of any explicit experimental data of this nature that might be used to answer this question. For the second solution $w = C$, where C is a non-zero constant, we may show that $\tau = C_1\kappa$, where C_1 is a further constant, so that $\mathcal{F}(\kappa, \tau) = A + B\kappa$, which coincides with the linear curvature case examined in detail by Feoli *et al.* (**14**). A closer analysis of the individual equations (2.5) and (2.6) reveals that both κ and τ must be constants, as is the case for the circular helices examined by Feoli *et al.* (**14**). These authors claim that the linear curvature case for the free-energy density uniquely determines these helical proteins. Our analysis does not conflict with this statement, except that we show helical proteins could also arise from a more general free energy $\mathcal{F}(\kappa, \tau) = -C + \kappa f(\tau/\kappa)$, noting that both constants κ and τ arise as a consequence of the Euler–Lagrange equations. Finally, in this paper, we examine some simple special forms of $\mathcal{F}(\kappa, \tau)$ to determine the resulting Euler–Lagrange constraints and we examine in some detail a particular conical helix and we derive the general form (5.8) of the energy density function $\mathcal{F}(\kappa, \tau)$ resulting from the Euler–Lagrange equations.

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APPENDIX A

In this appendix, we derive the variational quantities that are used for the determination of the Euler–Lagrange equations shown in Appendix B. The variation of $\mathbf{r}(s)$ is given by

$$\tilde{\mathbf{r}}(s) = \mathbf{r}(s) + \varepsilon_1\psi_1(s)\mathbf{T} + \varepsilon_2\psi_2(s)\mathbf{N} + \varepsilon_3\psi_3(s)\mathbf{B}, \tag{A.1}$$

where ε_i are small and $\psi_i(s)$ are arbitrary functions. By using the Frenet equations and $\mathbf{r}' = \mathbf{T}$, we have

$$\tilde{\mathbf{r}}' = [1 + \varepsilon_1\psi_1' - \varepsilon_2\kappa\psi_2]\mathbf{T} + [\varepsilon_1\kappa\psi_1 + \varepsilon_2\psi_2' - \varepsilon_3\tau\psi_3]\mathbf{N} + [\varepsilon_2\psi_2\tau + \varepsilon_3\psi_3']\mathbf{B} \tag{A.2}$$

and

$$|\tilde{\mathbf{r}}'|^2 = [1 + \varepsilon_1\psi_1' - \varepsilon_2\kappa\psi_2]^2 + [\varepsilon_1\kappa\psi_1 + \varepsilon_2\psi_2' - \varepsilon_3\tau\psi_3]^2 + [\varepsilon_2\psi_2\tau + \varepsilon_3\psi_3']^2. \tag{A.3}$$

Further, from (1.2) and (A.2), we find that

$$\begin{aligned}\tilde{\mathbf{r}}'' &= [\varepsilon_1(\psi_1'' - \psi_1\kappa^2) - \varepsilon_2(2\kappa\psi_2' + \kappa'\psi_2) + \varepsilon_3\psi_3\kappa\tau]\mathbf{T}\\ &\quad + [\kappa + \varepsilon_1(2\kappa\psi_1' + \psi_1\kappa') + \varepsilon_2(\psi_2'' - \psi_2\kappa^2 - \psi_2\tau^2) - \varepsilon_3(2\psi_3'\tau + \psi_3\tau')]\mathbf{N}\\ &\quad + [\varepsilon_1\kappa\tau\psi_1 + \varepsilon_2(2\psi_2'\tau + \psi_2\tau') + \varepsilon_3(\psi_3'' - \tau^2\psi_3)]\mathbf{B}. \end{aligned} \tag{A.4}$$

Next, from (A.2) and (A.4), we obtain

$$\begin{aligned}\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}'' &= [-\kappa(\varepsilon_2\psi_2\tau + \varepsilon_3\psi_3') + O(\varepsilon_i^2)]\mathbf{T}\\ &\quad - [\varepsilon_1\kappa\tau\psi_1 + \varepsilon_2(2\psi_2'\tau + \psi_2\tau') + \varepsilon_3(\psi_3'' - \tau^2\psi_3) + O(\varepsilon_i^2)]\mathbf{N}\\ &\quad + [\kappa + \varepsilon_1(3\kappa\psi_1' + \psi_1\kappa') + \varepsilon_2(\psi_2'' - 2\kappa^2\psi_2 - \tau^2\psi_2) - \varepsilon_3(2\tau\psi_3' + \tau'\psi_3) + O(\varepsilon_i^2)]\mathbf{B} \end{aligned} \tag{A.5}$$

so that we have

$$\begin{aligned}|\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|^2 &= [-\kappa(\varepsilon_2\psi_2\tau + \varepsilon_3\psi_3') + O(\varepsilon_i^2)]^2\\ &\quad + [\varepsilon_1\kappa\tau\psi_1 + \varepsilon_2(2\psi_2'\tau + \psi_2\tau') + \varepsilon_3(\psi_3'' - \tau^2\psi_3) + O(\varepsilon_i^2)]^2\\ &\quad + [\kappa + \varepsilon_1(3\kappa\psi_1' + \psi_1\kappa') + \varepsilon_2(\psi_2'' - 2\kappa^2\psi_2 - \tau^2\psi_2) - \varepsilon_3(2\tau\psi_3' + \tau'\psi_3) + O(\varepsilon_i^2)]^2. \end{aligned} \tag{A.6}$$

