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CONTINUUM DYNAMICS OF A PEPTIDE CHAIN

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SUMMARY

In this paper we derive equations for the dynamics of a peptide chain in a quadrilateral chip model, assuming dipole interactions between adjacent peptide units and passing to the continuous limit. Dihedral interactions are included and, when strong, are seen to ensure stability. Hydrogen bonds, on the other hand, are not taken into account in the main calculation. All interactions are local in this model. These factors are sufficient to yield helical shapes as exact solutions. Hydrogen bonds are needed, however, to obtain eigenfrequencies, and when this (distinct) calculation is performed, peptide oscillations with frequencies of the order of $10^{13}\ s^{-1}$ are obtained, in agreement with observation. Solitons are only found in very restricted cases, so far.

External forces, such as those due to the solvent, can be included in the model.

INTRODUCTION

The dynamic of the peptide chain constitutes a much research and open field of present day biophysics. The amount of experimental, theoretical and numerical work on structure, stability and folding is staggering. However, there is no widely known analytical model derived from first principles. Empirical terms are usually introduced. Here we will try as far as possible to avoid this.

Before outlining the approach of this paper, a few words about the vast literature on peptide dynamics, even if limited to the last few years, is in order. A somewhat more complete picture could be gained by consulting bibliographies of the very few papers we will be able to quote here.

On line of theoretical and numerical research follows the introduction of empirical elements into the potential energy function. This trend has been important for decades. For recent results and references see Olsen et al. (1989), Mazur, Dorofeev and Abagyan (1991), and Ramanathan and Shakhnovich (1994); and e.g., Karplus and McCammon (1986) or Chin et al. (1988) for reports on computations. For general background see McCammon and Harvey (1987).

The concept of solitons propagating and transferring energy along the bonded spines of a helix is conceptually very attractive and usually comes under the heading of "Davydov solitons" (Davydov 1985). Models similar to or else just extending Davydov's have been developed by others (Yomosa 1983, 1985, Bolterauer and Henkel 1986). All these authors obtain soliton solutions, as do many others (Scott, Chu and Mc Laughlin 1973, Scott 1983, Lawrence et al. 1987, Hochstrasser, Martens and Buttner 1989, Fedderson 1993). However, Davydov's approach leans heavily and hydrogen bonding, rendering the problem virtually one dimensional. We believe that the microscopic properties of the chain, such as the internal degrees of freedom and the kinematic restrictions at the C_2 atoms should enter the equations in an essential manner, not just through phenomenological constants. Also, three dimensionality would seem to be of more basic importance. Davydov's theory has also been criticized from other points of view (Pang Xiaofeng 1993 criticizes the mechanisms for energy transport in the model). This is not to negate the simplicity and elegance of Davydov's approach.

The approach in this paper to the dynamics of a peptide chain is classical. Peptide units are treated as quadrilateral chips. We take into account the local kinematical features of the chain. These include the rigidity of the peptide unit and the constraints at the C_2 atoms restricting the relative motion of the adjacent units to changes of two dihedral angles. A second factor is the dipole interaction between adjacent units. The energy of bending and twisting at the joints between units is also taken into account. External forces, such as those due to the solvent, can be included in our model.

Transition to the continuum restricts the validity of our theory, though it is hard to know a priori to what extent (for example a calculation in which the continuum limit kills solutions that were present in the discrete case in known, Lomdahl, Olsen and Samuelsen 1991; in other cases little is lost, see Zorski and Infeld 1992). However, our continuum model, in which the chain is an inextensible line with rotations of the peptide units as the internal degrees of freedom, does have its assets. It leads to a system of dynamical equations yielding exact solutions, in particular cases. The most interesting of these solutions is of course the helix. Given the locality of the theory, general expressions for the internal energy can be constructed. This energy is invariant with respect to rigid rotations and translations of the chain as whole. Thus, a simple expression for the density of the internal energy, which is quadratic in appropriate dynamic and field variables, describes not only the dipole interactions but also those due to bending and twisting of the chain. When these dihedral interactions are strong, stability is ensured.

Our theory has its limitations. One is the continuum limit mentioned above. Also, the hydrogen bonds between molecules separated by finite distance are non-local in our continuum theory and are not included here. They are of course one of the stabilizing factors, though perhaps not the most important one (Sundralingham et al. 1987). Other stabilizing factors may be more important (e.g., Ooi 1987, Privalov 1987, Regan and De Grado 1988, Austin 1988). Be that as it may, it is interesting that dihedral interactions on their own can in theory achieve the desired interactions on their own can in theory achieve the desired stabilization. Importantly, however, we have not yet obtained eigenfrequencies from our theory. Solitons have so far also failed to make appearance in the general three dimensional chain. We now address these two shortcomings.

Hydrogen bonds are absent ~~for~~ from our theory and we find that eigenoscillations only follow from simple considerations such as the above when these bonds are reintroduced in some manner. Here by doing so we obtain a basic picture of electrical vibrations of an α-helix, extending an idea of Fröhlich (1970, 1972, 1973). Finite dipole lengths are taken into account. An angular frequency for the basic mode of collective oscillations is found. It is almost $10^{13}\ s^{-1}$ for a typical protein. In spite of the simple geometry assumed (simpler than for the main model), the order of magnitude so obtained agrees with experiment.

Finally, when considerations are restricted to two dimensions and the neighbouring

dipoles are allowed to rotate freely, dipole interactions remain and soliton solutions are obtained from our model. Previous results of Zorski and Infeld (1992), and Infeld et al. (1995), including their equation, are recovered. However, this takes us so far afield from our α-helix that it is hardly cause for claiming that solitons can propagate energy in our fully three dimensional and hydrogen-bond-free model. This so far remains an open question.

In the last Chapter two-dimensional problems are examined. It turns out that in the considered here particular case the governing equations are the same as in the Kirchoff-Clebsch theory of rods (Coleman et al, 1991, 1993).

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§1. Peptide chain and its states

A peptide unit (Fig. 1) is a system of five atoms: two carbon (C_α and C'), one nitrogen (N), one hydrogen (H) and one oxygen (O). Identical peptide units are linked at the carbon atoms C_α to yield a peptide chain (Fig. 2). The units are numbered by $n = 0, 1, 2, \ldots, N-1$. An atom in the n-th unit will be generally denoted by $P^{(n)}$, e.g. $P^{(n)} = H$ or $P^{(n)} = N$. The upper carbon atom $C_\alpha^{(n+1)}$ belongs to the next, $(n+1)$-st unit. The masses of the atoms are denoted by $m(C)$, etc. so that the total mass of the unit is $m^{(n)} = m = 2m(C) + m(H) + m(O) + m(N)$. The position vectors are $\mathbf{r}(P^{(n)}, t)$ and the time variable will usually be suppressed; we shall also use the notation $\overset{\circ}{\mathbf{r}}(P^{(n)} = \mathbf{r}(P^{(n)}, 0)$ to represent the position vector in a natural state identical with the state at $t = 0$.

The peptide chain at time t is generated from a single peptide unit completed by its upper C_α atom in the following way: to determine the position of the n-th peptide unit $(n = 0, 1, 2, \ldots, N-1)$ displace the lower C_α atom to $C_\alpha^{(n)}$ and rotate the unit by means of the rotation tensor $\boldsymbol{Q}^{(n)}$. The upper C_α atom of the n-th unit and the lower C_α of the $(n+1)$-st unit (Fig. 2) coincide. Fig.1

The following are the two kinematic assumptions on which the dynamics is based.

1. The peptide unit and upper C_α atom move as a rigid system of material points. The standard bond lengths and angles, constant during the motion are shown in Fig. 1 (see e.g. [2]). The rigidity and moreover planarity (the latter is not assumed in our analysis) are due to the double bond character of $C' - N$ which excluded rotation about the $C' - N$ line.

2. The relative rotation of the adjacent peptide units, say $(n-1)$-st and n-th, linked at the carbon atom $C_\alpha^{(n)}$, is restricted to the following two rotations (Fig. 2): i) around the bond between the atom N in the $(n-1)$-st unit and $C_\alpha^{(n)}$, by angle $\phi^{(n-1)}$, ii) around the bond between $C_\alpha^{(n)}$ and C' in the n-th unit, by an angle $\psi^{(n)}$. The angles $\phi^{(n-1)}$ and $\psi^{(n)}$ are called dihedral angles. The two above axes of rotation are fixed in the $(n-1)$-st and n-th units respectively, they are therefore material axes and if the two unit vectors defining them are denoted by $\boldsymbol{b}^{(n-1)}$ and $\boldsymbol{a}^{(n)}$, respectively, we have $\boldsymbol{b}^{(n-1)} = \boldsymbol{Q}^{(n-1)} \cdot \overset{\circ}{\boldsymbol{b}}$ and $\boldsymbol{a}^{(n)} = \boldsymbol{Q}^{(n)} \cdot \overset{\circ}{\boldsymbol{a}}$ where $\overset{\circ}{\boldsymbol{a}}$ and $\overset{\circ}{\boldsymbol{b}}$ are constant vectors determined Fig.2

by the geometry of the unit. Thus, the peptide chain is a kinematic chain [16]. No side chains are considered here. It is assumed that they are sufficiently small, like in glycine, to be regarded as attached rigidly to the C_α atom, increasing its mass only.

The vectors $\boldsymbol{a}^{(n)}, \boldsymbol{b}^{(n-1)}$ are examples of material vectors; generally speaking, any vector $\boldsymbol{\alpha}$ transformed by $\boldsymbol{Q}$ in accordance with the rule $\boldsymbol{\alpha} = \boldsymbol{Q} \cdot \mathring{\boldsymbol{\alpha}}$ where $\mathring{\boldsymbol{\alpha}}$ is constant in time, is called material. Similarly, a material tensor $\boldsymbol{\alpha}$ transforms as follows: $\boldsymbol{\alpha} = \boldsymbol{Q} \cdot \mathring{\boldsymbol{\alpha}} \cdot \boldsymbol{Q}^T$. The set of quantities $\mathring{\boldsymbol{\alpha}}$ can be regarded as the set of components of the vector or the tensor, constant in the coordinate system moving rigidly with the peptide unit.

Let now $(P^{(n)}, P, n = 1, 2, \ldots)$ be a system of points moving rigidly, the rotation tensor being $\boldsymbol{Q}$ (App. A). Thus, the rigidity condition is

$$\boldsymbol{r}(P^{(n)}) = \boldsymbol{r}(P) + \boldsymbol{Q} \cdot \mathring{\boldsymbol{\rho}}\,(P^{(n)}) \tag{1.1}$$

where

$$\mathring{\boldsymbol{\rho}}\,(P^{(n)}) = \mathring{\boldsymbol{r}}\,(P^{(n)}) - \mathring{\boldsymbol{r}}\,(P)$$

and $\mathring{\boldsymbol{r}}\,(P^{(n)})$ is the position vector of $P^{(n)}$ at time $t = 0$. $\mathring{\boldsymbol{\rho}}\,(P^{(n)})$ is the position vector of $\boldsymbol{r}^{(n)}$ in the coordinate system moving with the considered system of points and the origin at P . Differentiating (1.1) we obtain the velocities

$$\boldsymbol{v}(P^{(n)}) = \boldsymbol{v}(P) + \dot{\boldsymbol{Q}} \cdot \mathring{\boldsymbol{\rho}}\,(P^{(n)}) \tag{1.2}$$

The kinetic energy is

$$K = \frac{1}{2} \sum_{P^{(n)}} |\boldsymbol{v}(P) + \dot{\boldsymbol{Q}} \cdot \mathring{\boldsymbol{\rho}}\,(P^{(n)})|^2 m(P^{(n)}) = \frac{1}{2} m |\boldsymbol{v}(P)|^2 + \boldsymbol{v}(P) \cdot \dot{\boldsymbol{Q}} \cdot \mathring{\boldsymbol{\sigma}} + \frac{1}{2} tr(\dot{\boldsymbol{Q}}\, \mathring{\boldsymbol{I}}\, \dot{\boldsymbol{Q}}^T) \tag{1.3}$$

where

$$\mathring{\boldsymbol{\sigma}} = \sum_{P^{(n)}} m(P^{(n)})\, \mathring{\boldsymbol{\rho}}\,(P^{(n)}) = m[\mathring{\boldsymbol{r}}\,(CG) - \mathring{\boldsymbol{r}}\,(P)] \quad m = \sum_{P^{(n)}} m(P^{(n)})$$

$$\mathring{\boldsymbol{I}} = \sum_{P^{(n)}} m(P^{(n)})\, \mathring{\boldsymbol{\rho}}\,(P^{(n)})\, \mathring{\boldsymbol{\rho}}\,(P^{(n)})$$

are the static and inertia moments, respectively. We shall later use also the inertia moment $\mathring{\boldsymbol{I}} = \mathring{\boldsymbol{I}} - \frac{1}{m} \mathring{\boldsymbol{\sigma}} \mathring{\boldsymbol{\sigma}}$.

The linear and angular momenta are defined as follows $(\boldsymbol{v}(P) = \boldsymbol{v})$:

$$\boldsymbol{p} = \frac{\partial K}{\partial \boldsymbol{v}} = m\boldsymbol{v} + \dot{\boldsymbol{Q}} \cdot \mathring{\boldsymbol{\sigma}}\,, \qquad \pi_i = \frac{\partial K}{\partial \alpha_i} = \frac{\partial Q_{pq}}{\partial \alpha_i} (v_p\, \mathring{\sigma}_q + \mathring{I}_{qr}\, \dot{Q}_{pr}), \tag{1.4}$$

Since $\dot{Q}_{ij} = \dfrac{\partial Q_{ij}}{\partial \alpha_m}\dot{\alpha}_m$ where α_i are the three independent parameters in any representation of $\boldsymbol{Q}$ (see [16] or [20]). Substituting for $\boldsymbol{v} = \dfrac{1}{m}(\boldsymbol{p} - \dot{\boldsymbol{Q}}\cdot \overset{\circ}{\boldsymbol{\sigma}})$ into the expression for the kinetic energy we obtain

$$K = \frac{1}{2m}|\boldsymbol{p}|^2 + \frac{1}{2}\dot{\boldsymbol{\alpha}}\cdot \overset{\sigma}{\boldsymbol{K}}\cdot\dot{\boldsymbol{\alpha}} \tag{1.5}$$

where $\overset{\sigma}{K}_{ij} = \dfrac{\partial Q_{pq}}{\partial \alpha_i}\overset{\sigma}{I}_{qr}\dfrac{\partial Q_{pr}}{\partial \alpha_j}$. Since both terms in K are positive definite and $\boldsymbol{p}$ and $\boldsymbol{\alpha}$ are independent, the matrix $\overset{\sigma}{\boldsymbol{K}}$ is invertible whence

$$\begin{aligned} v_i &= \frac{1}{m}(p_i - \frac{\partial Q_{ip}}{\partial \alpha_n}\overset{\circ}{\alpha}_q\overset{\circ}{\sigma}_p) = \frac{1}{m}(p_i - \frac{\partial Q_{ip}}{\partial \alpha_m}\overset{\circ}{\sigma}_p\overset{\sigma}{K}{}^{-1}_{mn}\tilde{\pi}_n) \\ \dot{\alpha}_i &= \overset{\sigma}{K}{}^{-1}_{im}(\pi_m - \frac{1}{m}\frac{\partial Q_{pq}}{\partial \alpha_m}p_p\overset{\circ}{\sigma}_q) = \overset{\sigma}{\boldsymbol{K}}{}^{-1}\cdot\tilde{\boldsymbol{\pi}} \end{aligned} \tag{1.6}$$

where $\tilde{\pi}_i = \pi_i - \dfrac{1}{m}\dfrac{\partial Q_{pq}}{\partial \alpha_i}p_p\overset{\circ}{\sigma}_q$ and therefore, substituting for $\dot{\boldsymbol{\alpha}}$ in K

$$K = \frac{1}{2m}|\boldsymbol{p}|^2 + \frac{1}{2}\tilde{\boldsymbol{\pi}}\cdot\overset{\sigma}{\boldsymbol{K}}{}^{-1}\cdot\tilde{\boldsymbol{\pi}} \tag{1.7}$$

i.e. the kinetic energy in terms of the linear and angular momenta. The Hamiltonian and the Lagrangian are now introduced in the usual way

$$L = K - \phi\,, \qquad H = -L + \boldsymbol{p}\cdot\boldsymbol{v} + \boldsymbol{\pi}\cdot\dot{\boldsymbol{\alpha}} = K + \phi \tag{1.8}$$

where ϕ is independent of $\boldsymbol{v}$ and $\dot{\boldsymbol{\alpha}}$ and will be treated in Chapter 6; thus the definitions (1.4) take the usual form

$$\boldsymbol{p} = \frac{\partial H}{\partial \boldsymbol{v}}\,, \qquad \boldsymbol{\pi} = \frac{\partial H}{\partial \dot{\boldsymbol{\alpha}}} \tag{1.9}$$

We note that $\tilde{\boldsymbol{\pi}}$ is linear in $\boldsymbol{p}$ and $\boldsymbol{\pi}$ and K is quadratic in these moments.

The Hamiltonian equations have the standard form

$$\dot{\boldsymbol{r}} = \frac{\partial H}{\partial \boldsymbol{p}}\,, \qquad \dot{\boldsymbol{p}} = -\frac{\partial H}{\partial \boldsymbol{r}}\,; \qquad \dot{\boldsymbol{\alpha}} = \frac{\partial H}{\partial \boldsymbol{\pi}}\,, \qquad \dot{\boldsymbol{\pi}} = -\frac{\partial H}{\partial \boldsymbol{\alpha}} \tag{1.10}$$

and hence the Lagrangian equations are the following:

$$\begin{aligned} &\frac{d^2}{dt^2}(mr_i + Q_{ip}\overset{\circ}{\sigma}_p) = -\frac{\partial \phi}{\partial r_i} \\ &\overset{\sigma}{I}_{qr}\frac{\partial Q_{pq}}{\partial \alpha_i}\ddot{Q}_{pr} = -\frac{\partial \phi}{\partial \alpha_i} + \frac{1}{m}\overset{\circ}{\sigma}_q\frac{\partial Q_{pq}}{\partial \alpha_i}\frac{\partial \phi}{\partial r_p} \end{aligned} \tag{1.11}$$

The equation for the angular momentum can be reduced to the conventional Eulerian form by introducing the rotation tensor $\boldsymbol{\Omega} = \dot{\boldsymbol{Q}}\boldsymbol{Q}^T$ and the rotation vector $\omega_i = \frac{1}{2}\varepsilon_{ipq}\Omega_{pq}$. Then (cf. [16] or [20])

$$\omega_i = a_{ip}^{-1}\dot{c}_p \tag{1.12}$$

where

$$a_{ip}^{-1} = \frac{1}{2}\varepsilon_{iqr}\frac{\partial Q_{qn}}{\partial \alpha_p}Q_{rn}$$

is an invertible tensor and moreover

$$\ddot{Q}_{ij} = (\dot{\Omega}_{ip} + \Omega_{qp}\Omega_{iq})Q_{pj} = [\varepsilon_{ipq}\dot{\omega}_q - (\delta_{ip}|\omega|^2 - \omega_i\omega_p)]Q_{pj} .$$

The final equations are conventionally written for the rotation vector $\boldsymbol{\omega}, \boldsymbol{\omega} = \boldsymbol{Q}\cdot\boldsymbol{\omega}$:

$$\overset{\circ}{J}_{ip}\dot{\bar{\omega}}_p - \varepsilon_{ipq}\overset{\circ}{J}_{qr}\bar{\omega}_p\bar{\omega}_r = a_{pq}Q_{qi}\left(-\frac{\partial\phi}{\partial\alpha_p} + \frac{1}{m}\overset{\circ}{\sigma}_r\frac{\partial Q_{qs}}{\partial\alpha_p}\frac{\partial\phi}{\partial r_s}\right) \tag{1.13}$$

where the new inertia tensor is

$$\overset{\circ}{J}_{ij} = \delta_{ij}\, tr\,\overset{\circ}{\boldsymbol{I}} - \overset{\circ}{I}_{ij} \tag{1.14}$$

A more explicit form of the equations of motion in the canonical variables follows by performing the required differentiation in (1.11):

$$\overset{\circ}{K}_{im}\ddot{\alpha}_m + \overset{\circ}{L}_{imn}\dot{\alpha}_m\dot{\alpha}_n = -\frac{\partial\phi}{\partial\alpha_i} + \frac{1}{m}\overset{\circ}{\sigma}_q\frac{\partial Q_{pq}}{\partial\alpha_i}\frac{\partial\phi}{\partial r_p} \tag{1.15}$$

where

$$\overset{\circ}{L}_{imn} = \frac{1}{2}\left(\frac{\partial\overset{\circ}{K}_{im}}{\partial\alpha_n} + \frac{\partial\overset{\circ}{K}_{in}}{\partial\alpha_m} - \frac{\partial\overset{\circ}{K}_{mn}}{\partial\alpha_i}\right) .$$

Clearly, all above equations are considerably simplified when the reference point P is the centre of gravity. Then $\overset{\circ}{\boldsymbol{\sigma}} = 0$, $\overset{\circ}{\boldsymbol{I}} = \overset{\circ}{\boldsymbol{I}}$, $\overset{\circ}{K}_{ij} = \overset{\circ}{K}_{ij} = \frac{\partial Q_{pi}}{\partial\alpha_i}\overset{\circ}{I}_{qr}\frac{\partial Q_{pr}}{\partial\alpha_j}$, $\dot{\boldsymbol{\pi}} = \boldsymbol{\pi}$ and

$$v_i = \frac{1}{m}p_i , \qquad \dot{\alpha}_i = \overset{\circ}{\boldsymbol{K}}^{-1}\cdot\boldsymbol{\pi} \tag{1.16}$$

The equations of motion are now

$$\begin{aligned} m\ddot{r}_i &= -\frac{\partial\Phi}{\partial r_i} \\ \overset{\circ}{I}_{qr}\frac{\partial Q_{pi}}{\partial\alpha_i}\ddot{Q}_{pr} &= -\frac{\partial\Phi}{\partial\alpha_i} \end{aligned} \tag{1.17}$$

We shall now show that the Lagrangian equations of motion follow from a variational principle. The variables are now r_i and Q_{ij} with the constraint $\boldsymbol{Q}\boldsymbol{Q}^T = \boldsymbol{\delta}$. The Lagrangian is completed by the term $\frac{1}{2}\boldsymbol{\lambda} : (\boldsymbol{Q}\boldsymbol{Q}^T - \boldsymbol{\delta})$ where λ_{ij} is a Lagrange multiplier, symmetric in its indices:

$$L = \frac{1}{2}m|\boldsymbol{v}|^2 + \boldsymbol{v}\cdot\dot{\boldsymbol{Q}}\cdot\mathring{\boldsymbol{\sigma}} + \frac{1}{2}\,tr\,\dot{\boldsymbol{Q}}\,\mathring{\boldsymbol{I}}\,\dot{\boldsymbol{Q}}^T + \boldsymbol{\lambda} : (\boldsymbol{Q}\boldsymbol{Q}^T - \boldsymbol{\delta}) - \phi \tag{1.18}$$

The equations of motion are

$$\left(\frac{\partial L}{\partial \boldsymbol{v}}\right)^{\cdot} - \frac{\partial L}{\partial \boldsymbol{r}} = 0\,, \qquad \left(\frac{\partial L}{\partial \dot{\boldsymbol{Q}}}\right)^{\cdot} - \frac{\partial L}{\partial \boldsymbol{Q}} = 0\,.$$

Since

$$\frac{\partial L}{\partial r_i} = -\frac{\partial \phi}{\partial r_i}\,, \qquad \frac{\partial L}{\partial v_i} = m v_i + \dot{Q}_{ip}\,\mathring{\sigma}_p$$

the equation of linear momentum follows immediately. Now

$$\frac{\partial L}{\partial Q_{ij}} = \lambda_{ip}Q_{pj}\,, \qquad \frac{\partial L}{\partial \dot{Q}_{ij}} = \dot{Q}_{ip}\,\mathring{I}_{jp} + v_i\,\mathring{\sigma}_j$$

whence

$$\ddot{Q}_{ir}\,\mathring{I}_{jr} + \dot{v}_i\,\mathring{\sigma}_j - \lambda_{ip}Q_{pj} = -\frac{\partial \phi}{\partial Q_{ij}}$$

and multiplying by Q_{lj},

$$\ddot{Q}_{ir}Q_{ls}\,\mathring{I}_{sr} + \dot{v}_i Q_{ls}\,\mathring{\sigma}_s + \frac{\partial \phi}{\partial Q_{is}}Q_{ls} - \lambda_{il} = 0\,. \tag{1.19}$$

The symmetric part of the above equation yields λ_{ij}; to obtain the angular momentum equation we multiply (1.19) by ε_{ail}, use the formula

$$\varepsilon_{ilp}Q_{ls} = \frac{\partial Q_{is}}{\partial \alpha_m}a_{mt}$$

and the fact that a is invertible. Thus, we arrive at (1.17).

§2. The kinematic constrain at C_α and the local rigidity

By the assumption in Chapter I the n-th and $(n-1)$-st peptide units can rotate with respect to each other about the axes $\boldsymbol{a}^{(n)}$ and $\boldsymbol{b}^{(n-1)}$ by the dihedral angles $\varphi^{(n)}$

$\phi^{(n-1)}$, respectively. The axes $a^{(n)}$ and $b^{(n-1)}$ are material i.e. $a^{(n)} = Q^{(n)} \cdot \mathring{a}$ and $b^{(n-1)} = Q^{(n-1)} \cdot \mathring{b}$. The required kinematic constraint can be written in the form

$$R^{(n)}(\psi^{(n)}, a^{(n)}) R^{(n-1)}(\phi^{(n-1)}, b^{(n-1)}) = Q^{(n)} Q^{(n-1)T} \tag{2.1}$$

where $R^{(n)}$ and $R^{(n-1)}$ are rotation tensors with the rotation axes and angles indicated as arguments. We are faced here with an equality of two orthogonal tensors, (2.1) is therefore a system of three independent equations. Treating the system (2.1) as a system of three nonlinear algebraic equations for two dihedral angles $\psi^{(n)}$ and $\phi^{(n-1)}$ (which are not dynamical variables in our approach) we observe that a solution exists only if the right-hand side of (2.1) satisfies an algebraic condition and then the latter constitutes a constraint in the variational principle. The matrices $Q^{(n)}$ and $Q^{(n-1)}$ can be removed from the left-hand side of (2.1); in fact, for an arbitrary orthogonal tensor $R(\psi, a)$, $a = Q \cdot \mathring{a}$ we have the formula

$$R(\psi, a) = Q R(\psi, \mathring{a}) Q^T$$

Applying this to $R^{(n)}$ and $R^{(n-1)}$ we obtain

$$Q^{(n)} R^{(n)} Q^{(n)T} Q^{(n-1)} R^{(n-1)} Q^{(n-1)T} = Q^{(n)} Q^{(n-1)T} \text{ , i.e. } R^{(n)} Q^{(n)T} Q^{(n-1)} R^{(n-1)} = \delta$$

where now $R^{(n)} = R^{(n)}(\psi^{(n)}, \mathring{a})$, $R^{(n-1)} = R^{(n-1)}(\phi^{(n-1)}, \mathring{b})$. Multiplying on the left by $R^{(n)T}$ and on the right by $R^{(n-1)T}$ we have

$$R^{(n-1)}(\phi^{(n-1)}, \mathring{b}^{(n-1)}) R^{(n)}(\psi^{(n)}, \mathring{a}^{(n)}) = Q^{(n-1)T} Q^{(n)} \tag{2.2}$$

The conditions (2.1) and (2.2) are equivalent, the latter however is more convenient in the variational formalism since the tensor $Q^{(n)}$, constituting the basic dynamical variable, appears in a simple manner in the right-hand side only.

Introduce now the tensor $\Gamma^{(n,n-1)}$ by the formula

$$Q^{(n)} Q^{(n-1)T} = \delta + \Gamma^{(n,n-1)}$$

and the vector $\gamma^{(n,n-1)}$ defined by the antisymmetric part of $\Gamma^{(n,n-1)}$.

$$\gamma_i^{(n,n-1)} = \frac{1}{2} \varepsilon_{ipq} \Gamma_{pq}^{(n,n-1)}$$

In terms of the latter vector the constraint takes the form (arguments are suppressed)

$$\varepsilon_{ipq} R^{(n)}_{pr} R^{(n-1)}_{rq} = 2\gamma_i^{(n,n-1)} . \tag{2.3}$$

We shall now present the continuum version of (2.3). Since the dihedral angles $\psi^{(n)}$ and $\phi^{(n-1)}$ are relative angles of rotation, to within a small parameter ε we have

$$\psi^{(n)} = \varepsilon\psi' , \qquad \phi^{(n-1)} = \varepsilon\phi'$$

the prime denoting differentiation with respect to the parameter s on the curve. Hence (we use the notation $\mathbf{1} \times \boldsymbol{a} = \varepsilon_{imj} a_m$)

$$\boldsymbol{R}^{(n)}(\psi^{(n)}, \boldsymbol{a}^{(n)}) = \boldsymbol{\delta} + \varepsilon\psi'(\mathbf{1} \times \boldsymbol{a}) , \qquad \boldsymbol{R}^{(n-1)}(\phi^{(n-1)}, \boldsymbol{b}^{(n-1)}) = \boldsymbol{\delta} + \varepsilon\phi'(\mathbf{1} \times \boldsymbol{b})$$

where $\boldsymbol{a} = \boldsymbol{Q} \cdot \overset{\circ}{\boldsymbol{a}}$, $\boldsymbol{b} = \boldsymbol{Q} \cdot \overset{\circ}{\boldsymbol{b}}$. Since $\boldsymbol{Q}^{(n-1)} = \boldsymbol{Q} - \varepsilon\boldsymbol{Q}'$ the condition (2.2) takes the form

$$\boldsymbol{Q}(\boldsymbol{Q}^T - \varepsilon\boldsymbol{Q}'^T) = \boldsymbol{\delta} + \varepsilon[\psi'(\mathbf{1} \times \boldsymbol{a}) + \phi'(\mathbf{1} \times \boldsymbol{b})]$$

and equating terms of order ε

$$\boldsymbol{Q}'\boldsymbol{Q}^T = \psi'\mathbf{1} \times \boldsymbol{a} + \phi'\mathbf{1} \times \boldsymbol{b} .$$

The definition of $\Gamma^{(n,n-1)}$ yields

$$\boldsymbol{\Gamma}^{(n,n-1)} = -\varepsilon\boldsymbol{Q}\boldsymbol{Q}'^T = \varepsilon\boldsymbol{Q}'\boldsymbol{Q}^T = \varepsilon\boldsymbol{\Gamma}$$

where $\boldsymbol{\Gamma} = \boldsymbol{Q}'\boldsymbol{Q}^T$ is an antisymmetric tensor. It constitutes the spatial counterpart of the rotation tensor $\boldsymbol{\Omega} = \dot{\boldsymbol{Q}}\boldsymbol{Q}^T$. Similarly we obtain $\dot{\boldsymbol{\Gamma}} = \boldsymbol{Q}^T\boldsymbol{Q}'$ and

$$\boldsymbol{\Gamma} = \boldsymbol{Q}\dot{\boldsymbol{\Gamma}}\boldsymbol{Q}^T , \qquad \dot{\boldsymbol{\gamma}} = \boldsymbol{Q}^T \cdot \boldsymbol{\gamma}$$

where $\boldsymbol{\gamma} = \mathrm{vect}\boldsymbol{\Gamma}$, i.e. $\gamma_i = \frac{1}{2}\varepsilon_{ipq}\Gamma_{pq}$. Thus (2.3) takes the form

$$\boldsymbol{\gamma} + (\psi'\boldsymbol{a} + \phi'\boldsymbol{b}) = 0 \tag{2.4}$$

or equivalently

$$\dot{\boldsymbol{\gamma}} + (\psi'\overset{\circ}{\boldsymbol{a}} + \phi'\overset{\circ}{\boldsymbol{b}}) = 0 \tag{2.5}$$

(2.4) or (2.5) implies a constraint on the dynamic variable Q necessary and sufficient for the existence of the dihedral angles $\psi(s,t)$, $\phi(s,t)$, namely γ must lie in the plane spanned by the vectors a and b defined by the geometry of the chain:

$$\gamma \cdot (a \times b) = 0 \tag{2.6}$$

or

$$\tilde{\gamma} \cdot (\overset{\circ}{a} \times \overset{\circ}{b}) = 0 \tag{2.7}$$

Knowing Q and hence also γ satisfying (2.6) we can calculate uniquely the derivatives of the dihedral angles from (2.4) or (2.5):

$$\psi' = \frac{-1}{1-(a\cdot b)^2}(a \times b)\cdot(\gamma \times b) = \frac{-1}{1-(\overset{\circ}{a}\cdot\overset{\circ}{b})^2}(\overset{\circ}{a}\times\overset{\circ}{b})\cdot(\tilde{\gamma}\times\overset{\circ}{b}) =$$

$$\frac{1}{1-(\overset{\circ}{a}\cdot\overset{\circ}{b})^2}[-\overset{\circ}{a}+(\overset{\circ}{a}\cdot\overset{\circ}{b})\overset{\circ}{b}]\cdot\tilde{\gamma} \overset{def}{=} \overset{\circ}{h}{}^{\psi}\cdot\tilde{\gamma}$$

$$\phi' = \frac{-1}{1-(a\cdot b)^2}(b \times a)\cdot(\gamma \times a) = \frac{-1}{1-(\overset{\circ}{a}\cdot\overset{\circ}{b})^2}(\overset{\circ}{b}\times\overset{\circ}{a})\cdot(\tilde{\gamma}\times\overset{\circ}{a}) =$$

$$\frac{1}{1-(\overset{\circ}{a}\cdot\overset{\circ}{b})^2}[-\overset{\circ}{b}+(\overset{\circ}{a}\cdot\overset{\circ}{b})\overset{\circ}{a}]\cdot\tilde{\gamma} \overset{def}{=} \overset{\circ}{h}{}^{\phi}\cdot\tilde{\gamma}$$

To end this part of the Chapter we introduce a useful triad at a point s : define a material unit vector

$$e^{\perp} = \frac{a\times b}{|a\times b|} = Q\cdot\overset{\circ}{e}{}^{\perp} , \qquad \overset{\circ}{e}{}^{\perp} = \frac{\overset{\circ}{a}\times\overset{\circ}{b}}{|\overset{\circ}{a}\times\overset{\circ}{b}|}$$

and its derivative

$$e^{\perp\prime} = Q'\cdot\overset{\circ}{e}{}^{\perp} = \Gamma Q\cdot\overset{\circ}{e}{}^{\perp} = \Gamma\cdot e^{\perp} = e^{\perp}\times\gamma .$$

Then we have an orthogonal triad $(\gamma, e^{\perp}, e^{\perp\prime})$ where $|e^{\perp\prime}| = |\gamma|$.

The condition (2.6) and (2.7) can now be written in the form

$$\gamma\cdot e^{\perp} = 0$$

or

$$\tilde{\gamma}\cdot\overset{\circ}{e}{}^{\perp} = 0$$

§3. Local rigidity conditions

We now proceed to the local rigidity condition. One of our kinematic assumptions (Chapter 1) is that the peptide units are rigid, i.e. for an arbitrary atom $P^{(n)}$ of the n-th unit

$$\boldsymbol{r}(P^{(n)}) - \boldsymbol{r}(C_\alpha^{(n)}) = \boldsymbol{Q}^{(n)} \cdot \overset{\circ}{\boldsymbol{\rho}}\,(P^{(n)})$$

To derive its continuum counterpart we assume that the unit's diagonal is of order ε, i.e. $\overset{\circ}{\boldsymbol{c}}{}^{(n)} = \varepsilon \hat{\boldsymbol{c}}^{(n)}$ where $\hat{\boldsymbol{c}}^{(n)}$ is the unit vector, ε tends to zero and we denote by $\hat{\boldsymbol{c}} = \hat{\boldsymbol{c}}(s)$ the limit of the diagonal, identifying it with the unit tangent vector to the smooth curve $\boldsymbol{r}(s)$ passing through the centres of gravity of the peptide units. Consider now two adjacent units and apply the rigidity formula (1.1) to their centres of gravity

$$\boldsymbol{r}(G^{(n)}) = \boldsymbol{r}(C_\alpha^{(n)}) + \boldsymbol{Q}^{(n)} \cdot \overset{\circ}{\boldsymbol{\rho}}\,(G^{(n)})$$

$$\boldsymbol{r}(G^{(n-1)}) = \boldsymbol{r}(C_\alpha^{(n-1)}) + \boldsymbol{Q}^{(n-1)} \cdot \overset{\circ}{\boldsymbol{\rho}}\,(G^{(n-1)})\,.$$

Subtracting, taking into account that $\boldsymbol{r}(C_\alpha^{(n)}) - \boldsymbol{r}(C_\alpha^{(n-1)}) = \boldsymbol{Q}^{(n-1)} \cdot \overset{\circ}{\boldsymbol{c}}{}^{(n-1)}$, after simple transformations we obtain

$$\boldsymbol{r}(G^{(n)}) - \boldsymbol{r}(G_\alpha^{(n-1)}) = \boldsymbol{Q}^{(n)} \cdot \overset{\circ}{\boldsymbol{\rho}}\,(G^{(n)}) + \boldsymbol{Q}^{(n-1)} \cdot [\overset{\circ}{\boldsymbol{c}}{}^{(n-1)} - \overset{\circ}{\boldsymbol{\rho}}\,(G^{(n-1)})]\,.$$

Passing to the continuum limit we set $\boldsymbol{r}(G^{(n)}) = \boldsymbol{r}(s)$, $\boldsymbol{r}(G^{(n-1)}) = \boldsymbol{r}(s) - \varepsilon \boldsymbol{r}'(s)$, $\boldsymbol{Q}^{(n)} = \boldsymbol{Q}^{(s)}$, $\boldsymbol{Q}^{(n-1)} = \boldsymbol{Q}(s) - \varepsilon \boldsymbol{Q}'(s)$; then neglecting terms of order ε^2 we obtain

$$\varepsilon \boldsymbol{r}' = \varepsilon \boldsymbol{Q} \cdot \overset{\circ}{\hat{\boldsymbol{c}}} = \varepsilon \boldsymbol{Q} \cdot \overset{\circ}{\boldsymbol{r}}{}' \qquad \text{i.e.} \qquad \boldsymbol{r}' = \hat{\boldsymbol{c}} = \boldsymbol{Q} \cdot \overset{\circ}{\hat{\boldsymbol{c}}} = \boldsymbol{Q} \cdot \overset{\circ}{\boldsymbol{r}}{}'$$

which is the required local rigidity condition. It connects the two dynamical variables $\boldsymbol{r}(s)$, $\boldsymbol{Q}(s)$ and therefore constitutes a side kinematic condition in the variational principle.