From (A.3) and (A.6), we note the following relations:

$$\begin{aligned} \left.\frac{\partial|\tilde{\mathbf{r}}'|^2}{\partial\varepsilon_1}\right|_{\bar{\varepsilon}=0} &= 2\psi_1', & \left.\frac{\partial|\tilde{\mathbf{r}}'\times\tilde{\mathbf{r}}''|^2}{\partial\varepsilon_1}\right|_{\bar{\varepsilon}=0} &= 2\kappa(3\kappa\psi_1' + \psi_1\kappa'),\\ \left.\frac{\partial|\tilde{\mathbf{r}}'|^2}{\partial\varepsilon_2}\right|_{\bar{\varepsilon}=0} &= -2\kappa\psi_2, & \left.\frac{\partial|\tilde{\mathbf{r}}'\times\tilde{\mathbf{r}}''|^2}{\partial\varepsilon_2}\right|_{\bar{\varepsilon}=0} &= 2\kappa(\psi_2'' - 2\kappa^2\psi_2 - \tau^2\psi_2),\\ \left.\frac{\partial|\tilde{\mathbf{r}}'|^2}{\partial\varepsilon_3}\right|_{\bar{\varepsilon}=0} &= 0, & \left.\frac{\partial|\tilde{\mathbf{r}}'\times\tilde{\mathbf{r}}''|^2}{\partial\varepsilon_3}\right|_{\bar{\varepsilon}=0} &= -2\kappa(2\tau\psi_3' + \psi_3\tau'), \end{aligned}$$

where $\bar{\varepsilon} = 0$ denotes evaluation at $\varepsilon_1 = \varepsilon_2 = \varepsilon_3 = 0$. From $|\tilde{\mathbf{r}}'|^2|_{\bar{\varepsilon}=0} = 1$, $|\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|^2|_{\bar{\varepsilon}=0} = \kappa^2$ and

$$\frac{\partial|\tilde{\mathbf{r}}'|}{\partial\varepsilon_i} = \frac{1}{2|\tilde{\mathbf{r}}'|}\frac{\partial|\tilde{\mathbf{r}}'|^2}{\partial\varepsilon_i},$$

we obtain

$$\begin{aligned} \left.\frac{\partial|\tilde{\mathbf{r}}'|}{\partial\varepsilon_1}\right|_{\bar{\varepsilon}=0} &= \psi_1', & \left.\frac{\partial|\tilde{\mathbf{r}}'\times\tilde{\mathbf{r}}''|}{\partial\varepsilon_1}\right|_{\bar{\varepsilon}=0} &= 3\kappa\psi_1' + \psi_1\kappa',\\ \left.\frac{\partial|\tilde{\mathbf{r}}'|}{\partial\varepsilon_2}\right|_{\bar{\varepsilon}=0} &= -\kappa\psi_2, & \left.\frac{\partial|\tilde{\mathbf{r}}'\times\tilde{\mathbf{r}}''|}{\partial\varepsilon_2}\right|_{\bar{\varepsilon}=0} &= \psi_2'' - 2\kappa^2\psi_2 - \tau^2\psi_2,\\ \left.\frac{\partial|\tilde{\mathbf{r}}'|}{\partial\varepsilon_3}\right|_{\bar{\varepsilon}=0} &= 0, & \left.\frac{\partial|\tilde{\mathbf{r}}'\times\tilde{\mathbf{r}}''|}{\partial\varepsilon_3}\right|_{\bar{\varepsilon}=0} &= -2\tau\psi_3' - \psi_3\tau'. \end{aligned} \tag{A.7}$$

Next, we need to determine $\det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')$ noting that $\tilde{\mathbf{r}}'''$ is given by

$$\begin{aligned}
\tilde{\mathbf{r}}''' = {} & [-\kappa^2 + \varepsilon_1(-3\kappa^2\psi_1' - 3\kappa\kappa'\psi_1 + \psi_1''') - \varepsilon_2(3\kappa\psi_2'' + 3\kappa'\psi_2' + \kappa''\psi_2 - \kappa^3\psi_2 - \tau^2\kappa\psi_2) \\
& + \varepsilon_3(\kappa'\tau\psi_3 + 2\kappa\tau'\psi_3 + 3\kappa\tau\psi_3')]\mathbf{T} + [\kappa' + \varepsilon_1(3\kappa\psi_1'' + 3\kappa'\psi_1' - \psi_1\kappa^3 - \psi_1\kappa\tau^2 + \kappa''\psi_1) \\
& + \varepsilon_2(\psi_2''' - 3\tau^2\psi_2' - 3\kappa^2\psi_2' - 3\kappa\kappa'\psi_2 - 3\tau\tau'\psi_2) \\
& + \varepsilon_3(-3\tau\psi_3'' - 3\tau'\psi_3' + \kappa^2\tau\psi_3 + \tau^3\psi_3 - \tau''\psi_3)]\mathbf{N} \\
& + [\kappa\tau + \varepsilon_1(3\kappa\tau\psi_1' + 2\kappa'\tau\psi_1 + \kappa\tau'\psi_1) + \varepsilon_2(3\psi_2''\tau - \tau\kappa^2\psi_2 - \tau^3\psi_2 + 3\tau'\psi_2' + \tau''\psi_2) \\
& + \varepsilon_3(\psi_3''' - 3\tau^2\psi_3' - 3\tau\tau'\psi_3)]\mathbf{B}. \qquad \text{(A.8)}
\end{aligned}$$

Thus from (A.2), (A.4) and (A.8), we can find that $\det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')$ is given by

$$\det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''') = \begin{vmatrix} M_{11} & M_{12} & M_{13} \\ M_{21} & M_{22} & M_{23} \\ M_{31} & M_{32} & M_{33} \end{vmatrix}, \qquad \text{(A.9)}$$

where M_{ij} $(i, j = 1, 2, 3)$ represent the coefficients of vectors **T**, **N** and **B** in $\tilde{\mathbf{r}}'$, $\tilde{\mathbf{r}}''$ and $\tilde{\mathbf{r}}'''$. As a result, we have

$$\det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''') = [1 + \varepsilon_1\psi_1' - \varepsilon_2\kappa\psi_2]M_1 - [\varepsilon_1\kappa\psi_1 + \varepsilon_2\psi_2' - \varepsilon_3\tau\psi_3]M_2 + [\varepsilon_2\psi_2\tau + \varepsilon_3\psi_3']M_3, \quad \text{(A.10)}$$

where $M_1 = M_{22}M_{33} - M_{23}M_{32}$, $M_2 = M_{21}M_{33} - M_{23}M_{31}$ and $M_3 = M_{21}M_{32} - M_{22}M_{31}$. From (A.10), we may deduce

$$\begin{aligned}
\left.\frac{\partial \det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')}{\partial \varepsilon_1}\right|_{\bar{\varepsilon}=0} &= \left.\frac{\partial M_1}{\partial \varepsilon_1}\right|_{\bar{\varepsilon}=0} + \psi_1' M_1|_{\bar{\varepsilon}=0} - \kappa\psi_1 M_2|_{\bar{\varepsilon}=0}, \\
\left.\frac{\partial \det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')}{\partial \varepsilon_2}\right|_{\bar{\varepsilon}=0} &= \left.\frac{\partial M_1}{\partial \varepsilon_2}\right|_{\bar{\varepsilon}=0} - \kappa\psi_2 M_1|_{\bar{\varepsilon}=0} - \psi_2' M_2|_{\bar{\varepsilon}=0} + \psi_2\tau M_3|_{\bar{\varepsilon}=0}, \qquad \text{(A.11)} \\
\left.\frac{\partial \det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')}{\partial \varepsilon_3}\right|_{\bar{\varepsilon}=0} &= \left.\frac{\partial M_1}{\partial \varepsilon_3}\right|_{\bar{\varepsilon}=0} + \tau\psi_3 M_2|_{\bar{\varepsilon}=0} + \psi_3' M_3|_{\bar{\varepsilon}=0},
\end{aligned}$$

thus, from (A.2), (A.4) and (A.8), we finally obtain

$$\begin{aligned}
\left.\frac{\partial \det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')}{\partial \varepsilon_1}\right|_{\bar{\varepsilon}=0} &= 6\kappa^2\tau\psi_1' + (2\tau\kappa\kappa' + \kappa^2\tau')\psi_1, \\
\left.\frac{\partial \det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')}{\partial \varepsilon_2}\right|_{\bar{\varepsilon}=0} &= 4\kappa\tau\psi_2'' + (3\kappa\tau' - 2\tau\kappa')\psi_2' + (\kappa\tau'' - 2\kappa^3\tau - 2\kappa\tau^3 - \kappa'\tau')\psi_2, \qquad \text{(A.12)} \\
\left.\frac{\partial \det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')}{\partial \varepsilon_3}\right|_{\bar{\varepsilon}=0} &= \kappa\psi_3''' - \kappa'\psi_3'' + (\kappa^3 - 5\kappa\tau^2)\psi_3' + (\kappa'\tau^2 - 4\kappa\tau\tau')\psi_3.
\end{aligned}$$

We note that $\tilde{\mathbf{r}}'|_{\bar{\varepsilon}=0} = \mathbf{T}$, $\tilde{\mathbf{r}}''|_{\bar{\varepsilon}=0} = \kappa\mathbf{N}$ and $\tilde{\mathbf{r}}'''|_{\bar{\varepsilon}=0} = -\kappa^2\mathbf{T} + \kappa'\mathbf{N} + \kappa\tau\mathbf{B}$ as such it can be shown that $\det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')|_{\bar{\varepsilon}=0} = \kappa^2\tau$.

APPENDIX B

Here, we derive the Euler–Lagrange equations (2.1) and (2.2) and the alternative boundary conditions. In the case when the energy depends on the curvature, the torsion and the derivatives of curvature and torsion, the total variation becomes

$$\frac{\partial}{\partial \varepsilon_i} \int \mathcal{F}(\kappa, \tau, \kappa', \tau') |\tilde{\mathbf{r}}'| ds \bigg|_{\bar{\varepsilon}=0} = 0 \quad (i = 1, 2, 3). \tag{B.1}$$

Equation (B.1) can be expanded as

$$\int \frac{\partial \mathcal{F}}{\partial \kappa} \frac{\partial \kappa}{\partial \varepsilon_i} |\tilde{\mathbf{r}}'| \bigg|_{\bar{\varepsilon}=0} ds + \int \frac{\partial \mathcal{F}}{\partial \tau} \frac{\partial \tau}{\partial \varepsilon_i} |\tilde{\mathbf{r}}'| \bigg|_{\bar{\varepsilon}=0} ds + \int \frac{\partial \mathcal{F}}{\partial \kappa'} \frac{\partial \kappa'}{\partial \varepsilon_i} |\tilde{\mathbf{r}}'| \bigg|_{\bar{\varepsilon}=0} ds$$

$$+ \int \frac{\partial \mathcal{F}}{\partial \tau'} \frac{\partial \tau'}{\partial \varepsilon_i} |\tilde{\mathbf{r}}'| \bigg|_{\bar{\varepsilon}=0} ds + \int \mathcal{F} \frac{\partial |\tilde{\mathbf{r}}'|}{\partial \varepsilon_i} \bigg|_{\bar{\varepsilon}=0} ds = 0. \tag{B.2}$$

Since the curvature κ and the torsion τ are given, respectively, by $\kappa = |\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|/|\tilde{\mathbf{r}}'|^3$ and $\tau = \det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')/|\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|^2$, we may deduce

$$\frac{\partial \kappa}{\partial \varepsilon_i} = \frac{1}{|\tilde{\mathbf{r}}'|^6} \left[|\tilde{\mathbf{r}}'|^3 \frac{\partial |\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|}{\partial \varepsilon_i} - 3|\tilde{\mathbf{r}}'|^2 |\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''| \frac{\partial |\tilde{\mathbf{r}}'|}{\partial \varepsilon_i} \right], \tag{B.3}$$

$$\frac{\partial \tau}{\partial \varepsilon_i} = \frac{1}{|\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|^4} \left[|\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|^2 \frac{\partial \det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')}{\partial \varepsilon_i} - 2|\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''| \det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''') \frac{\partial |\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|}{\partial \varepsilon_i} \right].$$