We have chosen here a curve passing through the centres of gravity of the peptide units. Another possibility is a curve passing through the C_α atoms, in this case however, due to the appearance of the static moment in the expression for the kinetic energy (1.3), the resulting equations are more complicated. This difference should be borne in mind in spite of the fact that some macroscopic results may be identical. For instance it can be shown that in both cases, one of the static solutions of the final system of equations is a helix.

§4. The variational principle and the equations of motion

We recall that there are two kinematic conditions at a point s, namely i) the condition of existence of the dihedral angles

$$\boldsymbol{\gamma} \cdot \boldsymbol{e}^{\perp} = 0 \tag{4.1}$$

and ii) the local rigidity condition

$$\boldsymbol{r}' = \boldsymbol{Q} \cdot \overset{\circ}{\hat{\boldsymbol{c}}} = \hat{\boldsymbol{c}} \tag{4.2}$$

Furthermore, since the rotation tensor $\boldsymbol{Q}(s,t)$ is to be one of the dynamic variables, there is the third constarint

$$\boldsymbol{Q}\boldsymbol{Q}^{\mathsf{T}} = \boldsymbol{\delta} \tag{4.3}$$

Thus we start from the Lagrangian

$$\mathcal{L} = \int_{t_1}^{t_2} dt \int_{0}^{l} ds L \tag{4.4}$$

where l is the length of the chain and the density of the Lagrangian is

$$L = K + \frac{1}{2}\lambda_{pq}(Q_{pr}Q_{qr} - \delta_{pq}) + \mu_p(r'_p - Q_{pr}\overset{0}{\hat{c}}_r) - \Lambda\boldsymbol{\gamma} \cdot \boldsymbol{e}^{\perp} - \phi \tag{4.5}$$

where $\boldsymbol{\lambda}$ (a symmetric tensor), $\boldsymbol{\mu}$ and Λ are Lagrangian multipliers. ϕ is the internal energy which in general contains interactions between the peptide units and external factors, e.g. the influence of the solvent. For the time being we assume that ϕ depends on $\boldsymbol{r}, \boldsymbol{r}'$ and $\boldsymbol{Q}, \boldsymbol{Q}'$. We will return (Chapter 6) to this important quantity later. The kinetic energy was given before (Chapter 1)

$$K = \frac{1}{2}\overset{\circ}{\rho}\,|\boldsymbol{v}|^2 + \frac{1}{2}\overset{\circ}{\rho}\ \mathrm{tr}\,(\dot{\boldsymbol{Q}}\,\overset{\circ}{\boldsymbol{I}}\,\dot{\boldsymbol{Q}}^{\mathsf{T}}) \tag{4.6}$$

The Lagrangian equations of motion have the usual from

$$\begin{aligned} \frac{\delta L}{\delta \boldsymbol{r}} &= \left(\frac{\partial L}{\partial \dot{\boldsymbol{r}}}\right)^{\cdot} + \left(\frac{\partial L}{\partial \boldsymbol{r}'}\right)' - \frac{\partial L}{\partial \boldsymbol{r}} = 0 \\ \frac{\delta L}{\delta \boldsymbol{Q}} &= \left(\frac{\partial L}{\partial \dot{\boldsymbol{Q}}}\right)^{\cdot} + \left(\frac{\partial L}{\partial \boldsymbol{Q}'}\right)' - \frac{\partial L}{\partial \boldsymbol{Q}} = 0\,. \end{aligned} \tag{4.7}$$

They express the conservation of the linear and angular momentum, respectively, and will be called the translational and rotational equations.

Since

$$\frac{\partial L}{\partial \boldsymbol{v}} = \overset{\circ}{\rho}\,\boldsymbol{v}\,, \qquad \frac{\partial L}{\partial \boldsymbol{r}} = -\frac{\partial \phi}{\partial \boldsymbol{r}}\,, \qquad \frac{\partial L}{\partial \boldsymbol{r}'} = \boldsymbol{\mu} - \frac{\partial \phi}{\partial \boldsymbol{r}'}$$

the translational equation takes the form

$$\overset{\circ}{\rho}\,\dot{\boldsymbol{v}} + \left(\boldsymbol{\mu}' - \frac{\delta \phi}{\delta \boldsymbol{r}}\right) = 0\,. \tag{4.8}$$

To derive the required form of the rotational equation we first note that

$$\frac{\partial \gamma_p}{\partial Q'_{ij}} = -\frac{1}{2}\varepsilon_{ipq} Q_{qj}$$

and then

$$\frac{\partial L}{\partial \dot{\boldsymbol{Q}}} = \overset{\circ}{\rho}\,\dot{\boldsymbol{Q}}\,\overset{\circ}{\boldsymbol{I}}\,, \qquad \frac{\partial L}{\partial \boldsymbol{Q}} = \boldsymbol{\lambda Q} - \boldsymbol{\mu}\hat{\overset{\circ}{\boldsymbol{c}}} - \frac{\partial \phi}{\partial \boldsymbol{Q}}\,, \qquad \frac{\partial L}{\partial \boldsymbol{Q}'_{ij}} = \frac{1}{2}\Lambda \varepsilon_{ipq} e^{\perp}_p Q_{pj}\,.$$

Hence

$$\overset{\circ}{\rho}\,\bar{Q}_{ip}\,\overset{\circ}{I}_{jp} - \lambda_{ip} Q_{pj} + \mu_i \hat{\overset{\circ}{c}}_j = \frac{\delta \phi}{\delta Q_{ij}} + \Lambda \frac{\delta(\boldsymbol{\gamma}\cdot \boldsymbol{e}^{\perp})}{\delta Q_{ij}} - \frac{1}{2}\Lambda' \varepsilon_{ipq} Q_{qj} e^{\perp}_p\,; \tag{4.9}$$

multiplying the above equation by Q_{rj} we have

$$\overset{\circ}{\rho}\,Q_{rj}\,\overset{\circ}{I}_{qj}\,\bar{Q}_{iq} - \lambda_{ri} + \mu_i \hat{c}_r = Q_{rj}\frac{\delta \phi}{\delta Q_{ij}} + \Lambda Q_{rj}\frac{\delta(\boldsymbol{\gamma}\cdot \boldsymbol{e}^{\mathsf{T}})}{\delta Q_{ij}} - \frac{1}{2}\Lambda' \varepsilon_{ipr} e^{\perp}_p\,.$$

The symmetric part of the latter equation yields $\boldsymbol{\lambda}$ whereas multiplying it by ε_{lri} and taking into account that

$$\varepsilon_{lri} Q_{rj}\frac{\delta(\boldsymbol{\gamma}\cdot \boldsymbol{e}^{\perp})}{\delta Q_{ij}} = -e^{\perp\prime}_l$$

we arrive at the required rotational equation

$$\varepsilon_{ipq} Q_{pr}\left(\overset{\circ}{I}_{sr}\,\bar{Q}_{qs} + \frac{1}{\overset{\circ}{\rho}}\mu_q \hat{\overset{\circ}{c}}_r - \frac{1}{\overset{\circ}{\rho}}\frac{\delta \phi}{\delta Q_{qr}}\right) = -\frac{1}{\overset{\circ}{\rho}}(\Lambda e^{\perp}_i)' \tag{4.10}$$

The system of equations (4.8) and (4.10) completed by the constraints (4.1), (4.2) and (4.3) constitutes a system of 16 differential-algebraic equations for the 16 unknowns $\boldsymbol{r}, \boldsymbol{Q}, \boldsymbol{\mu}$ and Λ. The scalar Lagrangian multiplier Λ can easily be eliminated from the system but $\boldsymbol{\mu}$ cannot. Furthermore for any representation of the orthogonal matrix $\boldsymbol{Q}(\boldsymbol{g})$ the constraint (4.3) is satisfied identically and the new unknowns are the $\boldsymbol{g's}$. Another procedure eliminating $\boldsymbol{Q}$ and leading to a Eulerian form of the equations of motion, is the following.

First we note that

$$\ddot{Q} - (\dot{\Omega} + \Omega^2)Q = [\varepsilon_{ipm}\dot{\omega}_m - (\delta_{ip}|\omega|^2 - \omega_i\omega_p)]Q_{pj}$$

whence, after simple transformations

$$\varepsilon_{ipq}Q_{pr}\,\overset{\circ}{I}_{sr}\,\ddot{Q}_{qs} = -(J_{ip}\dot{\omega}_p + \varepsilon_{ipq}J_{rp}\omega_q\omega_r) = -(J_{ip}\omega_p)^{\cdot} \tag{4.11}$$

where the new inertia tensor

$$J = tr(\overset{\circ}{I})\delta - Q\,\overset{\circ}{I}\,Q^{\mathsf{T}}\,.$$

Thus (4.11) is the first term in (4.10) and it is a time derivative. The second term

$$\frac{1}{\overset{\circ}{\rho}}\hat{c} \times \mu = \frac{1}{\overset{\circ}{\rho}}r' \times \mu$$

is not a space derivative. However, multiplying vectorially the translational equation (4.8) by r and adding to the rotational equation (which amounts to replacing the balance of the angular momentum by the balance of the total angular momentum), we obtain

$$(-J \cdot \omega + r \times v)^{\cdot} + \frac{1}{\overset{\circ}{\rho}}(r \times \mu + \Lambda e^{\perp})' = \frac{1}{\overset{\circ}{\rho}}\left(Q \times \frac{\delta\phi}{\delta Q} + r \times \frac{\delta\phi}{\delta r}\right)$$

where we have introduced the notation $\varepsilon_{ipq}Q_{pr}\dfrac{\delta\phi}{\delta Q_{qr}} = Q \times \dfrac{\delta\phi}{\delta Q}$. Now the left-hand side is in divergence form. The right-hand side is the sum of the momentum due to external and internal interactions, and the vector product of the arm r by the interaction force. Collecting all equations and adding the compatibility condition for γ and ω (since $\gamma =$ vect $\Gamma =$ vect $Q'Q^{\mathsf{T}}$ and $\omega =$ vect $\Omega =$ vect$\dot{Q}Q^{\mathsf{T}}$, the relation $(\dot{Q})' = (Q')^{\cdot}$ yields (4.12[3])) we arrive at a system of 13 algebraic-differential equations for 13 unknowns ω, γ, r, μ and Λ

$$\begin{aligned}
&(-J \cdot \omega + r \times v)^{\cdot} + \frac{1}{\overset{\circ}{\rho}}(r \times \mu + \Lambda e^{\perp})' = \frac{1}{\overset{\circ}{\rho}}\left(Q \times \frac{\delta\phi}{\delta Q} + r \times \frac{\delta\phi}{\delta r}\right)\\
&\dot{r} + \frac{1}{\overset{\circ}{\rho}}\mu' = \frac{1}{\overset{\circ}{\rho}}\frac{\delta\phi}{\delta r}\\
&\dot{\gamma} + \frac{1}{2}\omega \times \gamma = \omega' + \frac{1}{2}\gamma \times \omega\\
&r' = \hat{c}\\
&\gamma \cdot e^{\perp} = 0
\end{aligned} \tag{4.12}$$

The above system of equations is purely Eulerian, i.e. it contains no reference to the initial state. The vectors $\hat{c}$, $e^{\perp}$ and the tensor J are material quantities and obey equations of the form $e^{\perp\prime} = e^{\perp} \times \gamma$, in fact therefore there are 12 additional first order equations (6 for J , 3 for $\hat{c}$ and for $e^{\perp}$). If the internal energy $\phi(r, r', Q, Q')$ can be expressed in terms of r, r', γ and A where A is any set of material quantities, the system is closed; it will be shown in Chapter 6 that this is in fact the case for many important interactions. However, except for some particular cases (e.g. when e in constant) in order to fully determine Q we must known ϑ and e which for known ω and γ obey a system of ordinary differential equations (App. C).

The energy balance can be derived on the basis of Eqs (4.8) and (4.9) following from the variational principle, making use of the formulae

$$tr(\dot{Q} \overset{\circ}{I} \ddot{Q}^{\mathsf{T}}) = \frac{1}{2}(tr\ \dot{Q} \overset{\circ}{I} \dot{Q}^{\mathsf{T}})^{\cdot}$$

$$tr\ (\dot{Q}Q^{\mathsf{T}}\boldsymbol{\lambda}) = \frac{1}{2}\boldsymbol{\lambda} : (QQ^{\mathsf{T}} - \delta)^{\cdot}$$

$$\boldsymbol{\mu} \cdot \dot{Q} \cdot \hat{\hat{c}} = \boldsymbol{\mu} \cdot \boldsymbol{v}'$$

$$\dot{Q} \ : \frac{\delta\phi}{\delta Q} = \left(\dot{Q} \ : \frac{\partial\phi}{\partial Q'}\right)' - \dot{\phi} + \left(\frac{\partial\phi}{\partial r} \cdot \boldsymbol{v} + \frac{\partial\phi}{\partial r'} \cdot \boldsymbol{v}'\right)$$

$$\dot{Q} : \frac{\delta}{\delta Q}(\gamma \cdot e^{\perp}) = \omega \cdot e^{\perp\prime}$$

$$\varepsilon_{ipq}\dot{Q}_{ij}Q_{qj}e^{\perp}_{p} = -2\omega \cdot e^{\perp}$$

Thus, multiplying the first (rotation) equation by $\dot{Q}_{ij}$ and the second by v_i we find after some simple transformation

$$\frac{1}{2}\overset{\circ}{\rho}\, tr\ (\dot{Q} \overset{\circ}{I} \dot{Q}^{\mathsf{T}})^{\cdot} - \frac{1}{2}\boldsymbol{\lambda} : (QQ^{\mathsf{T}} - \delta)^{\cdot} + \boldsymbol{\mu} \cdot \boldsymbol{v}' =$$

$$-\dot{\phi} + \left(\dot{Q} \ : \frac{\partial\phi}{\partial Q'}\right)' + \left(\frac{\partial\phi}{\partial r} \cdot \boldsymbol{v} + \frac{\partial\phi}{\partial r'} \cdot \boldsymbol{v}'\right) + (\Lambda\omega \cdot e^{\perp})' - \Lambda(\gamma \cdot e^{\perp})$$

$$\frac{1}{2}(|\boldsymbol{v}|^2)^{\cdot} + \boldsymbol{\mu}' \cdot \boldsymbol{v} = \boldsymbol{v} \cdot \left[\left(\frac{\partial\phi}{\partial r'}\right)' - \frac{\partial\phi}{\partial r}\right] .$$

Adding the above equations and bearing in mind the constraints we finally obtain the required energy balance

$$\dot{E} + R' = 0 \tag{4.13}$$

where $E = K + \phi$ is the total energy of the system and the energy flux has the form

$$R = -\dot{\boldsymbol{Q}} \; : \frac{\partial \phi}{\partial \boldsymbol{Q}'} - \frac{\partial \phi}{\partial \boldsymbol{r}'} \cdot \boldsymbol{v} + \boldsymbol{\mu} \cdot \boldsymbol{v} - \Lambda(\boldsymbol{\omega} \cdot \boldsymbol{e}^{\perp}) \; ; \tag{4.14}$$

this contains the Lagrangian multipliers.

The second balance (of the field momentum) equation is derived in a similar manner, multiplying the rotation and translation equations by Q'_{ij} and r'_i, respectively. The result is

$$\dot{E}_* + R'_* = 0 \tag{4.15}$$

where

$$E_* = \overset{\circ}{\rho}\, tr\,(\boldsymbol{Q}'\, \overset{\circ}{\boldsymbol{I}}\, \dot{\boldsymbol{Q}}^{\mathrm{T}}) = \overset{\circ}{\rho}\, tr\,(\boldsymbol{\Gamma}\, \overset{\circ}{\boldsymbol{I}}\, \boldsymbol{\Omega}^{\mathrm{T}}) \tag{4.16}$$

$$R_* = -L + \boldsymbol{\mu} \cdot \hat{\boldsymbol{c}} - \left(\boldsymbol{Q}' \; : \frac{\partial \phi}{\partial \boldsymbol{Q}'} + \hat{\boldsymbol{c}} \cdot \frac{\partial \phi}{\partial \boldsymbol{r}'} \right) . \tag{4.17}$$

The system (4.12) of 13 equations for $\boldsymbol{\omega}, \boldsymbol{\gamma}, \boldsymbol{\mu}, \boldsymbol{r}$ and Λ is an algebraic-differential system, since the last equation does not contain any derivatives. However, differentiating it with respect to s, we have

$$\boldsymbol{\gamma}' \cdot \boldsymbol{e}^{\perp} + \boldsymbol{\gamma} \cdot \boldsymbol{e}^{\perp\prime} = \boldsymbol{\gamma}' \cdot \boldsymbol{e}^{\perp} + \boldsymbol{\gamma}' \cdot (\boldsymbol{e}^{\perp} \times \boldsymbol{\gamma}) = \boldsymbol{\gamma}' \cdot \boldsymbol{e}^{\perp} = 0 \tag{4.18}$$

Furthermore, in order to eliminate all second order derivatives we introduce the velocity $\boldsymbol{v} = \dot{\boldsymbol{r}}$ as a new variable. We confine ourselves to an invariant internal energy independent of $\boldsymbol{r}$ (Chapter 6); hence

$$\boldsymbol{Q} \times \frac{\delta \phi}{\delta \boldsymbol{Q}} = -\left(\frac{\partial \phi}{\partial \boldsymbol{\gamma}} \right)' , \qquad \frac{\delta \phi}{\delta \boldsymbol{r}} = 0$$

Changing the order of equations in the considered system and differentiating the constraint