From $|\tilde{\mathbf{r}}'|^2|_{\bar{\varepsilon}=0} = 1$, $|\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|^2|_{\bar{\varepsilon}=0} = \kappa^2$ and $\det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')|_{\bar{\varepsilon}=0} = \kappa^2 \tau$, we then derive

$$\frac{\partial \kappa}{\partial \varepsilon_i} \bigg|_{\bar{\varepsilon}=0} = \frac{\partial |\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|}{\partial \varepsilon_i} \bigg|_{\bar{\varepsilon}=0} - 3\kappa \frac{\partial |\tilde{\mathbf{r}}'|}{\partial \varepsilon_i} \bigg|_{\bar{\varepsilon}=0}, \tag{B.4}$$

$$\frac{\partial \tau}{\partial \varepsilon_i} \bigg|_{\bar{\varepsilon}=0} = \frac{1}{\kappa^2} \frac{\partial \det(\tilde{\mathbf{r}}', \tilde{\mathbf{r}}'', \tilde{\mathbf{r}}''')}{\partial \varepsilon_i} \bigg|_{\bar{\varepsilon}=0} - \frac{2\tau}{\kappa} \frac{\partial |\tilde{\mathbf{r}}' \times \tilde{\mathbf{r}}''|}{\partial \varepsilon_i} \bigg|_{\bar{\varepsilon}=0}.$$

As a result, using (A.7), (A.12) and (B.4), we obtain

$$\frac{\partial \kappa}{\partial \varepsilon_1} \bigg|_{\bar{\varepsilon}=0} = \kappa' \psi_1, \quad \frac{\partial \kappa}{\partial \varepsilon_2} \bigg|_{\bar{\varepsilon}=0} = \psi_2'' + (\kappa^2 - \tau^2)\psi_2, \quad \frac{\partial \kappa}{\partial \varepsilon_3} \bigg|_{\bar{\varepsilon}=0} = -2\tau \psi_3' - \tau' \psi_3 \tag{B.5}$$

and

$$\frac{\partial \tau}{\partial \varepsilon_1} \bigg|_{\bar{\varepsilon}=0} = \tau' \psi_1, \quad \frac{\partial \tau}{\partial \varepsilon_2} \bigg|_{\bar{\varepsilon}=0} = \frac{2\tau}{\kappa} \psi_2'' + \left(\frac{3\tau'}{\kappa} - \frac{2\tau\kappa'}{\kappa^2} \right) \psi_2' + \left(2\kappa\tau + \frac{\tau''}{\kappa} - \frac{\kappa'\tau'}{\kappa^2} \right) \psi_2,$$

$$\frac{\partial \tau}{\partial \varepsilon_3} \bigg|_{\bar{\varepsilon}=0} = \frac{1}{\kappa} \psi_3''' - \frac{\kappa'}{\kappa^2} \psi_3'' + \left(\kappa - \frac{\tau^2}{\kappa} \right) \psi_3' + \left(-\frac{2\tau\tau'}{\kappa} + \frac{\kappa'\tau^2}{\kappa^2} \right) \psi_3. \tag{B.6}$$

While formulae (1.1) are valid in any parametrisation, it is essential to note that

$$\kappa' = \frac{d\kappa}{ds}\frac{ds}{d\tilde{s}}, \quad \tau' = \frac{d\tau}{ds}\frac{ds}{d\tilde{s}},$$

where $d/d\tilde{s}$ is the intrinsic derivative of the varied curve. Here, $\tilde{s}$, the arc length of the varied curve, is related to s via $\tilde{s} = \int |\tilde{\mathbf{r}}'(s)|ds$. In particular, $ds/d\tilde{s} = 1/|\tilde{\mathbf{r}}'(s)|$. Consequently, we have

$$\frac{\partial\kappa'}{\partial\varepsilon_i} = \frac{d\kappa}{ds}\frac{\partial}{\partial\varepsilon_i}\left(\frac{1}{|\tilde{\mathbf{r}}'|}\right) + \frac{1}{|\tilde{\mathbf{r}}'|}\frac{\partial}{\partial\varepsilon_i}\left(\frac{d\kappa}{ds}\right) = -\frac{1}{|\tilde{\mathbf{r}}'|^2}\frac{\partial|\tilde{\mathbf{r}}'|}{\partial\varepsilon_i}\frac{d\kappa}{ds} + \frac{1}{|\tilde{\mathbf{r}}'|}\frac{\partial}{\partial\varepsilon_i}\left(\frac{d\kappa}{ds}\right),$$

$$\frac{\partial\tau'}{\partial\varepsilon_i} = \frac{d\tau}{ds}\frac{\partial}{\partial\varepsilon_i}\left(\frac{1}{|\tilde{\mathbf{r}}'|}\right) + \frac{1}{|\tilde{\mathbf{r}}'|}\frac{\partial}{\partial\varepsilon_i}\left(\frac{d\tau}{ds}\right) = -\frac{1}{|\tilde{\mathbf{r}}'|^2}\frac{\partial|\tilde{\mathbf{r}}'|}{\partial\varepsilon_i}\frac{d\tau}{ds} + \frac{1}{|\tilde{\mathbf{r}}'|}\frac{\partial}{\partial\varepsilon_i}\left(\frac{d\tau}{ds}\right),$$

and hence,

$$\left.\frac{\partial\kappa'}{\partial\varepsilon_i}\right|_{\bar{\varepsilon}=0} = -\kappa'\left.\frac{\partial|\tilde{\mathbf{r}}'|}{\partial\varepsilon_i}\right|_{\bar{\varepsilon}=0} + \left.\frac{\partial\kappa'}{\partial\varepsilon_i}\right|_{\bar{\varepsilon}=0}, \quad \left.\frac{\partial\tau'}{\partial\varepsilon_i}\right|_{\bar{\varepsilon}=0} = -\tau'\left.\frac{\partial|\tilde{\mathbf{r}}'|}{\partial\varepsilon_i}\right|_{\bar{\varepsilon}=0} + \left.\frac{\partial\tau'}{\partial\varepsilon_i}\right|_{\bar{\varepsilon}=0}. \tag{B.7}$$