$\mathbf{r}' = \hat{\mathbf{c}}$ with respect to time $(\phi = \frac{1}{2}\gamma \cdot \phi \cdot \gamma)$

$$\begin{aligned} J \cdot \dot{\omega} - \frac{1}{\overset{\circ}{\rho}} \phi \cdot \gamma' - \Lambda e^{\perp\prime} &= \dots \\ \dot{v} + \frac{1}{\overset{\circ}{\rho}} \mu' &= \dots \\ \dot{r} &= \dots \\ v' &= \dots \\ -\omega' + \dot{\gamma} &= \dots \\ \gamma' \cdot e^{\perp} &= \dots \end{aligned} \tag{4.19}$$

where the right-hand sides are algebraic in all unknowns. We denote by $\Omega(s,t) = 0$ the characteristic surface and employ the standard methods to find the 16×16 determinant. After elementary transformations, making use of some ~~standard~~ properties of block matrices, we obtain

$$D = \frac{1}{\overset{\circ}{\rho}{}^3} \dot{\Omega}^3 \Omega'^3 \begin{vmatrix} & e_i^{\perp} & \\ \dot{\Omega}^2 J_{ip} \gamma_p - \frac{\Omega'^2}{\overset{\circ}{\rho}} \phi_{ip} \gamma_p \\ \dot{\Omega}^2 J_{ip} e^{\perp\prime}{}_p - \frac{\Omega'^2}{\overset{\circ}{\rho}} \phi_{ip} e^{\perp\prime}{}_p \end{vmatrix} = 0$$

where $i = 1,2,3$ numbers the columns. Introducing the notation

$$L = \overset{\circ}{\rho} \frac{\dot{\Omega}^2}{\Omega'^2} J - \phi$$

we have

$$D = \frac{1}{\overset{\circ}{\rho}{}^5} \dot{\Omega}^3 \Omega'^3 e^{\perp} \cdot [(L \cdot \gamma) \times (L \cdot e^{\perp\prime})] = 0$$

which is the required equation for the characteristic surface. Since one of the equations was differentiated with respect to s and one with respect to t the solutions $\Omega' = 0$, $\dot{\Omega} = 0$ are spurious and we finally have

$$\dot{\Omega}^2 \Omega'^3 e^{\perp} \cdot [(L \cdot \gamma) \times (L \cdot e^{\perp\prime})] = 0 \tag{4.20}$$

There are still solutions $\dot{\Omega}^2 = 0$, $\Omega'^8 = 0$ representing characteristics parallel to the s and t axes, whereas the equation

$$e^{\perp} \cdot [(L \cdot \gamma) \times (L \cdot e^{\perp'})] = 0 \tag{4.21}$$

stating that the volume spanned by the vectors $e^{\perp}$, $L \cdot \gamma$ and $L \cdot e^{\perp'}$ vanishes, yields non-degenerate solutions. Eq. (4.21) is quadratic in $\lambda^2 = \frac{\dot{\Omega}^2}{\Omega'^2}$ and in general its coefficients are functions of s and t. Nevertheless, it can be proved that the solutions λ^2 are constants and therefore all characteristics are straight lines. To prove this statement we first observe that (4.21) is equivalent to the existence of two scalar functions A and B, such that

$$e^{\perp} = A(L \cdot \gamma) + B(L \cdot e^{\perp'})$$

Consider first the case of an invertible matrix L : $\det L \neq 0$ and λ^2 does not belong to the spectrum of the matrix $J^{-1}\phi$. Then

$$L^{-1} \cdot e^{\perp} = A\gamma + Be^{\perp'}$$

multiplying this equation in turn by $e^{\perp}$, γ and $e^{\perp'}$ we have

$$e^{\perp} \cdot L^{-1} \cdot e^{\perp} = 0$$

$$|\gamma|^2 A = \gamma \cdot L^{-1} \cdot e^{\perp}, \qquad |\gamma|^2 B = e^{\perp'} \cdot L^{-1} \cdot e^{\perp}.$$

The last two equations determine A and B which in general depend on s and t, in view of the fact however that L is a material matrix, the first equation can be written in the form

$$\overset{\circ}{e}{}^{\perp} \cdot \overset{\circ}{L}{}^{-1} \cdot \overset{\circ}{e}{}^{\perp} = \overset{\circ}{e}{}^{\perp} \cdot (\overset{\circ}{\rho}\lambda^2 \overset{\circ}{J} - \overset{\circ}{\phi})^{-1} \cdot \overset{\circ}{e}{}^{\perp} = 0$$

and λ^2 so determined is a constant. It remains to examine the case of singular L; $\det L = 0$ or, since it is material, $\det \overset{\circ}{L} = 0$:

$$\det(\overset{\circ}{\rho}\lambda^2 \overset{\circ}{J} - \overset{\circ}{\phi}) = 0$$

Thus, again all λ^2 are constant, for they belong to the spectrum of $\overset{\circ}{L}$.

We note finally that in the two-dimensional case λ^2 can be calculated explicitly, namely there is only one solution

$$\lambda^2 = \frac{1}{\overset{\circ}{\rho}\, tr_2 \overset{\circ}{I}} \overset{\circ}{\phi}_{33}, \qquad tr_2 \overset{\circ}{I} = \overset{\circ}{I}_{11} + \overset{\circ}{I}_{22}$$

besides the solutions $\dot{\Omega} = 0,\ \Omega' = 0$.

§5. Particular solutions for the internal energy quadratic in γ. The helix.

We assume now that (Chapter 6) $\phi = \frac{1}{2}\gamma \cdot \phi \cdot \gamma$ where the matrix ϕ is material i.e. $\phi = Q \overset{\circ}{\phi} Q^{\mathsf{T}}$. Then $Q \times \frac{\delta \phi}{\delta Q} = -(\phi \cdot \gamma)'$ and $\frac{\delta \phi}{\delta r} = 0$ whence

$$
\begin{aligned}
&(-J \cdot \omega + r \times v)^{\cdot} + \frac{1}{\overset{\circ}{\rho}}(r \times \mu + \phi \cdot \gamma + \Lambda e^{\perp})' = 0 \\
&\dot{r} + \frac{1}{\overset{\circ}{\rho}}\mu' = 0 \\
&\dot{\gamma} + \frac{1}{2}\omega \times \gamma = \omega' + \frac{1}{2}\gamma \times \omega \qquad (5.1) \\
&r' = \hat{c} \\
&\gamma \cdot e^{\perp} = 0 .
\end{aligned}
$$

Assume now that all quantities depend on one variable $\xi = s - Vt$. We recall that s is a material coordinate. Then

$$
\Omega = -VQ'Q^{\mathsf{T}}, \qquad \omega = -V\gamma \qquad (5.2)
$$

and the compatibility condition $(5.1)^3$ is satisfied identically. Moreover,

$$
r \times v = -Vr \times r' = -Vr \times \hat{c}
$$

The first two equations in (5.1) can be integrated once with respect to ξ; denoting the integration constants by $\frac{1}{\overset{\circ}{\rho}}\overset{\circ}{C}$ and $\frac{1}{\overset{\circ}{\rho}}\overset{\circ}{\mu}$, we can determine μ from the second equation, namely

$$
\frac{1}{\overset{\circ}{\rho}}\mu = \frac{1}{\overset{\circ}{\rho}}\overset{\circ}{\mu} - V^2\hat{c} \qquad (5.3)
$$

which we substitute into the first equation and we arrive at a system of 7-algebraic-ordinary differential equations for r, γ, Λ (differentiation appears in the second equation only)

$$
\begin{aligned}
&L \cdot \gamma = (\overset{\circ}{C} + r \times \overset{\circ}{\mu}) + \Lambda e^{\perp} = 0 \\
&r' = \hat{c} \qquad (5.4) \\
&\gamma \cdot e^{\perp} = 0
\end{aligned}
$$

where $\boldsymbol{L} = \overset{\circ}{\rho}\, V^2 \boldsymbol{J} - \boldsymbol{\phi}$ is a symmetric in general indefinite matrix. In the static case ($V = 0$), $\boldsymbol{L} = -\boldsymbol{\phi}$ and if $\boldsymbol{\phi}$ is positive definite, $\boldsymbol{L}$ is negative-definite. For sufficiently large V, $\boldsymbol{L}$ is positive definite. Since $\boldsymbol{L}$ is a material matrix the rotation equation multiplied by $\boldsymbol{Q}^{\mathsf{T}}$ has the form

$$\overset{\circ}{\boldsymbol{L}}\, \boldsymbol{Q}^{\mathsf{T}} \cdot \boldsymbol{\gamma} = \boldsymbol{Q}^{\mathsf{T}} \cdot (\overset{\circ}{\boldsymbol{C}} + \boldsymbol{r} \times \overset{\circ}{\boldsymbol{\mu}}) + \Lambda\, \overset{\circ}{\boldsymbol{e}}{}^{\perp}$$

and our system is

$$\overset{\circ}{\boldsymbol{L}}\, \boldsymbol{Q}^{\mathsf{T}} \cdot \boldsymbol{\gamma} = \boldsymbol{Q}^{\mathsf{T}} \cdot (\overset{\circ}{\boldsymbol{C}} + \boldsymbol{r} \times \overset{\circ}{\boldsymbol{\mu}}) + \Lambda\, \overset{\circ}{\boldsymbol{e}}{}^{\perp}$$

$$\boldsymbol{r}' = \dot{\boldsymbol{c}} \tag{5.5}$$

$$\boldsymbol{\gamma} \cdot \boldsymbol{e}^{\perp} = 0$$

A class of interesting solutions can be deduced for $\overset{\circ}{\boldsymbol{\mu}} = 0$. Then the rotation equation does not contain the position vector and the latter is found from the constraint $\boldsymbol{r}' = \dot{\boldsymbol{c}}$ after having determined $\boldsymbol{\gamma}$ and hence the rotation matrix (see App. C). Thus

$$\overset{\circ}{\boldsymbol{L}}\, \boldsymbol{Q}^{\mathsf{T}} \cdot \boldsymbol{\gamma} = \boldsymbol{Q}^{\mathsf{T}} \cdot \overset{\circ}{\boldsymbol{C}} + \Lambda\, \overset{\circ}{\boldsymbol{e}}{}^{\perp} \tag{5.6}$$

Eliminating Λ by multiplying the above equation by $\overset{\circ}{\boldsymbol{e}}{}^{\perp}$ we have $\Lambda = \overset{\circ}{\boldsymbol{e}}{}^{\perp} \cdot (\overset{\circ}{\boldsymbol{L}}\, \boldsymbol{Q}^{\mathsf{T}} \cdot \boldsymbol{\gamma} - \boldsymbol{Q}^{\mathsf{T}} \cdot \overset{\circ}{\boldsymbol{C}})$ and

$$\overset{\circ}{\boldsymbol{P}} \cdot (\overset{\circ}{\boldsymbol{L}}\, \boldsymbol{Q}^{\mathsf{T}} \cdot \boldsymbol{\gamma} - \boldsymbol{Q}^{\mathsf{T}} \cdot \overset{\circ}{\boldsymbol{C}}) = 0 \tag{5.7}$$

where $\overset{\circ}{\boldsymbol{P}} = \boldsymbol{\delta} - \overset{\circ}{\boldsymbol{e}}{}^{\perp}\, \overset{\circ}{\boldsymbol{e}}{}^{\perp}$ is a constant, symmetric idempotent matrix. Particular solutions of this equation follow from the assumptions

i) the rotation axis is constant, $\boldsymbol{e} = \boldsymbol{e}^{(0)}$.

ii) the constant $\overset{\circ}{\boldsymbol{C}}$ is codirectional with $\boldsymbol{e}^{(0)}$.

The assumption i) and the definition of $\boldsymbol{\gamma}$ imply that

$$\boldsymbol{\gamma} = \boldsymbol{\gamma}^{(0)} = -\vartheta^{(0)\prime} \boldsymbol{e}^{(0)} \tag{5.8}$$

where $\vartheta^{(0)\prime}$ is a constant gradient of rotation around $\boldsymbol{e}^{(0)}$. $\vartheta^{(0)\prime} = 0$ yields a straight line; we hereafter consider the case $\vartheta^{(0)\prime} \neq 0$. In accordance with ii) we set

$$\overset{\circ}{\boldsymbol{C}} = -\overset{\circ}{K}\, (\vartheta^{(0)\prime})^2 \boldsymbol{e}^{(0)} \tag{5.9}$$

where $\overset{\circ}{K}$ is a scalar constant. Substituting (5.8) and (5.9) into (5.7) and bearing in mind that $e^{(0)}$ is an eigenvector of the rotation tensor $Q^{(0)} = Q(e^{(0)}, \vartheta^{(0)})$ and of its transpose, with unit eigenvalue

$$Q^{(0)} \cdot e^{(0)} = Q^{(0)\top} \cdot e^{(0)} = e^{(0)}$$

we obtain

$$(\overset{\circ}{P}\overset{\circ}{L} - \lambda^{(0)}\delta) \cdot e^{(0)} = 0 \tag{5.10}$$

where $\lambda^{(0)} = \overset{\circ}{K}\vartheta^{(0)\prime}$. The constraint condition $(5.5)^3$ takes now the form

$$e^{(0)} \cdot \overset{\circ}{e}{}^{\perp} = 0 \tag{5.11}$$

and follows from (6.10) for $\lambda^{(0)} \neq 0$ by multiplying the entire equation by $\overset{\circ}{e}{}^{\perp}$. Thus we have arrived at an eigenvalue problem for the matrix $\overset{\circ}{P}\overset{\circ}{L}$ with vanishing determinant which means zero is an eigenvalue. All eigenvalues of (6.10) are real. In fact, it can be written in the form

$$(\overset{\circ}{P}\overset{\circ}{L} + \overset{\circ}{L}\overset{\circ}{P} - \overset{\circ}{L}\overset{\circ}{P} - \lambda^{(0)}\delta) \cdot e^{(0)} = 0$$

but since $e^{(0)} \cdot \overset{\circ}{e}{}^{\perp} = 0$, $\overset{\circ}{L}\overset{\circ}{P} \cdot e^{(0)} = \overset{\circ}{L} \cdot e^{(0)}$ and we obtain the following equivalent eigenvalue problem:

$$(\overset{\circ}{P}\overset{\circ}{L} + \overset{\circ}{L}\overset{\circ}{P} - \overset{\circ}{L} - \lambda^{(0)}\delta) \cdot e^{(0)} = 0$$

with the symmetric matrix $\overset{\circ}{P}\overset{\circ}{L} + \overset{\circ}{L}\overset{\circ}{P} - \overset{\circ}{L}$.

Equating to zero the determinant of $\overset{\circ}{P}\overset{\circ}{L} - \lambda^{(0)}\delta$ leads to an equation for the eigenvalues

$$\lambda^{(0)}(\lambda^{(0)2} - S_1\lambda^{(0)} + S_2) = 0 \tag{5.12}$$

where $S_1 = tr\ \overset{\circ}{P}\overset{\circ}{L}$, $S_2 = \frac{1}{2}[(tr\ \overset{\circ}{P}\overset{\circ}{L})^2 - tr(\overset{\circ}{P}\overset{\circ}{L})^2]$ whence the two non-vanishing eigenvalues are

$$\lambda^{(0)}_{1,2} = \frac{1}{2}\left[(tr\ \overset{\circ}{P}\overset{\circ}{L}) \pm \sqrt{2tr(\overset{\circ}{P}\overset{\circ}{L})^2 - (tr\ \overset{\circ}{P}\overset{\circ}{L})^2}\right] . \tag{5.13}$$

We are now in a position to find the position vector $\mathbf{r}'(\xi) = \mathbf{r}' = Q^{(0)} \cdot \hat{\mathbf{c}}$; introducing the notation $k^{(0)}_{1,2} = \vartheta^{(0)\prime}_{1,2} = \frac{1}{\overset{\circ}{K}}\lambda^{(0)}_{1,2}$ we have for $k^{(0)} = k^{(0)}_1$ or $k^{(0)} = k^{(0)}_2$

$$Q^{(0)} = \delta\cos(k^{(0)}\xi) + (1 - \cos(k^{(0)}\xi))e^{(0)}e^{(0)} + \sin(k^{(0)}\xi)\mathbf{1} \times e^{(0)} \tag{5.14}$$

Hence, introducing a suitable integration constant

$$r_i(\xi) = [\xi e_i^{(0)} e_p^{(0)} + (\delta_{ip} - e_i^{(0)} e_p^{(0)}) \frac{\sin(k^{(0)}\xi)}{k^{(0)}} + \frac{1 - \cos(k^{(0)}\xi)}{\cos k^{(0)}} \varepsilon_{imp} e_m^{(0)}] \overset{\circ}{c}_p + r_2(0) \qquad (5.15)$$

Our solution is therefore a helix. In fact we have two helices for $k_{1,2}^{(0)}$ which naturally will be called the right and left helix, respectively.

For prescribed $\overset{\circ}{e}{}^{\perp}$ (and hence $\overset{\circ}{P}$) and $\overset{\circ}{L}$ (in fact we need only $\overset{\circ}{P}\overset{\circ}{L}$ to get $\lambda_{1,2}^{(0)}$ from (5.13)) we still have an arbitrary constant $\overset{\circ}{K}$. Its value can be determined from the known number of peptide units per turn of the helix (e.g. 3.6) which we denote by $n^{(0)}$. Let $l^{(0)}$ be the length of the helix per turn. Then, for say the right helix

$$l_1^{(0)} = \frac{2\pi}{k_1^{(0)}} = n^{(0)} | \overset{\circ}{c} |$$

or since $k_1^{(0)} = \dfrac{\lambda_1^{(0)}}{\overset{\circ}{K}}$,

$$\overset{\circ}{K} = \frac{1}{2\pi} \lambda_1^{(0)} n^{(0)} | \overset{\circ}{c} | .$$

It is frequently convenient to deal with a helix around a vertical cylinder rather than in a general position. Set now $e^{(0)} = (0,0,1)$, $\overset{\circ}{c} = (\overset{\circ}{c}_1, 0, \overset{\circ}{c}_2)$, choose $r_1(0) = 0$, $r_2(0) = -\dfrac{1}{k^{(0)}}$, $r_3(0) = 0$ and introduce a new angle $\phi = \xi k^{(0)} - \dfrac{\pi}{2}$. Then, denoting by R the radius of the cylinder, we obtain the equations of the helix

$$r_1 = R\cos\phi, \qquad r_2 = R\sin\phi, \qquad r_3 = \sqrt{1 - R^2 k^{(0)2}}\,\xi \qquad (5.16)$$

It is important to examine the stability of the above helix solution. We shall therefore linearize Eq. (5.7)

$$\overset{\circ}{P} \cdot (\overset{\circ}{L}\, Q^{\mathrm{T}} \cdot \gamma - Q^{\mathrm{T}} \cdot \overset{\circ}{C}) = 0 \qquad (5.17)$$

around the solution $Q = Q^{(0)} = Q(e^{(0)}, \vartheta^{(0)})$, $\gamma = \gamma^{(0)} = -\vartheta^{(0)\prime} e^{(0)}$, $\overset{\circ}{C} = -\overset{\circ}{K}\,(\vartheta^{(0)\prime})^2 e^{(0)}$. To this end we assume that

$$Q = Q^{(1)} Q^{(0)} \qquad (5.18)$$

where $Q^{(1)}$ is a small rotation tensor superposed on $Q^{(0)}$:

$$Q^{(1)} = \delta + \varepsilon \vartheta^{(1)} 1 \times e^{(1)} = \delta + \varepsilon 1 \times e\,, \qquad e = \vartheta^{(1)} e^{(1)}\,, \qquad |\vartheta^{(1)}| = |e|\,. \qquad (5.19)$$

Thus

$$\Gamma = Q'Q^{\mathsf{T}} = \Gamma^{(0)} + \varepsilon\Gamma^{(1)}$$

where

$$\Gamma^{(1)}_{ij} = \varepsilon_{imp}e_m\Gamma^{(0)}_{pj} - \Gamma^{(0)}_{ip}\varepsilon_{pmj}e_m + \varepsilon_{imj}e'_m$$

and

$$\gamma_i = \frac{1}{2}\varepsilon_{ipq}\Gamma_{pq} = \gamma^{(0)}_i + \varepsilon\gamma^{(1)}_i$$

where

$$\gamma^{(1)} = -(e' + \gamma^{(0)} \times e) \,. \tag{5.20}$$

Substituting for Q^{T}, γ and $\mathring{C}$ into (5.17) we have

$$\mathring{P} \cdot [\mathring{L}\, Q^{(0)\mathsf{T}} \cdot e' + \mathring{K}\, (\vartheta^{(0)\prime})^2 Q^{(0)\mathsf{T}} \cdot (e \times e^{(0)})] = 0 \,. \tag{5.21}$$