We also note that

$$\left.\frac{\partial\kappa'}{\partial\varepsilon_i}\right|_{\bar{\varepsilon}=0} = \frac{d}{ds}\left(\left.\frac{\partial\kappa}{\partial\varepsilon_i}\right|_{\bar{\varepsilon}=0}\right), \quad \left.\frac{\partial\tau'}{\partial\varepsilon_i}\right|_{\bar{\varepsilon}=0} = \frac{d}{ds}\left(\left.\frac{\partial\tau}{\partial\varepsilon_i}\right|_{\bar{\varepsilon}=0}\right). \tag{B.8}$$

From (B.2), (B.5), (B.6), (B.7) and (B.8), the variation $(\partial/\partial\varepsilon_1)\int \mathcal{F}(\kappa,\tau,\kappa',\tau')|\tilde{\mathbf{r}}'|ds\big|_{\bar{\varepsilon}=0} = 0$ in the tangential direction gives rise to

$$\int \frac{\partial\mathcal{F}}{\partial\kappa}\kappa'\psi_1 ds + \int \frac{\partial\mathcal{F}}{\partial\tau}\tau'\psi_1 ds + \int \frac{\partial\mathcal{F}}{\partial\kappa'}\kappa''\psi_1 ds + \int \frac{\partial\mathcal{F}}{\partial\tau'}\tau''\psi_1 ds + \int \mathcal{F}\psi_1' ds = 0. \tag{B.9}$$

By integrating by parts the fifth integral in (B.9) and imposing the condition $\mathcal{F}\psi_1 = 0$ at the boundary, we find that the variation in the tangential direction is identically satisfied.

Further, the variation $(\partial/\partial\varepsilon_2)\int \mathcal{F}(\kappa,\tau,\kappa',\tau')|\tilde{\mathbf{r}}'|ds\big|_{\bar{\varepsilon}=0} = 0$ in the normal direction becomes, after using (B.2), (B.5), (B.6), (B.7) and (B.8),

$$\begin{aligned}
&\int \frac{\partial\mathcal{F}}{\partial\kappa}[\psi_2'' + (\kappa^2-\tau^2)\psi_2]ds + \int \frac{\partial\mathcal{F}}{\partial\tau}\left[\frac{2\tau}{\kappa}\psi_2'' + \left(\frac{3\tau'}{\kappa} - \frac{2\kappa'\tau}{\kappa^2}\right)\psi_2' + \left(2\kappa\tau + \frac{\tau''}{\kappa} - \frac{\kappa'\tau'}{\kappa^2}\right)\psi_2\right]ds \\
&+ \int \frac{\partial\mathcal{F}}{\partial\kappa'}[\psi_2''' + (\kappa^2-\tau^2)\psi_2' + (3\kappa\kappa' - 2\tau\tau')\psi_2]ds \\
&+ \int \frac{\partial\mathcal{F}}{\partial\tau'}\left[\frac{2\tau}{\kappa}\psi_2''' + \left(\frac{5\tau'}{\kappa} - \frac{4\tau\kappa'}{\kappa^2}\right)\psi_2'' + \left(2\kappa\tau + \frac{4\tau''}{\kappa} - \frac{6\kappa'\tau'}{\kappa^2} - \frac{2\tau\kappa''}{\kappa^2} + \frac{4\tau\kappa'^2}{\kappa^3}\right)\psi_2'\right. \\
&\left.+ \left(2\kappa'\tau + 3\tau'\kappa + \frac{\tau'''}{\kappa} - \frac{2\kappa'\tau''}{\kappa^2} - \frac{\kappa''\tau'}{\kappa^2} + \frac{2\tau'\kappa'^2}{\kappa^3}\right)\psi_2\right]ds - \int \mathcal{F}\kappa\psi_2 ds = 0.
\end{aligned} \tag{B.10}$$

Integrating by parts those terms in (B.10) involving ψ_2', ψ_2'' and ψ_2''' gives

$$\int \left\{ \frac{d^2}{ds^2}\left(\frac{\partial \mathcal{F}}{\partial \kappa} + \frac{2\tau}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau}\right) + \frac{d}{ds}\left(\frac{2\kappa'\tau}{\kappa^2}\frac{\partial \mathcal{F}}{\partial \tau} - \frac{3\tau'}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau}\right) + [\kappa^2 - \tau^2]\frac{\partial \mathcal{F}}{\partial \kappa} \right.$$

$$+ \left[2\kappa\tau + \frac{\tau''}{\kappa} - \frac{\kappa'\tau'}{\kappa^2}\right]\frac{\partial \mathcal{F}}{\partial \tau} + [3\kappa\kappa' - 2\tau\tau']\frac{\partial \mathcal{F}}{\partial \kappa'} - \frac{d}{ds}\left([\kappa^2 - \tau^2]\frac{\partial \mathcal{F}}{\partial \kappa'}\right)$$

$$- \frac{d^3}{ds^3}\left(\frac{\partial \mathcal{F}}{\partial \kappa'}\right) + \left[2\kappa'\tau + 3\tau'\kappa + \frac{\tau'''}{\kappa} - \frac{2\kappa'\tau''}{\kappa^2} - \frac{\kappa''\tau'}{\kappa^2} + \frac{2\tau'\kappa'^2}{\kappa^3}\right]\frac{\partial \mathcal{F}}{\partial \tau'}$$

$$- \frac{d}{ds}\left(\left[2\kappa\tau + \frac{4\tau''}{\kappa} - \frac{6\kappa'\tau'}{\kappa^2} - \frac{2\tau\kappa''}{\kappa^2} + \frac{4\tau\kappa'^2}{\kappa^3}\right]\frac{\partial \mathcal{F}}{\partial \tau'}\right) + \frac{d^2}{ds^2}\left(\left[\frac{5\tau'}{\kappa} - \frac{4\tau\kappa'}{\kappa^2}\right]\frac{\partial \mathcal{F}}{\partial \tau'}\right)$$

$$\left. - \frac{d^3}{ds^3}\left(\frac{2\tau}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau'}\right) - \kappa\mathcal{F} \right\} \psi_2 ds = 0, \tag{B.11}$$

which is obtained assuming that the following boundary condition is satisfied:

$$\left\{ \frac{d^2}{ds^2}\left(\frac{\partial \mathcal{F}}{\partial \kappa'} + \frac{2\tau}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau'}\right) - \frac{d}{ds}\left(\frac{\partial \mathcal{F}}{\partial \kappa} + \frac{2\tau}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau} + \left[\frac{5\tau'}{\kappa} - \frac{4\tau\kappa'}{\kappa^2}\right]\frac{\partial \mathcal{F}}{\partial \tau'}\right) \right.$$

$$\left. + \left[\frac{3\tau'}{\kappa} - \frac{2\tau\kappa'}{\kappa^2}\right]\frac{\partial \mathcal{F}}{\partial \tau} + [\kappa^2 - \tau^2]\frac{\partial \mathcal{F}}{\partial \kappa'} + \left[2\kappa\tau + \frac{4\tau''}{\kappa} - \frac{6\kappa'\tau'}{\kappa^2} - \frac{2\tau\kappa''}{\kappa^2} + \frac{4\tau\kappa'^2}{\kappa^3}\right]\frac{\partial \mathcal{F}}{\partial \tau'} \right\} \psi_2$$

$$+ \left\{ -\frac{d}{ds}\left(\frac{\partial \mathcal{F}}{\partial \kappa'} + \frac{2\tau}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau'}\right) + \frac{\partial \mathcal{F}}{\partial \kappa} + \frac{2\tau}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau} + \left[\frac{5\tau'}{\kappa} - \frac{4\tau\kappa'}{\kappa^2}\right]\frac{\partial \mathcal{F}}{\partial \tau'} \right\} \psi_2'$$

$$+ \left\{ \frac{\partial \mathcal{F}}{\partial \kappa'} + \frac{2\tau}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau'} \right\} \psi_2'' = 0. \tag{B.12}$$

Equation (B.11) holds for arbitrary ψ_2 if

$$\frac{d^2}{ds^2}\left(\frac{\partial \mathcal{F}}{\partial \kappa} + \frac{2\tau}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau}\right) + \frac{d}{ds}\left(\frac{2\kappa'\tau}{\kappa^2}\frac{\partial \mathcal{F}}{\partial \tau} - \frac{3\tau'}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau}\right) + [\kappa^2 - \tau^2]\frac{\partial \mathcal{F}}{\partial \kappa}$$

$$+ \left[2\kappa\tau + \frac{\tau''}{\kappa} - \frac{\kappa'\tau'}{\kappa^2}\right]\frac{\partial \mathcal{F}}{\partial \tau} + [3\kappa\kappa' - 2\tau\tau']\frac{\partial \mathcal{F}}{\partial \kappa'} - \frac{d}{ds}\left([\kappa^2 - \tau^2]\frac{\partial \mathcal{F}}{\partial \kappa'}\right)$$

$$- \frac{d^3}{ds^3}\left(\frac{\partial \mathcal{F}}{\partial \kappa'}\right) + \left[2\kappa'\tau + 3\tau'\kappa + \frac{\tau'''}{\kappa} - \frac{2\kappa'\tau''}{\kappa^2} - \frac{\kappa''\tau'}{\kappa^2} + \frac{2\tau'\kappa'^2}{\kappa^3}\right]\frac{\partial \mathcal{F}}{\partial \tau'}$$

$$- \frac{d}{ds}\left(\left[2\kappa\tau + \frac{4\tau''}{\kappa} - \frac{6\kappa'\tau'}{\kappa^2} - \frac{2\tau\kappa''}{\kappa^2} + \frac{4\tau\kappa'^2}{\kappa^3}\right]\frac{\partial \mathcal{F}}{\partial \tau'}\right) + \frac{d^2}{ds^2}\left(\left[\frac{5\tau'}{\kappa} - \frac{4\tau\kappa'}{\kappa^2}\right]\frac{\partial \mathcal{F}}{\partial \tau'}\right)$$

$$- \frac{d^3}{ds^3}\left(\frac{2\tau}{\kappa}\frac{\partial \mathcal{F}}{\partial \tau'}\right) - \kappa\mathcal{F} = 0. \tag{B.13}$$

Upon simplifying, (B.13) may be written as shown in (2.1). We note here that the boundary condition (B.12) is satisfied if $\psi_2 = \psi_2' = \psi_2'' = 0$ or the alternative boundary conditions may be obtained if the coefficients of ψ_2, ψ_2' and ψ_2'' are equal to zero at the boundary.