This is a system of three linear ordinary differential equations with periodic coefficients for the vector $e(s,t)$. As before, multiplication by $\mathring{e}^{\perp}$ yields an identity. The third equation follows from the constraint $\gamma \cdot e^{\perp} = 0$. In order to reduce the system to one with constant coefficients we expand the unknown vector e in the constant orthonormal triad

$$e = Ae^{(0)} + B\,\mathring{e}^{\perp} + Ce^{(0)} \times \mathring{e}^{\perp} \tag{5.22}$$

However, since the new unit vector along the rotation axis is now $e^{(0)} + \varepsilon e$, $|e^{(0)} + \varepsilon e| = 1$, $e^{(0)} \cdot e = 0$ and hence $A = 0$. Introduce the notation $\mathring{L}_{11} = e^{(0)} \cdot \mathring{L} \cdot e^{(0)}$, $\mathring{L}_{12} = e^{(0)} \cdot \mathring{L} \cdot \mathring{e}^{\perp}$, etc. and note that multiplication of the original equation by $e^{(0)} \times \mathring{e}^{\perp}$ yields $\mathring{L}_{13} = 0$. Then, inserting (5.22) into (5.21) we obtain two equations

$$\begin{aligned} &\mathring{L}_{12}\,(B' \cos\vartheta^{(0)} + C' \sin\vartheta^{(0)}) = 0 \\ &\mathring{L}_{23}\,(B' \cos\vartheta^{(0)} + C' \sin\vartheta^{(0)}) - \mathring{L}_{33}\,(B' \sin\vartheta^{(0)} - C' \cos\vartheta^{(0)}) \\ &- \mathring{K}\,(\vartheta^{(0)\prime})^2 (B \cos\vartheta^{(0)} + C \sin\vartheta^{(0)}) = 0 \end{aligned} \tag{5.23}$$

Writing the constraint in the form

$$(\gamma^{(0)} + \varepsilon\gamma^{(1)}) \cdot (Q^{(1)}Q^{(0)} \cdot \mathring{e}^{\perp}) = 0 \tag{5.24}$$

where in accordance with (5.20) $\gamma^{(1)} = -(e' + \gamma^{(0)} \times e)$, and using (5.19) and the expansion (5.22) we obtain

$$B' \cos \vartheta^{(0)} + C' \sin \vartheta^{(0)} = 0 \,. \tag{5.25}$$

Finally it is convenient to introduce two new unknowns by the invertible linear transformation

$$D = B \cos \vartheta^{(0)} + C \sin \vartheta^{(0)}, \qquad E = B \sin \vartheta^{(0)} - C \cos \vartheta^{(0)}$$

whence (5.26)

$$B = D \cos \vartheta^{(0)} + E \sin \vartheta^{(0)}, \qquad C = D \sin \vartheta^{(0)} - E \cos \vartheta^{(0)}$$

and then our system of three linear differential equations (homogeneous with constant coefficients) takes the form $(\vartheta^{(0)\prime} = k^{(0)})$

$$\begin{aligned} &D' + k^{(0)} E = 0 \\ &\mathring{L}_{33}\, E' + k^{(0)} (\mathring{K}\, k^{(0)} - \mathring{L}_{33}) D = 0 \,. \end{aligned} \tag{5.27}$$

Eliminating E we have

$$\mathring{L}_{33}\, D'' + (\mathring{L}_{33} - \mathring{K}\, k^{(0)}) k^{(0)2} D = 0 \tag{5.28}$$

Thus, the stability condition has the form

$$\mathring{L}_{33}\, (\mathring{L}_{33} - \mathring{K}\, k^{(0)}) > 0 \tag{5.29}$$

We shall now prove that for an arbitrary internal energy quadratic in γ, addition of an appropriate dihedral energy (see Chapter 6) even in its simplest quadratic form, stabilizes the helix. In fact, for the sum of the above energies, since $(e^{(0)} = \bar{\alpha}\, \mathring{a} + \bar{\beta}\, \mathring{b})$

$$\begin{aligned} \mathring{K}^a \cdot (e^{(0)} \times \mathring{e}^{\perp}) &= -\frac{|\, \mathring{a} \times \mathring{b}\, |}{1 - |\, \mathring{a} \times \mathring{b}\, |^2} (\mathring{a} \cdot \mathring{b}\, \bar{\alpha} + \bar{\beta}) \\ \mathring{K}^b \cdot (e^{(0)} \times \mathring{e}^{\perp}) &= -\frac{|\, \mathring{a} \times \mathring{b}\, |}{1 - |\, \mathring{a} \times \mathring{b}\, |^2} (\bar{\alpha} + \mathring{a} \cdot \mathring{b}\, + \bar{\beta}) \end{aligned} \tag{5.30}$$

the new $\mathring{L}_{33}$ is

$$(e^{(0)}\times \overset{\circ}{e}{}^{\perp})\cdot \overset{\circ}{\rho}\, V^2\, \overset{\circ}{J}\cdot(e^{(0)}\times \overset{\circ}{e}{}^{\perp}) - (e^{(0)}\times \overset{\circ}{e}{}^{\perp})\cdot \overset{\circ}{\phi}\cdot(e^{(0)}\times \overset{\circ}{e}{}^{\perp})$$

$$- \left(\frac{|\,\overset{\circ}{a}\times \overset{\circ}{b}\,|}{1-|\,\overset{\circ}{a}\times \overset{\circ}{b}\,|^2}\right)[(\overset{\circ}{a}\cdot \overset{\circ}{b}\,\bar{\alpha}+\bar{\beta})^2\,\overset{\circ}{W}{}^{a} + (\bar{\alpha}+\overset{\circ}{a}\cdot \overset{\circ}{b}+\bar{\beta})^2\,\overset{\circ}{W}{}^{b}]$$

where the scalars, defined in Chapter 6, are both positive:

$$\overset{\circ}{W}{}^{a}, \overset{\circ}{W}{}^{b} \quad > 0\,.$$

Thus for sufficiently large $\overset{\circ}{W}{}^{a}$ and $\overset{\circ}{W}{}^{b}$, we have $\overset{\circ}{L}_{33} < 0$ and the stability condition is satisfied whatever $\overset{\circ}{\phi}$ and $\overset{\circ}{\rho}\, V^2\, \overset{\circ}{J}$ are. It can also be proved that the considered helix can be stabilized by introducing the hydrogen bond. However, since this bond is non-local in the sense of the continuum theory, the calculations are much more complicated and will not be presented here.

§6. Energy of the continuous chain.

The form of the internal energy determines the system of equations governing the motion of the chain. In this Chapter we consider the local internal energy, i.e. the energy of interaction between adjacent elements of the chain, and the external energy. We assume that the internal energy depends on the dynamical variables Q, r and their first derivatives only:

$$W = W(Q, Q', r, r')\,. \tag{6.1}$$

We shall require that W be invariant with respect to a rigid translation of the chain $r \to r + a$, a constant

$$W(Q, Q', r + a, r') = W(Q, Q', r, r')\,,$$

which implies that $W = W(Q, Q', r')$. Furthermore, we note that the local rigidity constraint $r' = Q\cdot \overset{\circ}{c}$ makes it possible to eliminate r' from (6.1), whence

$$W = W(Q, Q')\,. \tag{6.2}$$

This quantity is required to be invariant with respect to a rigid rotation of the whole chain by an arbitrary constant tensor S:

$$W(Q, Q') = W(SQ, SQ')\,. \tag{6.3}$$

It is sufficient to take infinitesimal rotations only, i.e. $S = \delta + \bar{S} = \delta + \bar{\vartheta}\, 1 \times \bar{e}$, $\bar{\vartheta}$ small. Hence

$$W(Q,Q') = W(Q+\bar{S}Q, Q'+\bar{S}Q') = W(Q,Q') + \frac{\partial W(Q,Q')}{\partial Q} : (\bar{S}Q) + \frac{\partial W(Q,Q')}{\partial Q} : (\bar{S}Q')$$

and substituting for $\bar{S}$

$$\varepsilon_{imn}\left(\frac{\partial W}{\partial Q_{mp}}Q_{np} + \frac{\partial W}{\partial Q'_{mp}}Q'_{np}\right) = 0\,. \tag{6.4}$$

Since γ is one of the dynamical variables, we replace Q' in (6.4) by γ, bearing in mind that for a fixed Q the map $Q' \to \gamma(QQ')$ is linear and one to one. Setting $W(Q,Q') = \bar{W}(Q,\gamma(QQ'))$ we have

$$\frac{\partial W}{\partial Q_{ij}} = \frac{\partial \bar{W}}{\partial Q_{ij}} + \frac{\partial \bar{W}}{\partial \gamma_l}\frac{\partial \gamma_l}{\partial Q_{ij}}\,, \qquad \frac{\partial W}{\partial Q'_{ij}} = \frac{\partial \bar{W}}{\partial \gamma_l}\frac{\partial \gamma_l}{\partial Q'_{ij}}\,;$$

taking into account that

$$\frac{\partial \gamma_l}{\partial Q_{ij}} = \frac{1}{2}(\gamma_l Q_{ij} - \gamma_i Q_{lj})\,, \qquad \frac{\partial \gamma_l}{\partial Q'_{ij}} = \frac{1}{2}\varepsilon_{liq}Q_{qj}$$

and $Q'_{ij} = \varepsilon_{ipq}\gamma_q Q_{pj}$, after simple transformation (6.4) takes the form

$$\varepsilon_{imn}\left(\frac{\partial \bar{W}}{\partial Q_{mp}}Q_{np} - \gamma_m\frac{\partial \bar{W}}{\partial \gamma_n}\right) = 0 \tag{6.5}$$

The internal energy $\bar{W}(Q,\gamma)$ satisfying the above relation will be called invariant.

In the case of an invariant internal energy, taking into account (6.5) we can readily prove the following important formula for the variational derivative appearing in the equations of motion:

$$Q \times \frac{\delta W}{\delta Q} = -\left(\frac{\partial \bar{W}}{\partial \gamma}\right)'$$

i.e. it is a space derivative and if $\dfrac{\delta W}{\delta r} = 0$ all equations of motion can be written in the divergence form.

We shall not pursue the problem of a general solution of Eq. (6.5) we note however that every expression

$$W_{p_1\ldots p_l}\gamma_{p_1}\gamma_{p_2}\cdots\gamma_{p_l} \tag{6.6}$$

for $l = 1, 2, \ldots$ where $\bar{W}$ is material, is a solution. Since (6.6) is linear in $\bar{W}$ every series of such monomials is also a solution.

An important expression for the energy of interaction between adjacent peptide units possessing dipole moments

$$\bar{W} = \frac{1}{2}\boldsymbol{\gamma} \cdot \boldsymbol{W} \cdot \boldsymbol{\gamma} \tag{6.7}$$

is derived from the discrete case in App. B.

Another important and natural object in the local continuum theory of a deformable peptide chain, is that of energy depending directly on the gradients of the dihedral angles, called the dihedral energy,*

$$\phi' = \boldsymbol{K}^{\mathfrak{a}} \cdot \boldsymbol{\gamma}, \qquad \psi' = \boldsymbol{K}^{\mathfrak{b}} \cdot \boldsymbol{\gamma}$$

where the vectors $\boldsymbol{K}^{\mathfrak{a}}$ and $\boldsymbol{K}^{\mathfrak{b}}$ are material (Chapter 2)

$$\boldsymbol{K}^{\mathfrak{a}} = \boldsymbol{Q} \cdot \mathring{\boldsymbol{K}}^{\mathfrak{a}}, \qquad \boldsymbol{K}^{\mathfrak{b}} = \boldsymbol{Q} \cdot \mathring{\boldsymbol{K}}^{\mathfrak{b}}$$

and

$$\mathring{\boldsymbol{K}}^{\mathfrak{a}} = -\frac{1}{1 - (\mathring{\boldsymbol{a}} \times \mathring{\boldsymbol{b}})^2}(\mathring{\boldsymbol{a}} - \mathring{\boldsymbol{a}} \cdot \mathring{\boldsymbol{b}}\mathring{\boldsymbol{b}}), \qquad \mathring{\boldsymbol{K}}^{\mathfrak{b}} = -\frac{1}{1 - (\mathring{\boldsymbol{a}} \times \mathring{\boldsymbol{b}})^2}(\mathring{\boldsymbol{b}} - \mathring{\boldsymbol{a}} \cdot \mathring{\boldsymbol{b}}\mathring{\boldsymbol{a}}).$$

We shall consider the general expression

$$W = \bar{W}(\boldsymbol{K}^{\mathfrak{a}} \cdot \boldsymbol{\gamma}, \boldsymbol{K}^{\mathfrak{b}} \cdot \boldsymbol{\gamma}) = \bar{W}(\alpha, \beta) \tag{6.8}$$

which is invariant, for $\boldsymbol{K}^{\mathfrak{a}} \cdot \boldsymbol{\gamma}$ and $\boldsymbol{K}^{\mathfrak{b}} \cdot \boldsymbol{\gamma}$ are invariant. As before we have

$$\boldsymbol{Q} \times \frac{\delta W}{\delta \boldsymbol{Q}} = -\left(\frac{\partial \bar{W}}{\partial \boldsymbol{\gamma}}\right)' = -\left(\frac{\partial \bar{W}}{\partial \alpha}\boldsymbol{K}^{\mathfrak{a}} + \frac{\partial \bar{W}}{\partial \beta}\boldsymbol{K}^{\mathfrak{b}}\right)'$$

and since $\boldsymbol{K}^{\mathfrak{a}\prime} = \boldsymbol{K}^{\mathfrak{a}} \times \boldsymbol{\gamma}$,

$$\boldsymbol{Q} \times \frac{\delta W}{\delta \boldsymbol{Q}} = -\left[\left(\frac{\partial \bar{W}}{\partial \alpha}\right)' \boldsymbol{K}^{\mathfrak{a}} + \left(\frac{\partial \bar{W}}{\partial \beta}\right)' \boldsymbol{K}^{\mathfrak{b}}\right] - \left(\frac{\partial \bar{W}}{\partial \alpha}\boldsymbol{K}^{\mathfrak{a}} + \frac{\partial \bar{W}}{\partial \beta}\boldsymbol{K}^{\mathfrak{b}}\right) \times \boldsymbol{\gamma}. \tag{6.9}$$

This formula shows that unless $\boldsymbol{K}^{\mathfrak{a}}$ and $\boldsymbol{K}^{\mathfrak{b}}$ are parallel to $\boldsymbol{\gamma}$, there is always a local moment perpendicular to $\boldsymbol{\gamma}$. The rotational equation in this case retains its divergence form.

*It is frequently called the energy of "bending" and "twisting" of the chain.

A simple particular case of $\bar{W}$ is the quadratic form ($\overset{\circ}{W}{}^a > 0$, $\overset{\circ}{W}{}^b > 0$)

$$\bar{W} = \frac{1}{2}[\overset{\circ}{W}{}^a(K^a \cdot \gamma)^2 + \overset{\circ}{W}{}^b(K^b \cdot \gamma)^2] = \frac{1}{2}\gamma \cdot (\overset{\circ}{W}{}^a K^a K^a + \overset{\circ}{W}{}^b K^b K^b) \cdot \gamma \qquad (6.10)$$

i.e. an expression identical with that for the dipolar energy. Thus, the sum of all these energies is obtained by replacing $\overset{\circ}{\phi}$ in the dipolar energy by $\overset{\circ}{\phi} + 2\bar{W}$.

External energy. External forces and moments acting on the chain may be due for instance to the solvent in which the chain is moving. These forces and moments may be potential, we shall therefore consider some examples of simple external potentials, not necessarily invariant, leading to certain effects of interest.

1.

$$\phi^{(1)} = -\boldsymbol{r} \cdot \boldsymbol{f} \, . \qquad (6.11)$$

Here $\boldsymbol{f}$ is a material vector. Now

$$\frac{\delta\phi^{(1)}}{\delta \boldsymbol{r}} = \boldsymbol{f} \, , \qquad \frac{\delta\phi^{(1)}}{\delta \boldsymbol{Q}} = \boldsymbol{r}\,\overset{\circ}{\boldsymbol{f}} \quad \text{and} \quad \boldsymbol{Q} \times \frac{\delta\phi^{(1)}}{\delta \boldsymbol{Q}} + \boldsymbol{r} \times \frac{\delta\phi^{(1)}}{\delta \boldsymbol{r}} = 0$$

In other words we are faced with a material (follower) force and there is no contribution to the total moment.

2.

$$\phi^{(2)} = \boldsymbol{r}' \cdot \boldsymbol{g} = \hat{\boldsymbol{c}} \cdot \boldsymbol{g} \qquad (6.12)$$

where again $\boldsymbol{g} = \boldsymbol{Q} \cdot \overset{\circ}{\boldsymbol{g}}$. Hence

$$\frac{\delta\phi^{(2)}}{\delta \boldsymbol{r}'} = \boldsymbol{g}' = \boldsymbol{g} \times \boldsymbol{\gamma} \, , \qquad \boldsymbol{Q} \times \frac{\delta\phi^{(2)}}{\delta \boldsymbol{Q}} = \boldsymbol{r}' \times \boldsymbol{g}$$

and

$$\boldsymbol{Q} \times \frac{\delta\phi^{(2)}}{\delta \boldsymbol{Q}} + \boldsymbol{r} \times \frac{\delta\phi^{(2)}}{\delta \boldsymbol{r}} = (\boldsymbol{r} \times \boldsymbol{g})' \, .$$

In this example therefore both the force and the moment (local and total) are not material but both are derivatives with respect to s of $\boldsymbol{g}$ and $\boldsymbol{r} \times \boldsymbol{g}$, respectively. Consequently the divergence form of the equations of motion is preserved.

3. Let now $\phi^{(3)}(\boldsymbol{Q}, \boldsymbol{Q}')$ be invariant, $\phi^{(3)} = -\boldsymbol{\gamma} \cdot \boldsymbol{g}$, $\boldsymbol{g} = \boldsymbol{Q} \cdot \overset{\circ}{\boldsymbol{g}}$, i.e. $\boldsymbol{Q} \times \dfrac{\delta\phi^{(3)}}{\delta \boldsymbol{Q}} = -\left(\boldsymbol{Q} \times \dfrac{\delta\phi^{(3)}}{\delta \boldsymbol{\gamma}}\right)'$ and the moment is again a derivative with respect to s of a material vector.