Finally, the variation $(\partial/\partial\varepsilon_3)\int \mathcal{F}(\kappa, \tau, \kappa', \tau')|\tilde{\mathbf{r}}'|ds\big|_{\bar{\varepsilon}=0} = 0$ in the binormal direction, using (B.2), (B.5), (B.6), (B.7) and (B.8), gives rise to

$$-\int \frac{\partial\mathcal{F}}{\partial\kappa}[2\tau\psi_3' + \tau'\psi_3]ds + \int \frac{\partial\mathcal{F}}{\partial\tau}\left[\frac{1}{\kappa}\psi_3''' - \frac{\kappa'}{\kappa^2}\psi_3'' + \left(\kappa - \frac{\tau^2}{\kappa}\right)\psi_3' + \left(\frac{\kappa'\tau^2}{\kappa^2} - \frac{2\tau\tau'}{\kappa}\right)\psi_3\right]ds$$
$$-\int \frac{\partial\mathcal{F}}{\partial\kappa'}[2\tau\psi_3'' + 3\tau'\psi_3' + \tau''\psi_3]ds$$
$$+\int \frac{\partial\mathcal{F}}{\partial\tau'}\left[\frac{1}{\kappa}\psi_3'''' - \frac{2\kappa'}{\kappa^2}\psi_3''' + \left(\kappa - \frac{\tau^2}{\kappa} - \frac{\kappa''}{\kappa^2} + \frac{2\kappa'^2}{\kappa^3}\right)\psi_3'' + \left(\kappa' - \frac{4\tau\tau'}{\kappa} + \frac{2\kappa'\tau^2}{\kappa^2}\right)\psi_3'\right.$$
$$\left. + \left(-\frac{2\tau'^2}{\kappa} - \frac{2\tau\tau''}{\kappa} + \frac{4\tau\tau'\kappa'}{\kappa^2} + \frac{\kappa''\tau^2}{\kappa^2} - \frac{2\tau^2\kappa'^2}{\kappa^3}\right)\psi_3\right]ds = 0. \qquad \text{(B.14)}$$

Similarly to the above, we may integrate by parts the terms involving ψ_3', ψ_3'', ψ_3''' and ψ_3''''. As such, (B.14) becomes

$$\int\left\{-\frac{d^3}{ds^3}\left(\frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau}\right) - \frac{d^2}{ds^2}\left(\frac{\kappa'}{\kappa^2}\frac{\partial\mathcal{F}}{\partial\tau}\right) + \frac{d}{ds}\left(2\tau\frac{\partial\mathcal{F}}{\partial\kappa} + \frac{\tau^2}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau} - \kappa\frac{\partial\mathcal{F}}{\partial\tau}\right)\right.$$
$$-\tau'\frac{\partial\mathcal{F}}{\partial\kappa} + \left[\frac{\kappa'\tau^2}{\kappa^2} - \frac{2\tau\tau'}{\kappa}\right]\frac{\partial\mathcal{F}}{\partial\tau} - \tau''\frac{\partial\mathcal{F}}{\partial\kappa'} + \frac{d}{ds}\left(3\tau'\frac{\partial\mathcal{F}}{\partial\kappa'}\right) - \frac{d^2}{ds^2}\left(2\tau\frac{\partial\mathcal{F}}{\partial\kappa'}\right)$$
$$+\left[-\frac{2\tau'^2}{\kappa} - \frac{2\tau\tau''}{\kappa} + \frac{4\tau\tau'\kappa'}{\kappa^2} + \frac{\kappa''\tau^2}{\kappa^2} - \frac{2\tau^2\kappa'^2}{\kappa^3}\right]\frac{\partial\mathcal{F}}{\partial\tau'} - \frac{d}{ds}\left(\left[\kappa' - \frac{4\tau\tau'}{\kappa} + \frac{2\kappa'\tau^2}{\kappa^2}\right]\frac{\partial\mathcal{F}}{\partial\tau'}\right)$$
$$\left.+\frac{d^2}{ds^2}\left(\left[\kappa - \frac{\tau^2}{\kappa} - \frac{\kappa''}{\kappa^2} + \frac{2\kappa'^2}{\kappa^3}\right]\frac{\partial\mathcal{F}}{\partial\tau'}\right) - \frac{d^3}{ds^3}\left(-\frac{2\kappa'}{\kappa^2}\frac{\partial\mathcal{F}}{\partial\tau'}\right) + \frac{d^4}{ds^4}\left(\frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau'}\right)\right\}\psi_3 ds = 0, \quad \text{(B.15)}$$

where we assume that the condition

$$\frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau'}\psi_3''' + \left\{-\frac{d}{ds}\left(\frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau'}\right) + \frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau} - \frac{2\kappa'}{\kappa^2}\frac{\partial\mathcal{F}}{\partial\tau'}\right\}\psi_3''$$
$$+\left\{\frac{d^2}{ds^2}\left(\frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau'}\right) - \frac{d}{ds}\left(\frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau} - \frac{2\kappa'}{\kappa^2}\frac{\partial\mathcal{F}}{\partial\tau'}\right) - \frac{\kappa'}{\kappa^2}\frac{\partial\mathcal{F}}{\partial\tau} - 2\tau\frac{\partial\mathcal{F}}{\partial\kappa'} + \left[\kappa - \frac{\tau^2}{\kappa} - \frac{\kappa''}{\kappa^2} + \frac{2\kappa'^2}{\kappa^3}\right]\frac{\partial\mathcal{F}}{\partial\tau'}\right\}\psi_3'$$

$$+\left\{-\frac{d^3}{ds^3}\left(\frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau'}\right)+\frac{d^2}{ds^2}\left(\frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau}-\frac{2\kappa'}{\kappa^2}\frac{\partial\mathcal{F}}{\partial\tau'}\right)\right.$$

$$+\frac{d}{ds}\left(\frac{\kappa'}{\kappa^2}\frac{\partial\mathcal{F}}{\partial\tau}+2\tau\frac{\partial\mathcal{F}}{\partial\kappa'}-\left[\kappa-\frac{\tau^2}{\kappa}-\frac{\kappa''}{\kappa^2}+\frac{2\kappa'^2}{\kappa^3}\right]\frac{\partial\mathcal{F}}{\partial\tau'}\right)$$