In [14] and [15] an equation was derived and investigated, describing a chain of rigid dipoles in a plane, situated along a straight line, assuming that their centres of gravity do not move and the angle of rotation is ϑ. This equation has a kink solution and is under investigation by the Painlevé test [19]. We shall now prove that it can be derived along the lines of this paper from a three-dimensional case, provided we choose the internal energy $\phi(Q.Q')$ in an appropriate way. Since the centres of gravity do not move and the dipoles are allowed to rotate freely (there are no constraints) we set $\dot{r} = 0$, $\mu = 0$. Furthermore, since in the two-dimensional case.

$$Q = \begin{pmatrix} \cos\vartheta & -\sin\vartheta & 0 \\ \sin\vartheta & \cos\vartheta & 0 \\ 0 & & 1 \end{pmatrix},$$

$\omega_3 = -\dot{\vartheta}, \gamma_3 = -\vartheta'$; the only remaining equation in the system is the rotational equation for the angle ϑ. It can easily be shown that the kinetic energy of the chain is

$$K = \frac{1}{2} \overset{\circ}{\rho}\, tr(\dot{Q}\, \overset{\circ}{I}\, \dot{Q}^{\mathrm{T}}) = \frac{1}{2} \overset{\circ}{\rho}\, tr_2(\overset{\circ}{I})\dot{\vartheta}^2$$

where $tr_2\, \overset{\circ}{I} = \overset{\circ}{I}_{11} + \overset{\circ}{I}_{22}$. The external potential energy (not invariant) is assumed to be

$$\phi = \frac{1}{2}\gamma \cdot Q\phi Q^{\mathrm{T}} \cdot \gamma + a \cdot b$$

where $\phi_{ij} = Q_{pq}\, \overset{\circ}{\phi}_{ijpq}$ and $\overset{\circ}{\phi}_{ijpq}$ is constant, $b = Q \cdot \overset{\circ}{b}$, the zero indicating constant quantities. Assume that $\overset{\circ}{a}_3 = \overset{\circ}{b}_3 = 0$, $\overset{\circ}{a}_1\overset{\circ}{b}_1 + \overset{\circ}{a}_2\overset{\circ}{b}_2 = 1$, $\overset{\circ}{a}_1\overset{\circ}{b}_2 - \overset{\circ}{a}_2\overset{\circ}{b}_1 = 0$ and furthermore $\overset{\circ}{\phi}_{12} + \overset{\circ}{\phi}_{21} = -1$, $\overset{\circ}{\phi}_{12} = \overset{\circ}{\phi}_{21}$ and denote $\overset{\circ}{\phi}_{33} = \sigma$. Then the Lagrangian equation derived from the Lagrangian $L = K - \phi$ is

$$\overset{\circ}{\rho}\, tr_2(\overset{\circ}{I})\ddot{\vartheta} + (\cos\vartheta - \sigma)\vartheta'' + (1 - \frac{1}{2}\vartheta'^2)\sin\vartheta = 0$$

and differs from that in [15] in notation only. The term $a \cdot b$ leads to $\sin\vartheta$ in the equation while $(\cos\vartheta - \sigma)\vartheta'' - \frac{1}{2}\vartheta'^2 \sin\vartheta$ follows from the first term in the potential energy.

§7. Friction forces. Peptide chain in shear flow.

We consider in this Chapter the peptide chain in a solvent the flow of which is known; the interaction occurs by means of friction forces.

Each atom P of an elementary peptide unit is subject to the force

$$f^{(\eta)}(P) = \bar{\eta}(P)[v(P) - v^s(P)] \tag{7.1}$$

where $\bar{\eta}(P)$ is the coefficient of friction and $v^s(P)$ is the velocity of the solvent (say, water) at point P

$$v^s(P) = v_0 + \kappa \cdot r(P) \tag{7.2}$$

v_0 and κ being constant (cf. e.g. [13]) The peptide unit is rigid

$$r(P) = r(CG) + Q \cdot \overset{\circ}{\rho}(P)$$

where $\overset{\circ}{\rho}(P) = \overset{\circ}{r}(P) - \overset{\circ}{r}(CG)$ and

$$v(P) = v + \dot{Q} \cdot \overset{\circ}{\rho}(P), \qquad v = v(CG). \tag{7.3}$$

Similarly

$$v^s(P) = v_0 + \kappa \cdot [r + Q \cdot \overset{\circ}{\rho}(P)], \qquad r = r(CG) \tag{7.4}$$

Substituting (7.3) and (7.4) into (7.1) we arrive at the total friction force acting on the peptide unit

$$f^{(\eta)} = \sum_P f^{(\eta)}(P) = \eta[v - (v_0 + \kappa \cdot r) + (\dot{\sigma}^{(\eta)} - \kappa \cdot \sigma^{(\eta)})] = \eta[(r + \sigma(\eta) - v_0 t)^{\cdot} - \kappa \cdot (r + \sigma^{(\eta)})] \tag{7.5}$$

Here $\eta = \sum_P \bar{\eta}(P)$, $\sigma^{(\eta)} = Q \cdot \overset{\circ}{\sigma}{}^{(\eta)}$; $\overset{\circ}{\sigma}{}^{(\eta)} = \frac{1}{\eta} \sum_P \bar{\eta}(P) \overset{\circ}{\rho}(P)$ is the counterpart of the static moment of the unit. Using the definition of $r(CG)$ we have

$$\sigma^{(\eta)} = \sum_P \left[\frac{\bar{\eta}(P)}{\eta} - \frac{m(P)}{m} \right] r(P).$$

If the coefficient of friction $\bar{\eta}(P)$ is independent of the particle, $\overset{\circ}{\sigma}{}^{(\eta)} = 0$. Using the same interpretation of the forces as before, in passing to the continuum limit (7.5) is regarded as the friction force per unit length, provided η is replaced by $\frac{1}{|\overset{\circ}{c}|}\eta$, we shall not however change the notation.

The moment with respect to the centre of gravity exerted by the external flow (7.2) on a peptide unit can be derived in a similar manner. The definition of the moment on the atom P is

$$m^{(\eta)}(P) = \bar{\eta}(P)\rho(P) \times [v(P) - v^s(P)]. \tag{7.6}$$

Substituting for $\rho(P), v(P)$ and $v^s(P)$ we obtain after a simple transformation

$$m^{(\eta)} = \sum_P m^{(\eta)}(P) = \eta Q \times [(v - v_0 - \kappa \cdot r)\, \overset{\circ}{\sigma}{}^{(\eta)} + \dot{Q}\, \overset{\circ}{I}{}^{(\eta)} - \kappa Q\, \overset{\circ}{I}{}^{(\eta)}] \qquad (7.7)$$

where as before, for matrices A and B, $(A \times B)_i = \varepsilon_{ipq} A_{pm} B_{qm}$. If η is replaced by $\frac{1}{|\overset{\circ}{c}|}\eta$, (8.7) is the required expression for the moment exerted by the external flow per unit length of the chain. In the above formula

$$\overset{\circ}{I}{}^{(\eta)} = \frac{1}{\eta} \sum_P \bar{\eta}(P)\, \overset{\circ}{\rho}(P)\, \overset{\circ}{\rho}(P) \qquad (7.8)$$

is the counterpart of the inertia tensor $\overset{\circ}{I}$.

Expression (7.7) for $m^{(\eta)}$ can be transformed to a convenient form as follows. Bearing in mind that $\sigma^{(\eta)} = Q \cdot \overset{\circ}{\sigma}{}^{(\eta)}$ and $\dot{Q} = \Omega Q$, the second term takes the form

$$\varepsilon_{ipq} Q_{pm} \dot{Q}_{qn}\, \overset{\circ}{I}{}^{(\eta)}_{mn} = -J^{(\eta)} \cdot \omega$$

where

$$J^{(\eta)} = tr(I^{(\eta)})\delta - I^{(\eta)} \qquad (7.9)$$

while the last term

$$\varepsilon_{ipq} Q_{pm} \kappa_{qn} Q_{nl}\, \overset{\circ}{I}{}^{(\eta)}_{ml} = -\kappa \times I^{(\eta)}$$

Hence

$$m^{(\eta)} = \eta[-J^{(\eta)} \cdot \omega + \sigma^{(\eta)} \times ((v - v_0 - \kappa \cdot r) + \kappa \times \overset{\circ}{I}{}^{(\eta)}]$$

and the system of equations of motion is now

$$\begin{aligned}
&(-J \cdot \omega + r \times v)^{\cdot} + \frac{1}{\overset{\circ}{\rho}}(r \times \mu + \Lambda e^{\perp})' + m^{\eta} + r \times f^{(\eta)} = \frac{1}{\overset{\circ}{\rho}}\left(Q \times \frac{\delta\phi}{\delta Q} + r \times \frac{\delta\phi}{\delta r}\right) \\
&\dot{r} + \frac{1}{\overset{\circ}{\rho}}\mu' + f^{(\eta)} = \frac{1}{\overset{\circ}{\rho}}\frac{\delta\phi}{\delta r} \\
&\dot{\gamma} + \frac{1}{2}\omega \times \gamma = \omega' + \frac{1}{2}\gamma \times \omega \\
&r' = \hat{c} \\
&\gamma \cdot e^{\perp} = 0
\end{aligned} \qquad (7.10)$$

with the same unknowns. The equations of motion in the considered system cannot be represented in a divergence form.

The expressions for $\boldsymbol{f}^{(\eta)}$ and $\boldsymbol{m}^{(\eta)}$ are derived on the basis of the force $\boldsymbol{f}^{(\eta)}(P)$ on an atom in the peptide unit; in a simplified theory, neglecting the structure of the unit, we assume that the force on the unit (and hence per unit length of the chain) is given by

$$\boldsymbol{f}^{(\eta)} = \eta[\boldsymbol{v} - (\boldsymbol{v}_0 + \boldsymbol{\kappa} \cdot \boldsymbol{r})] \tag{7.11}$$

which is equivalent to assuming $\boldsymbol{\sigma}^{(\eta)} = 0$. Thus

$$\boldsymbol{m}^{(\eta)} = \eta(-\boldsymbol{J}^{(\eta)} \cdot \boldsymbol{\omega} + \boldsymbol{\kappa} \times \boldsymbol{I}^{(\eta)})$$

where $\boldsymbol{J}^{(\eta)}$ is given by (7.9) in terms of $\boldsymbol{I}^{(\eta)}$. Since $\boldsymbol{\sigma}^{(\eta)} = 0$ is equivalent to $\bar{\eta}(P) = \frac{1}{m}\eta m(P)$ we finally obtain

$$\boldsymbol{m}^{(\eta)} = \eta(-\boldsymbol{J} \cdot \boldsymbol{\omega} + \boldsymbol{\kappa} \times \boldsymbol{I}) . \tag{7.12}$$

The last term in this relation represents the interaction between the rotational part of $\boldsymbol{v}^s$ and the rotational inertia of the peptide unit.

§8. Two-dimensional problems

In this Chapter we examine the chain situated in the (x_1, x_2) plane. The rotation tensor has now the form

$$\boldsymbol{Q} = \begin{pmatrix} \cos\vartheta & -\sin\vartheta & 0 \\ \sin\vartheta & \cos\vartheta & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{8.1}$$

and the only rotational degree of freedom is the angle ϑ describing the ~~relative~~ rotation of the ~~adjacent~~ peptide units. It follows from the definitions that

$$\boldsymbol{\gamma} = (0, 0, -\vartheta') , \qquad \boldsymbol{\omega} = (0, 0, -\dot{\vartheta})$$

and $\overset{o}{e}{}_{\frac{1}{3}} = 0$. Hence the compatibility condition $(7.10)^3$ and the constraint condition $(7.10)^5$ are identically satisfied and we may set $\Lambda \equiv 0$. It turns out now that there is only one rotational equation (in the x_3 direction) and $-\boldsymbol{J} \cdot \boldsymbol{\omega} = tr_2(\overset{o}{\boldsymbol{I}})\ddot{\vartheta}$ where $tr_2(\overset{o}{\boldsymbol{I}}) = \overset{o}{I}_{11} + \overset{o}{I}_{22}$. We confine ourselves to the case of vanishing external potential forces.

i.e. we set $\frac{\delta\phi}{\delta r} = 0$ and to the invariant internal energy ϕ. When calculating the friction forces and moments we base on the simplified formulae (7.11) and (7.12). Furthermore, we assume that the only non-vanishing components of κ are κ_{12} and κ_{21} and $\kappa_{12} = -\kappa_{21}$

Thus we have

$$f_1^{(\eta)} = \eta[\dot{r}_1 - (v_{01} + \kappa_{12} r_2)], \quad f_2^{(\eta)} = \eta[\dot{r}_2 - (v_{02} - \kappa_{12} r_1)]$$
$$m^{(\eta)} = \eta t r_2 \overset{\circ}{I} (\dot{\vartheta} + \kappa_{12}) \tag{8.2}$$

Simple transformations now lead to the system (7.10) reduced to two dimensions

$$\begin{aligned}
&t r_2^{(\eta)} \overset{\circ}{I} (\bar{\vartheta} + \eta\dot{\vartheta}) - \overset{\circ}{\phi}_{33} \vartheta'' + \eta t r_2 \overset{\circ}{I} \kappa_{12} + \frac{1}{\overset{\circ}{\rho}}(\hat{c}_1\mu_2 - \hat{c}_2\mu_1) = 0 \\
&\bar{r}_1 + \frac{1}{\overset{\circ}{\rho}}\mu_1' + \eta[\dot{r}_1 - (v_{01} + \kappa_{12} r_2)] = 0 \\
&\bar{r}_2 + \frac{1}{\overset{\circ}{\rho}}\mu_2' + \eta[\dot{r}_2 - (v_{02} - \kappa_{12} r_1)] = 0 \\
&r_1' = \overset{\circ}{\hat{c}}_1 \cos\vartheta - \overset{\circ}{\hat{c}}_2 \sin\vartheta , \qquad r_2' = \overset{\circ}{\hat{c}}_1 \sin\vartheta + \overset{\circ}{\hat{c}}_2 \cos\vartheta .
\end{aligned} \tag{8.3}$$

This is a system of five partial differential equations for $\vartheta, r_1, r_2, \mu_1$ and μ_2. We may assume without loss of generality that $\overset{\circ}{\hat{c}} = (0, 1)$; it is also convenient to use dimensionless variables. To this end we set $t = \alpha\tilde{t}, s = \beta\tilde{s}, \mu = \gamma\tilde{\mu}, r = \beta\tilde{r}, \tilde{\eta} = \alpha\eta, \tilde{\kappa} = \alpha\kappa_{12}$ where $\alpha^2 = \overset{\circ}{\rho}\frac{(t r \overset{\circ}{I}_2)^2}{\overset{\circ}{\phi}_{33}}, \beta^2 = \overset{\circ}{\rho}\, t r_2 \overset{\circ}{I}, \gamma = \frac{\overset{\circ}{\phi}_{33}}{t r_2 \overset{\circ}{I}}$ and we drop the tildas so that now $(\dot{})$ denotes differentiation with respect to $\tilde{t}$, $(')$ with respect to $\tilde{s}$. We assume that $\overset{\circ}{\phi}_{33} > 0$, $\overset{\circ}{\mu} = 0$ and obtain

$$\begin{aligned}
&\bar{\vartheta} + \eta(\dot{\vartheta} + \kappa) - \vartheta'' - (\mu_1 \cos\vartheta + \mu_2 \sin\vartheta) = 0 \\
&\bar{r}_1 + \mu_1' + \eta[\dot{r}_1 - (v_{01} + \kappa r_2)] = 0 \\
&\bar{r}_2 + \mu_2' + \eta[\dot{r}_2 - (v_{02} - \kappa r_1)] = 0 \\
&r_1' = -\sin\vartheta , \qquad r_2' = \cos\vartheta .
\end{aligned} \tag{8.4}$$

We first note that in the conservative case $\eta = 0$, the system is reduced to the pendulum equation. In fact, in this case μ is determined to within a constant from the translational equations and substitution into the rotation equation yields the desired result.

The system (8.4) implies two non-trivial balance laws which in absence of friction express the laws of conservation of energy and field momentum. To derive them we multiply

When all unknowns depend on one variable $\zeta = s - Vt$,

the first three equations by $\dot{\vartheta}, \dot{r}_i$ and by ϑ', r_i', respectively, whence

$$\begin{aligned} \dot{E} + R' &= D^E \\ \dot{L} + (E - \mu \cdot r)' &= D^L \end{aligned} \tag{8.5}$$

where

$$\begin{aligned} E &= \frac{1}{2}[|\dot{r}|^2 + \dot{\vartheta}^2 + \vartheta'^2], \qquad R = \mu \cdot \dot{r} - \dot{\vartheta}\vartheta', \qquad L = -(\dot{r} \cdot r' + \dot{\vartheta}\vartheta') \\ D^E &= -\eta[|\dot{r}|^2 + \dot{\vartheta}^2 - (\dot{r} \cdot v_0) + \kappa(r_1\dot{r}_2 - \dot{r}_1 r_2 + \dot{\vartheta})] \\ D^L &= -\eta[r' \cdot \dot{r} + \vartheta'\dot{\vartheta} - (r' \cdot v_0) + \kappa(r_1 r_2' - r_1' r_2 + \vartheta')] . \end{aligned} \tag{8.6}$$

In general D^E can be both positive and negative, in the case however of a stationary solvent $(v_0 = 0,\ \kappa = 0)$ $D^E < 0$, as expected.

In the conservative case the system is Hamiltonian with constraints $r_1' + \sin\vartheta = 0$, $r_2' - \cos\vartheta = 0$ and the corresponding Lagrangian is

$$\mathcal{L} = \frac{1}{2}(|\dot{r}|^2 + \dot{\vartheta}^2) - \frac{1}{2}\vartheta'^2 + \mu_1(r_1' + \sin\vartheta) + \mu_2(r_2' - \cos\vartheta) . \tag{8.7}$$

The position vector r can be eliminated from the system (8.4). In fact, differentiating $(8.4)^2$ and $(8.4)^3$ with respect to s and using $(8.4)^4$ we arrive at the system of three equations for ϑ, μ_1 and μ_2 :

$$\begin{aligned} &\ddot{\vartheta} + \eta(\dot{\vartheta} + \kappa) - \vartheta'' - (\mu_1 \cos\vartheta + \mu_2 \sin\vartheta) = 0 \\ &(\sin\vartheta)\ddot{} + \eta(\dot{\vartheta} + \kappa)\cos\vartheta - \mu_1'' = 0 \\ &(\cos\vartheta)\ddot{} - \eta(\dot{\vartheta} + \kappa)\sin\vartheta + \mu_2'' = 0 \end{aligned} \tag{8.8}$$

Having solved (8.8) we calculate r from $(8.4)^4$.

In the considered particular two-dimensional case for the internal energy $\frac{1}{2}\gamma \cdot \phi \cdot \gamma$ for $\eta = 0$, our system (8.8) is identical modulo the notation with the equations describing the dynamics of elastic rods (see e.g. [22]). However, in the three dimensional case or for a different internal energy (or for $\eta \neq 0$) the systems are essentially different.