$$\left.-2\tau\frac{\partial\mathcal{F}}{\partial\kappa}+\left[\kappa-\frac{\tau^2}{\kappa}\right]\frac{\partial\mathcal{F}}{\partial\tau}-3\tau'\frac{\partial\mathcal{F}}{\partial\kappa'}+\left[\kappa'-\frac{4\tau\tau'}{\kappa}+\frac{2\tau^2\kappa'}{\kappa^2}\right]\frac{\partial\mathcal{F}}{\partial\tau'}\right\}\psi_3=0 \tag{B.16}$$

is satisfied at the boundary. Equation (B.15) is satisfied for arbitrary functions ψ_3 when

$$-\frac{d^3}{ds^3}\left(\frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau}\right)-\frac{d^2}{ds^2}\left(\frac{\kappa'}{\kappa^2}\frac{\partial\mathcal{F}}{\partial\tau}\right)+\frac{d}{ds}\left(2\tau\frac{\partial\mathcal{F}}{\partial\kappa}+\frac{\tau^2}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau}-\kappa\frac{\partial\mathcal{F}}{\partial\tau}\right)$$

$$-\tau'\frac{\partial\mathcal{F}}{\partial\kappa}+\left[\frac{\kappa'\tau^2}{\kappa^2}-\frac{2\tau\tau'}{\kappa}\right]\frac{\partial\mathcal{F}}{\partial\tau}-\tau''\frac{\partial\mathcal{F}}{\partial\kappa'}+\frac{d}{ds}\left(3\tau'\frac{\partial\mathcal{F}}{\partial\kappa'}\right)-\frac{d^2}{ds^2}\left(2\tau\frac{\partial\mathcal{F}}{\partial\kappa'}\right)$$

$$+\left[-\frac{2\tau'^2}{\kappa}-\frac{2\tau\tau''}{\kappa}+\frac{4\tau\tau'\kappa'}{\kappa^2}+\frac{\kappa''\tau^2}{\kappa^2}-\frac{2\tau^2\kappa'^2}{\kappa^3}\right]\frac{\partial\mathcal{F}}{\partial\tau'}-\frac{d}{ds}\left(\left[\kappa'-\frac{4\tau\tau'}{\kappa}+\frac{2\kappa'\tau^2}{\kappa^2}\right]\frac{\partial\mathcal{F}}{\partial\tau'}\right)$$

$$+\frac{d^2}{ds^2}\left(\left[\kappa-\frac{\tau^2}{\kappa}-\frac{\kappa''}{\kappa^2}+\frac{2\kappa'^2}{\kappa^3}\right]\frac{\partial\mathcal{F}}{\partial\tau'}\right)-\frac{d^3}{ds^3}\left(-\frac{2\kappa'}{\kappa^2}\frac{\partial\mathcal{F}}{\partial\tau'}\right)+\frac{d^4}{ds^4}\left(\frac{1}{\kappa}\frac{\partial\mathcal{F}}{\partial\tau'}\right)=0. \tag{B.17}$$

Equation (B.17) can be simplified giving rise to (2.2). Again, we note that the boundary condition (B.16) is satisfied either if $\psi_3=\psi_3'=\psi_3''=\psi_3'''=0$ or if the coefficients of ψ_3, ψ_3', ψ_3'' and ψ_3''' are equal to zero at the boundary, giving rise to the alternative boundary conditions.

APPENDIX C

For the case of the energy density depending only on the curvature, we show here that the integration of (2.3) and (2.4) can be resulted in general terms for any given $\mathcal{F}(\kappa)$. We note that the same result can also be found in Feoli *et al.* (**14**), but the procedure given here is far more direct and formal. To solve (2.3) and (2.4), we first simplify (2.4) as

$$\frac{d\tau}{ds}\frac{d\mathcal{F}(\kappa)}{d\kappa}+2\tau\frac{d^2\mathcal{F}(\kappa)}{d\kappa^2}\frac{d\kappa}{ds}=0$$

so that if we denote $\mathcal{F}_\kappa=d\mathcal{F}(\kappa)/d\kappa$, then the above equation can be rearranged as $-(1/\tau)d\tau=2[\mathcal{F}_{\kappa\kappa}/\mathcal{F}_\kappa]d\kappa$, which can be integrated to give an equation for determining τ, namely

$$\tau=\frac{C_1}{\mathcal{F}_\kappa^2}, \tag{C.1}$$

where C_1 is a constant of integration. Upon substituting (C.1) into (2.3) and simplifying, we deduce

$$\frac{d^2\mathcal{F}_\kappa}{ds^2} + \kappa[\kappa\mathcal{F}_\kappa - \mathcal{F}] = \frac{C_1^2}{\mathcal{F}_\kappa^3}. \tag{C.2}$$

By introducing $p = \mathcal{F}_\kappa$ and $\omega = \kappa\mathcal{F}_\kappa - \mathcal{F}$, we find $\kappa = d\omega/dp$ and with these substitutions, (C.2) reduces to

$$\frac{d^2 p}{ds^2} + \omega\frac{d\omega}{dp} = \frac{C_1^2}{p^3}. \tag{C.3}$$

With further substitution of $u = dp/ds$, (C.3) becomes

$$u\frac{du}{dp} + \omega\frac{d\omega}{dp} = \frac{C_1^2}{p^3}, \tag{C.4}$$

which may readily be integrated to give $u = \pm\{C_2 - \omega^2 - C_1^2 p^{-2}\}^{1/2}$, where C_2 denotes an arbitrary constant. Since $u = dp/ds$, we are left with the following formal integration:

$$\int \frac{p\,dp}{\sqrt{p^2(C_2 - \omega^2) - C_1^2}} + C_3 = \pm s, \tag{C.5}$$

where C_3 denotes a further arbitrary constant, $p = \mathcal{F}_\kappa$ and $\omega = \kappa\mathcal{F}_\kappa - \mathcal{F}$.