Coleman et al. [22], [23] observed that for $\eta = 0$, (8.8) can be written in a different very useful form. We proceed in a similar way for $\kappa = 0$ and $\eta \neq 0$, namely we introduce

two potentials ψ_1 and ψ_2 such that

$$\vartheta = \arctan \frac{\psi_1''}{\psi_2''}, \qquad (\psi_1'')^2 + (\psi_2'')^2 = 1$$
$$\mu_1 = \bar{\psi}_1 - \eta\dot{\psi}_1, \qquad \mu_2 = -(\bar{\psi}_2 - \eta\dot{\psi}_2). \tag{8.9}$$

Then $(8.8)^2$, $(8.8)^3$ are satisfied identically and Eq. $(8.8)^1$ is reduced to the following $(\dot{\vartheta} = \dot{\psi}_1''\psi_2'' - \psi_1''\dot{\psi}_2'',\ \bar{\vartheta} = \bar{\psi}_1''\psi_2'' - \psi_1''\bar{\psi}_2'')$:

$$\psi_2'' L\psi_1 - \psi_1'' L\psi_2 = 0 \tag{8.10}$$

where L is a linear non-self adjoint partial differential operator with constant coefficients

$$L = \frac{\partial^2}{\partial s^2}\Box^2 - \frac{\partial}{\partial t}\left[\frac{\partial}{\partial t} - \eta\left(\frac{\partial^2}{\partial s^2} + 1\right)\right], \qquad \Box^2 = \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial s^2} \tag{8.11}$$

Another form of Eq. (8.10) is obtained as follows: we have

$$\frac{1}{\psi_1''} L\psi_1 = \frac{1}{\psi_2''} L\psi_2 \overset{def}{=} \lambda$$

i.e. $L\psi_i = \lambda\psi_i''$. Squaring these equations and adding the results we find that $\lambda^2 = |L\psi|^2$. Thus finally

$$L\psi_i = |L\psi|\psi_i'' \qquad i = 1, 2 \tag{8.12}$$

which for $|L\psi| \neq 0$ implies $\psi_1''^2 + \psi_2''^2 = 1$. There is also a complex form of the considered equations for $\psi = \psi_1 + i\psi_2$, namely $L\psi = |L\psi|\psi''$ where now $|L\psi|$ is the modulus od the complex function $L\psi_1 + iL\psi_2 = L(\psi_1 + i\psi_2) = L\psi$. As before, the equation itself for $|L\psi| \neq 0$ implies $|\psi''| = 1$. Denoting $L\psi = z = re^{i\vartheta}$ we obtain the following form of the above equation: $\psi'' = e^{i\vartheta}$ where $\vartheta = \arctan \frac{L\psi_2}{L\psi_1}$.

In order to illustrate particular forms of ψ_1 and ψ_2 for $\eta = 0$ consider the solution $\overset{\circ}{\vartheta} = 0$ $\overset{\circ}{\mu}_1 = 0, \overset{\circ}{\mu}_2 = \text{const}$. Now we take $\overset{\circ}{\psi}_1{}'' = 0$, $\overset{\circ}{\psi}_2{}'' = 1$, $\overset{\circ}{\bar{\psi}}_1 = 0$, $\overset{\circ}{\bar{\psi}}_2 = -\overset{\circ}{\mu}_2$ or $\overset{\circ}{\psi}_1 = \alpha_1 + \beta_1 s + \gamma_1 t$, $\overset{\circ}{\psi}_2 = \frac{1}{2}(s^2 - \overset{\circ}{\mu}_2 t^2) + \alpha_2 + \beta_2 s + \gamma_2 t$. The linear parts in $\overset{\circ}{\psi}_1$ or $\overset{\circ}{\psi}_2$ can be neglected. To linearize the system around this solution we set $\psi_i = \overset{\circ}{\psi}_i + \varepsilon c_i e^{i(ks - \omega t)}$ with $\varepsilon \ll 1$ and it turns out that the dispersion equation is

$$\omega^2 = \frac{1}{1 + k^2} k^2 (k^2 - \overset{\circ}{\mu}_2)$$

i.e. the same as following directly from Eqs (8.8) for $\eta = 0$. We note that for $\omega^2 \geq 0, \overset{\circ}{\mu}_2 \leq k^2$.

There is a simple solution of (8.9) and (8.10) in the variable $(ks-\omega t)$, namely

$$\psi_1 = a\cos(ks-\omega t)+\frac{\sqrt{1-a^2k^4}}{k^2}\sin(ks-\omega t), \quad \psi_2 = \frac{\sqrt{1-a^2k^4}}{k^2}\cos(ks-\omega t)-a\sin(ks-\omega t)$$

for $a^2k^4 \leq 1$, $a = \text{const}$. Otherwise a, ω k are arbitrary. In this particular case $\mu_1\cos\vartheta + \mu_2\sin\vartheta = 0$ in the first equation. The position of a particle labelled by s can be calculated from (8.4)[4]; after integration we obtain, setting the integration constants equal to zero

$$r_1 = k\left[a\sin(ks-\omega t) - \frac{\sqrt{1-a^2k^4}}{k^2}\cos(ks-\omega t)\right]$$
$$r_2 = -k\left[\frac{1}{k^2}\sqrt{1-a^2k^4}\sin(ks-\omega t) + a\cos(ks-\omega t)\right].$$

Squaring the above formulae and adding them we eliminate the variable $ks-\omega t$ whence

$$r_1^2 + r_2^2 = \frac{1}{k^2}.$$

Thus, the peptide units move on a circle with radius $\frac{1}{k}$.

Another simple solution is a straight line $r_1 = a_1 s + r_1(0)$, $r_2 = a_2 s + r_2(0)$. Now $\psi_1 = \frac{1}{2}(c_1 t^2 + a_1 s^2)$, $\psi_2 = \frac{1}{2}(c_2 t^2 + a_2 s^2)$ where $a_1^2 + a_2^2 = 1, \frac{c_1}{c_2} = \frac{a_1}{a_2}$.

To linearize Eqs (8.8) for $\kappa = 0$ we set $\vartheta = \vartheta_0 + \varepsilon\vartheta_1$, $\mu_1 = \mu_{10} + \varepsilon a_1$, $\mu_2 = \mu_{20} + \varepsilon a_2$, assuming $\mu_{10} = 0$, $\mu_{20}' = 0$. The third equation does not contribute to the linear part; the first two take the form

$$\Box^2\vartheta_1 + \eta\dot{\vartheta}_1 - a_1 - \mu_{20}\dot{\vartheta}_1 = 0, \qquad \Box^2 = \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial s^2}$$
$$\ddot{\vartheta}_1 + \eta\dot{\vartheta}_1 - a_1'' = 0;$$

eliminating a_1 we have

$$\left(L - \mu_{20}\frac{\partial^2}{\partial s^2}\right)\vartheta_1 + \eta(\vartheta_1'' - \dot{\vartheta}_1)^{\cdot} = 0$$

where $L = \frac{\partial^2}{\partial s^2}\Box^2 - \frac{\partial^2}{\partial t^2}$. Assuming $\vartheta_1 = \Theta e^{i(ks-\omega t)}$ we obtain the dispersion relation

$$\omega = \frac{1}{2}\left[-i\eta \pm \sqrt{4\frac{k^2(k^2-\mu_{20})}{1+k^2} - \eta^2}\right]$$

depending essentially on the value of the Lagrangian multiplier in the basic state. For small wave numbers and large friction either $\omega = 0$ or $\omega = -i\eta$. For small friction and negative μ_{20}

$$\omega = \pm \mathring{\omega} - \frac{1}{2}\eta\left(i \pm \frac{1}{4}\frac{\eta^2}{\mathring{\omega}}\right)$$

where $\mathring{\omega} = k\sqrt{\dfrac{k^2 - \mu_{20}}{1 + k^2}}$ is the frequency for $\eta = 0$.

Approximate solutions of two-dimensional problems.

We shall now apply the standard multi-scale method (see e.g. [22]. [23]) to derive some asymptotic solutions of Eqs (8.8). We start from the conservative case

$$\begin{aligned} &\ddot{\vartheta} - \vartheta'' - (\mu_1 \cos\vartheta + \mu_2 \sin\vartheta) = 0 \\ &(\sin\vartheta)\ddot{} - \mu_1'' = 0 \\ &(\cos\vartheta)\ddot{} + \mu_2'' = 0 \end{aligned} \tag{8.13}$$

which has the solution $\vartheta = 0$, $\mu_1 = 0$, $\mu_2 = \mathring{\mu}_2 = \text{const}$. The slow variables are denoted by $S_1 = \varepsilon s$, $T_1 = \varepsilon t$, $S_2 = \varepsilon^2 s$, $T_2 = \varepsilon^2 t$ and we confine ourselves to second order in ε. Moreover, we set

$$\sin\vartheta = \vartheta - \frac{1}{6}\vartheta^3, \qquad \cos\vartheta = 1 - \frac{1}{2}\vartheta^2$$

and use the expansions

$$\vartheta = \varepsilon(\vartheta_0 + \varepsilon\vartheta_1 + \varepsilon^2\vartheta_2),\ \mu_1 = \varepsilon(a_0 + \varepsilon a_1 + \varepsilon^2 a_2),\ \mu_2 = \mathring{\mu}_2 + \varepsilon^2(b_1 + \varepsilon b_2)\,. \tag{8.14}$$

The term εb_0 in the expression for μ_2 has been omitted since it would follow that $b_0 = 0$ in order that the solution exists. We assume that

$$\begin{aligned} \vartheta_0 &= \Theta(S_1, T_1, S_2, T_2)e^{i(ks-\omega t)} + \text{c.c.} \\ a_0 &= A(S_1, T_1, S_2, T_2)e^{i(ks-\omega t)} + \text{c.c.} \\ b_1 &= B(S_1, T_1, S_2, T_2)e^{2i(ks-\omega t)} + \text{c.c.} \end{aligned} \tag{8.15}$$

The square of $e^{i(ks-\omega t)}$ in the expression for b_1 follows from the fact that $\cos\vartheta$ in Eq. $(8.13)^3$ starts from $e^{2i(ks-\omega t)}$. We recall that

$$(\dot{}) = \frac{\partial}{\partial t} + \varepsilon\frac{\partial}{\partial T_1} + \varepsilon^2\frac{\partial}{\partial T_2}, \qquad (\ddot{}) = \frac{\partial^2}{\partial t^2} + 2\varepsilon\frac{\partial^2}{\partial t \partial T_1} + \varepsilon^2\left(\frac{\partial^2}{\partial T_1^2} + 2\frac{\partial^2}{\partial t \partial T_2}\right),$$

etc., whence

$$\dot{\vartheta}_0 = (-i\omega\Theta + \varepsilon\Theta_{T_1} + \varepsilon^2\Theta_{T_2})e^{i(ks-\omega t)} + c.c. , \qquad \Theta_{T_1} = \frac{\partial\Theta}{\partial T_1}$$

and similar formulae for the other derivatives. Substituting the expansions (8.14) into Eqs (8.13) we obtain the following results: the terms of order ε yield

$$\begin{aligned} &(\omega^2 - k^2 - \mathring{\mu}_2)\Theta + A = 0 \\ &\omega^2\Theta - k^2 A = 0 \\ &\omega^2\Theta^2 - 2k^2 B = 0 . \end{aligned} \tag{8.16}$$

Thus, the first two equations lead to the dispersion relation

$$\omega^2 = \frac{1}{1+k^2}k^2(k^2 - \mathring{\mu}_2) \tag{8.17}$$

and hence

$$A = \frac{\omega^2}{k^2}\Theta \tag{8.18}$$

and

$$B = \frac{\omega^2}{2k^2}\Theta^2. \tag{8.19}$$

Note that $\omega^2 \geq 0$ only for $\mathring{\mu}_2 \leq k^2$ and $\omega^2 \geq 0$ for all negative $\mathring{\mu}_2$. It can be verified that it is sufficient to examine the first two equations only, for the third simply yields an expression for b_2'', namely

$$b_2'' = -4i(\omega\Theta\Theta_{T_1} + \frac{\omega^2}{k}\Theta\Theta_{S_1})e^{2i(ks-\omega t)} + c.c.$$

The terms of order ε^2 lead to the equations

$$(\Box^2 - \mathring{\mu}_2)\vartheta_1 - a_1 = 2i(\omega\Theta_{T_1} + k\Theta_{S_1})e^{i(ks-\omega t)} + c.c. , \qquad \Box^2 = \frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial s^2}$$

$$\frac{\partial^2\vartheta_1}{\partial t^2} - \frac{\partial^2 a_1}{\partial s^2} = 2i(\omega\Theta_{T_1} + kA_{S_1})e^{i(ks-\omega t)} + c.c. .$$

Eliminating a_1 and denoting $L = \dfrac{\partial^2}{\partial s^2}\Box^2$

$$\left(L - \mathring{\mu}_2\frac{\partial^2}{\partial s^2}\right)\vartheta_1 = -2i[\omega(1+k^2)\Theta_{T_1} + k^3\Theta_{S_1} + kA_{S_1}]e^{i(ks-\omega t)} + c.c.$$

and since in view of the dispersion relation (8.17) $(L-\overset{\circ}{\mu}_2\frac{\partial^2}{\partial s^2})e^{i(ks-\omega t)}=0$ we arrive at the secularity condition

$$\Theta_{T_1}+\omega'\Theta_{S_1}=0 \tag{8.20}$$

where $\omega'=\frac{d\omega(k)}{dk}$. Hence, as usual $\Theta(S_1,T_1)=\Theta(\xi_1)$, $\xi_1=S_1-\omega' T_1$. We may now set $\vartheta_1=0$ and then

$$a_1=-2i(k-\omega\omega')\Theta_{S_1}e^{i(ks-\omega t)}+c.c. \tag{8.21}$$

Finally the terms of order ε^3 yield $(\Box_1^2=\frac{\partial^2}{\partial T_1^2}-\frac{\partial^2}{\partial S_1^2})$

$$(\Box^2-\overset{\circ}{\mu}_2)\vartheta_2-a_2=-[\Box_1^2\Theta+\frac{\mu_2}{2}\Theta^2\bar{\Theta}-2i(\omega\Theta_{T_2}+k\Theta_{S_2})]e^{i(ks-\omega t)}+c.c.$$

$$-\frac{\overset{0}{\mu}_2}{6}\Theta^3e^{3i(ks-\omega t)}+c.c.$$

$$\frac{\partial^2\vartheta_2}{\partial t^2}-\frac{\partial^2 a_2}{\partial s^2}=[-(\Theta_{T_1T_1}-2i\omega\Theta_{T_2})+(A_{S_1S_1}+2ikA_{S_2})-$$

$$\frac{3}{2}\omega^2\Theta^2\bar{\Theta}]e^{i(ks-\omega t)}-\frac{3}{2}\omega^2\Theta^3e^{3i(ks-\omega t)}+c.c.+2\frac{\partial^2 a_1}{\partial s\partial S_1}\,.$$

As before, we eliminate a_2 from the above equations and after some transformations we arrive at the conventional nonlinear Schrödinger equation as a nonsecularity condition

$$\Theta_{T_2}+\omega'\Theta_{S_2}-\frac{i}{2}\omega''\Theta_{\xi_1\xi_1}+\frac{1}{2}i\frac{k^4(1+\overset{0}{\mu}_2)}{\omega(1+k^2)^2}|\Theta|^2\Theta=0\,. \tag{8.22}$$

In order to examine the influence of small but finite friction we set $\kappa=0$ (the solvent does not move) and replace η by $\varepsilon^2\eta$. Then friction enters terms of order ε^3 only, and the only difference as compared with the conservative case, is the replacement of (8.22) by an equation of the Ginzburg-Landau type

$$\Theta_{T_2}+\omega'\Theta_{S_2}-\frac{i}{2}\omega''\Theta_{\xi_1\xi_1}+\frac{1}{2}i\frac{k^4(1+\overset{0}{\mu}_2)}{\omega(1+k^2)^2}|\Theta|^2\Theta+\frac{1}{2}\eta\Theta=0\,. \tag{8.23}$$

Introducing a new dependent function $C(\xi_1,S_2,T_2)=\Theta(\xi_1,S_2,T_2)e^{\frac{1}{2}\eta T_2}$ we reduce the above equation to the form

$$C_{T_2}+\omega'C_{S_2}-\frac{i}{2}\omega''C_{\xi_1\xi_1}+\frac{1}{2}i\frac{k^4(1+\overset{0}{\mu}_2)}{\omega(1+k^2)^2}|C|^2Ce^{-\frac{1}{2}\eta T_2}=0 \tag{8.24}$$

indicating "a decay in time $T_2 = \varepsilon^2 t$" of the nonlinear term.

Returning to the conservative case $\eta = 0$ we note that

$$\omega' = \frac{d\omega(k)}{dk} = \frac{1}{\omega(1+k^2)}\left(\frac{\omega^2}{k} + k^3\right) = \sqrt{\frac{k^2+1}{k^2 - \mathring{\mu}_2}}\left[1 - \frac{1+\mathring{\mu}_2}{(k^2+1)^2}\right],$$

$$\frac{1}{k}(k^2+1)^{5/2}\omega''(k^2 - \mathring{\mu}_2)^{3/2} = -(1+\mathring{\mu}_2)(k^4 - 2k^2 + 3\,\mathring{\mu}_2)$$

and the Benjamin-Feir instability (cf. [23], [22]) occurs when

$$(1+\mathring{\mu}_2)^2(k^4 - 2k^2 + 3\,\mathring{\mu}_2) > 0\,. \tag{8.25}$$

For $\mathring{\mu}_2 = 0$ instability occurs when $k^2 > 2$ i.e. for waves short (as compared with the length of the peptide unit) which may be outside the range of validity of the continuum theory. Bearing in mind that $\omega^2 \geq 0$ if and only if $\mathring{\mu}_2 \leq k^2$ the instability condition takes the form

$$(1+\mathring{\mu}_2)^2(k^4 - 2k^2 + 3\,\mathring{\mu}_2) > 0\,, \quad \mathring{\mu}_2 < k^2\,. \tag{8.26}$$

These conditions restrict the constant Lagrange multiplier for a given wave number.

Appendix A

We employ in this paper the conventional representation of the rotation tensor

$$\boldsymbol{Q} = \boldsymbol{\delta}\cos\vartheta + (1-\cos\vartheta)\boldsymbol{e}\boldsymbol{e} + \sin\vartheta\,\boldsymbol{1}\times\boldsymbol{e}\,, \qquad |\boldsymbol{e}| = 1 \tag{A.1}$$

where $\boldsymbol{1}\times\boldsymbol{e} = \varepsilon_{imj}e_m$. The unit vector $\boldsymbol{e}$ defines the direction of the axis of instantaneous rotation and ϑ is the angle of rotation around it.

From (A.1) it follows that

$$\boldsymbol{Q} = (\boldsymbol{R}e^{i\vartheta} + \boldsymbol{S}) + \text{c.c.} \tag{A.2}$$

where

$$\boldsymbol{R} = \frac{1}{2}[(\boldsymbol{\delta} - \boldsymbol{e}\boldsymbol{e}) - i\boldsymbol{1}\times\boldsymbol{e}] = -\frac{1}{2}\boldsymbol{q}(\boldsymbol{q} + i\boldsymbol{\delta})\,, \qquad \boldsymbol{S} = \frac{1}{2}\boldsymbol{e}\boldsymbol{e}$$

and $\boldsymbol{q} = \boldsymbol{1}\times\boldsymbol{e}$. The above complex tensors satisfy some useful relations, e.g. $\boldsymbol{R}^n = \boldsymbol{R}$ for $n = 1, 2, \ldots$ ($\boldsymbol{R}$ is idempotent), $\bar{\boldsymbol{R}} = \boldsymbol{R}^T$, $\boldsymbol{R}\bar{\boldsymbol{R}} = 0$, $\boldsymbol{R}\boldsymbol{S} = 0$, $\boldsymbol{S}^n = 2^{-(n-1)}\boldsymbol{S}$, etc.

$\boldsymbol{Q}$ can also be represented in terms of its generator by the formula

$$\boldsymbol{Q} = e^{\vartheta\boldsymbol{q}}\,; \tag{A.3}$$

we note that $q^{2n} = (-1)^n(\delta - ee)$, $q^{2n-1} = (-1)^{n-1}q$ for $n = 1,2,\ldots$. For small angles of rotation $Q = \delta + \mathbf{1} \times e + O(\vartheta^2)$.

We note that e is both right and left eigenvector of Q with unit eigenvalue: $Q \cdot e = e \cdot Q = e$.

Another useful representation in terms of its scalar and vector invariants $trQ = 1 + 2\cos\vartheta$ and $r = -2e\sin\vartheta (r_i = \varepsilon_{ipq}Q_{pq})$ is easily derived from (A.1) by substituting for ϑ and e:

$$Q = \frac{1}{2}\left[\delta(trQ - 1) - \frac{1}{4(trQ + 1)}rr - \mathbf{1} \times r\right] . \tag{A.4}$$

The above invariants are not independent, namely they satisfy the relation

$$|r|^2 = (3 - trQ)(1 + trQ) .$$

Appendix B

The expression for the internal (interaction) energy of a peptide chain having dipole moments, can be derived from elementary microscopic considerations. In the continuum limit the derived formula is exact. Only nearest neighbour interactions are taken into account.

We assume that each (say, n-th) unit of the chain has a negative charge at $P^{-(n)}$ and a positive one at $P^{+(n)}$, initially therefore the dipole has a finite length (Fig. 3).

In view of the rigidity of the peptide unit

$$r(P^{+(n)}) = r(C_\alpha^{(n)}) + Q^{(n)} \cdot \overset{\circ}{\rho}(P^{+(n)})$$

$$r(P^{-(n)}) = r(C_\alpha^{(n)}) + Q^{(n)} \cdot \overset{\circ}{\rho}(P^{-(n)})$$

where as before $\overset{\circ}{\rho}(P^{+(n)}) = \overset{\circ}{r}(P^{+(n)}) - \overset{\circ}{r}(C_\alpha^{(n)})$, etc. There are of course similar formulae for the $(n-1)$ th unit. For $C_\alpha^{(n+1)}$ and $C_\alpha^{(n)}$, $r(C_\alpha^{(n+1)}) - r(C_\alpha^{(n)}) = c^{(n)} = Q^{(n)} \cdot \overset{\circ}{c}{}^{(n)}$ and since all units are assumed to be identical we may set without loss of generality $\overset{\circ}{c}{}^{(n)} = \overset{\circ}{c}$

and $\overset{\circ}{\rho}(P^{+(n)}) = \overset{\circ}{\rho}(P^{+}) = \overset{\circ}{\rho}{}^{+}$, etc. Hence

$$\overset{++}{r}{}_{(n-1,n)} = r(P^{+(n)}) - r(P^{+(n-1)}) = Q^{(n-1)} \cdot \overset{\circ}{c}{}^{(n)} + (Q^{(n)} - Q^{(n-1)})\,\overset{\circ}{\rho}{}^{+}$$

$$\overset{+-}{r}{}_{(n-1,n)} = Q^{(n-1)} \cdot \overset{\circ}{c} + (Q^{(n)} \cdot \overset{\circ}{\rho}{}^{+} - Q^{(n-1)} \cdot \overset{\circ}{\rho}{}^{-})$$

$$\overset{-+}{r}{}_{(n-1,n)} = Q^{(n-1)} \cdot \overset{\circ}{c} + (Q^{(n)} \cdot \overset{\circ}{\rho}{}^{-} - Q^{(n-1)} \cdot \overset{\circ}{\rho}{}^{+})$$

$$\overset{--}{r}{}_{(n-1,n)} = Q^{(n-1)} \cdot \overset{\circ}{c} + (Q^{(n)} - Q^{(n-1)}) \cdot \overset{\circ}{\rho}{}^{-}$$

In order to pass to the continuous chain we write to the order of $\varepsilon^2 (\varepsilon = |\overset{\circ}{c}|)$: $Q^{(n)} = Q(s)$, $Q^{(n-1)} = Q(s) - \varepsilon Q'(s) + \frac{1}{2}\varepsilon^2 Q''(s)$. Introducing the notation $\overset{\circ}{\rho}{}^{+} = \overset{+}{\alpha} \cdot \overset{\circ}{c}$, $\rho^{+} = Q \cdot \overset{\circ}{\rho}{}^{+}$, etc. we have

$$\overset{++}{r} = \overset{++,0}{r} + \varepsilon\,\overset{++,0}{\rho}, \quad \overset{++,0}{r} = Q \cdot \overset{\circ}{c}, \quad \overset{++,0}{\rho} = -(Q' - \tfrac{1}{2}\varepsilon Q'')(\delta - \overset{+}{\alpha}) \cdot \overset{\circ}{c}$$

$$\overset{+-}{r} = \overset{+-,0}{r} + \varepsilon\,\overset{+-,0}{\rho}, \quad \overset{+-,0}{r} = Q(\delta + \overset{+}{\alpha} - \bar{\alpha}) \cdot \overset{\circ}{c}, \quad \overset{+-,0}{\rho} = -(Q' - \tfrac{1}{2}\varepsilon Q'')(\delta - \bar{\alpha}) \cdot \overset{\circ}{c}$$

$$\overset{-+}{r} = \overset{-+,0}{r} + \varepsilon\,\overset{-+,0}{\rho}, \quad \overset{-+,0}{r} = Q(\delta + \bar{\alpha} - \overset{+}{\alpha}) \cdot \overset{\circ}{c}, \quad \overset{-+,0}{\rho} = -(Q' - \tfrac{1}{2}\varepsilon Q'')(\delta - \overset{+}{\alpha}) \cdot \overset{\circ}{c}$$

$$\overset{--}{r} = \overset{--,0}{r} + \varepsilon\,\overset{--,0}{\rho}, \quad \overset{--,0}{r} = Q \cdot \overset{\circ}{c}, \quad \overset{--,0}{\rho} = -(Q' - \tfrac{1}{2}\varepsilon Q'')(\delta - \bar{\alpha}) \cdot \overset{\circ}{c}\ .$$

Observe that $|\overset{++\,\prime 0}{r}| = |\overset{--\,\prime 0}{r}| = |\overset{\circ}{c}|$, $|\overset{+-,0}{r}| = |(\delta + \overset{+}{\alpha} - \bar{\alpha}) \cdot \overset{\circ}{c}|$, $|\overset{-+,0}{r}| = |(\delta + \bar{\alpha} - \overset{+}{\alpha}) \cdot \overset{\circ}{c}|$.

Consider now an internal energy $\phi(r)$ where r is the vector joining any two points. We have

$$\phi(r + \varepsilon\rho) = \phi(r) + \varepsilon\rho \cdot \frac{\partial\phi(r)}{\partial r} + \frac{1}{2}\varepsilon^2 \rho \cdot \frac{\partial^2\phi(r)}{\partial r \partial r} \cdot \rho$$

and for central interactions with $\phi(r) = \phi(|r|)$, since

$$\frac{\partial\phi(|r|)}{\partial r} = r\frac{\phi'(|r|)}{|r|}, \quad \frac{\partial^2\phi(|r|)}{\partial r \partial r} = \delta\frac{\phi'(|r|)}{|r|} + rr\frac{1}{|r|}\left(\frac{\phi'(|r|)}{|r|}\right)'$$

we obtain for the internal energy

$$\overset{++}{\phi} = \phi(|\overset{\circ}{c}|) - \varepsilon\frac{\phi'(|\overset{\circ}{c}|)}{|\overset{\circ}{c}|}(c - \rho^{+})' \cdot c + \frac{1}{2}\varepsilon^2 \left\{ \frac{\phi'(|\overset{\circ}{c}|)}{|\overset{\circ}{c}|}(c - \rho^{+})'' \cdot c + \left[\frac{\phi'(|\overset{\circ}{c}|)}{|\overset{\circ}{c}|}\delta + \right.\right.$$

$$\left.\left. + \frac{1}{|\overset{\circ}{c}|}\left(\frac{\phi'(|\overset{\circ}{c}|)}{|\overset{\circ}{c}|}\right)' cc \right] : (c - \rho^{+})'(c - \rho^{+})' \right\}$$

The constant $\phi(|\overset{\circ}{\mathbf{c}}|)$ may be neglected. Furthermore the terms of order ε cancel when we add the energy of the $(n+1)$-st unit. For the same reason to obtain the energy density the term proportional to ε^2 must be doubled. Thus, bearing in mind that $\mathbf{c} = \mathbf{Q}\cdot\overset{\circ}{\mathbf{c}}$, $\rho^+ = \mathbf{Q}\cdot\overset{\circ}{\rho}{}^+$, $\rho^- = \mathbf{Q}\cdot\overset{\circ}{\rho}{}^-$, after transformations

$$\frac{1}{\varepsilon}\overset{++}{\phi} = \frac{1}{2}[\overset{++}{\phi}{}^{(1)}Q'_{pq}Q'_{pr}(\overset{\circ}{c}_q - \overset{\circ}{\rho}{}^+_q)\overset{\circ}{\rho}{}^+_r + \overset{++}{\phi}{}^{(2)}(Q'_{pq}Q_{pr}\overset{\circ}{c}_q\overset{\circ}{\rho}{}^+_r)^2]$$

$$\frac{1}{\varepsilon}\overset{+-}{\phi} = \frac{1}{2}[\overset{+-}{\phi}{}^{(1)}Q'_{pq}Q'_{pr}(\overset{\circ}{c}_q - \overset{\circ}{\rho}{}^-_q)\overset{\circ}{\rho}{}^+_r + \overset{+-}{\phi}{}^{(2)}(Q'_{pq}Q_{pr}(\overset{\circ}{c}_q - \overset{\circ}{\rho}{}^-_q)\overset{\circ}{\rho}{}^+_r)^2]$$

$$\frac{1}{\varepsilon}\overset{-+}{\phi} = \frac{1}{2}[\overset{-+}{\phi}{}^{(1)}Q'_{pq}Q'_{pr}(\overset{\circ}{c}_q - \overset{\circ}{\rho}{}^+_q)\overset{\circ}{\rho}{}^-_r + \overset{-+}{\phi}{}^{(2)}(Q'_{pq}Q_{pr}(\overset{\circ}{c}_q - \overset{\circ}{\rho}{}^+_q)\overset{\circ}{\rho}{}^-_r)^2]$$

$$\frac{1}{\varepsilon}\overset{--}{\phi} = \frac{1}{2}[\overset{--}{\phi}{}^{(1)}Q'_{pq}Q'_{pr}(\overset{\circ}{c}_q - \overset{\circ}{\rho}{}^-_q)\overset{\circ}{\rho}{}^-_r + \overset{--}{\phi}{}^{(2)}(Q'_{pq}Q_{pr}\overset{\circ}{c}_q\overset{\circ}{\rho}{}^-_r)^2]$$

where the scalar material coefficients are given by the formulae

$$\overset{++}{\phi}{}^{(1)} = -2\varepsilon\frac{\phi'(|\overset{\circ}{\mathbf{c}}|)}{|\overset{\circ}{\mathbf{c}}|},\quad \overset{++}{\phi}{}^{(2)} = \frac{2\varepsilon}{|\overset{\circ}{\mathbf{c}}|}\left(\frac{\phi'(|\overset{\circ}{\mathbf{c}}|)}{|\overset{\circ}{\mathbf{c}}|}\right)',\quad \overset{--}{\phi}{}^{(1)} = \overset{++}{\phi}{}^{(1)},\ \overset{--}{\phi}{}^{(2)} = \overset{++}{\phi}{}^{(2)}$$

$$\overset{+-}{\phi}{}^{(1)} = -2\varepsilon\frac{\phi'(|\overset{+-}{\mathbf{r}}{}^0|)}{|\overset{+-}{\mathbf{r}}{}^0|},\quad \overset{+-}{\phi}{}^{(2)} = \frac{2\varepsilon}{|\overset{+-}{\mathbf{r}}{}^0|}\left(\frac{\phi'(|\overset{+-}{\mathbf{r}}{}^0|)}{|\overset{+-}{\mathbf{r}}{}^0|}\right)',$$

$$\overset{-+}{\phi}{}^{(1)} = -2\varepsilon\frac{\phi'(|\overset{-+}{\mathbf{r}}{}^0|)}{|\overset{-+}{\mathbf{r}}{}^0|},\quad \overset{-+}{\phi}{}^{(2)} = \frac{2\varepsilon}{|\overset{-+}{\mathbf{r}}{}^0|}\left(\frac{\phi'(|\overset{-+}{\mathbf{r}}{}^0|)}{|\overset{-+}{\mathbf{r}}{}^0|}\right)'.$$

In order to obtain the total internal energy ϕ per unit length we sum the above expressions; if $\phi(|\mathbf{r}|)$ is the Coulomb energy $\frac{q^+q^-}{|\mathbf{r}|}$, the sign of $\overset{+-}{\phi}$ and $\overset{-+}{\phi}$ has to be changed, which we do below. For other phenomenological energies such as the Lennard-Jones energy, the signs remain the same. Finally

$$\phi = \frac{1}{2}[\phi^{(1)}_{qr}Q'_{pq}Q'_{pr} + \sum_{\alpha=1}^{4}(\overset{\alpha}{\phi}{}^{(2)}_{qr}Q'_{pq}Q_{pr})^2]\,. \tag{B.1}$$

$\phi^{(1)}$ is a symmetric and $\phi^{(2)}$ an antisymmetric tensor. Both are constant:

$$\phi^{(1)}_{qr} = \overset{++}{\phi}{}^{(1)}(\overset{\circ}{c}_{[q} - \overset{\circ}{\rho}{}^+_{(q)})\overset{\circ}{\rho}{}^+_{r)} - \overset{+-}{\phi}{}^{(1)}(\overset{\circ}{c}_{[q} - \overset{\circ}{\rho}{}^-_{(q)})\overset{\circ}{\rho}{}^+_{r)} - \overset{-+}{\phi}{}^{(1)}(\overset{\circ}{c}_{[q} - \overset{\circ}{\rho}{}^+_{(q)})\overset{\circ}{\rho}{}^-_{r)} + \overset{--}{\phi}{}^{(1)}(\overset{\circ}{c}_{[q} - \overset{\circ}{\rho}{}^-_{(q)})\overset{\circ}{\rho}{}^-_{r)}$$

$$\overset{1}{\phi}{}^{(2)}_{qr} = \sqrt{\overset{++}{\phi}{}^{(2)}}\,\overset{\circ}{c}_{[q}\overset{\circ}{\rho}{}^+_{r]},\quad \overset{2}{\phi}{}^{(2)}_{qr} = i\sqrt{\overset{+-}{\phi}{}^{(2)}}(\overset{\circ}{c}_{[q} - \overset{\circ}{\rho}{}^-_{[q})\overset{\circ}{\rho}{}^+_{r]},\quad \overset{3}{\phi}{}^{(2)}_{qr} =$$

$$= i\sqrt{\overset{-+}{\phi}{}^{(2)}}(\overset{\circ}{c}_{[q} - \overset{\circ}{\rho}{}^+_{[q})\overset{\circ}{\rho}{}^-_{r]},\quad \overset{4}{\phi}{}^{(2)}_{qr} = \sqrt{\overset{--}{\phi}{}^{(2)}}\,\overset{\circ}{c}_{[q}\overset{\circ}{\rho}{}^-_{r]}\,. \tag{B.2}$$

Introducing $\gamma_i = \frac{1}{2}\varepsilon_{ipq}\Gamma_{pq}$ $\boldsymbol{\Gamma}$, $\boldsymbol{\Gamma} = \boldsymbol{Q}'\boldsymbol{Q}^{\mathrm{T}}$ we arrive at a simpler form of (B.1), namely

$$\boldsymbol{\phi} = \frac{1}{2}\boldsymbol{\gamma}\cdot\boldsymbol{\phi}\cdot\boldsymbol{\gamma} \tag{B.3}$$

where

$$\phi_{pq} = Q_{pm}Q_{qn}\overset{\circ}{\phi}_{mn}$$

$$\overset{\circ}{\phi}_{mn} = (tr(\boldsymbol{\phi}^{(1)})\delta_{mn} - \phi^{(1)}_{mn}) + 4\sum_{\alpha+1}^{4}\overset{\alpha}{\phi}{}^{(2)}_{m}\overset{\alpha}{\phi}{}^{(2)}_{n}\,,\quad \overset{\circ}{\boldsymbol{\phi}}{}^{(2)} = \operatorname{vect}\overset{\circ}{\boldsymbol{\phi}}\,.$$

Thus, ϕ_{pq} is a material tensor. An inspection of (B.3) proves that in general $\boldsymbol{\phi}$ is not positive-definite.

Appendix C

It can be shown directly from the definitions of $\boldsymbol{\gamma}$ and $\boldsymbol{\omega}$ that

$$-\vartheta'\boldsymbol{e} + (1-\cos\vartheta)\boldsymbol{e}'\times\boldsymbol{e} - \sin\vartheta\boldsymbol{e}' = \boldsymbol{\gamma} \tag{C.1}$$

$$|\boldsymbol{e}| = 1$$

$$-\dot{\vartheta}\boldsymbol{e} + (1-\cos\vartheta)\dot{\boldsymbol{e}}\times\boldsymbol{e} - \sin\vartheta\dot{\boldsymbol{e}} = \boldsymbol{\omega} \tag{C.2}$$

The above two systems are identical systems of three ordinary differential equations of first order for ϑ and $\boldsymbol{e}$, provided $\boldsymbol{\gamma}$ and $\boldsymbol{\omega}$ are known. We refer the Reader to [16, Sec. 3.2] for various results on the kinematics of rotation. We note here that (C.1) (or (C.2)) is not in its normal form but can be reduced to it, provided $\sin\frac{\vartheta}{2} \neq 0$. In fact, scalar and vector multiplication of (C.1) by $\boldsymbol{e}$ yield $\vartheta' = -\boldsymbol{e}\cdot\boldsymbol{\gamma}$ and

$$\sin\vartheta\boldsymbol{e}' + (1-\cos\vartheta)\boldsymbol{e}\times\boldsymbol{e}' = -\boldsymbol{e}\times(\boldsymbol{\gamma}\times\boldsymbol{e})$$

$$-(1-\cos\vartheta)\boldsymbol{e}' + \sin\vartheta\boldsymbol{e}\times\boldsymbol{e}' = -\boldsymbol{e}\times\boldsymbol{\gamma}\,.$$

Regarding this system as algebraic for $\boldsymbol{e}'$ and $\boldsymbol{e}\times\boldsymbol{e}'$, we find that the determinant is $4\sin^2\frac{\vartheta}{2}$ and the solution for $\sin\frac{\vartheta}{2} \neq 0$ leads to the normal form of the system

$$\boldsymbol{e}' - \frac{1}{2}\operatorname{ctg}\frac{\vartheta}{2}(\boldsymbol{e}\boldsymbol{e}\cdot\boldsymbol{\gamma} - \boldsymbol{\gamma}) - \frac{1}{2}\boldsymbol{e}\times\boldsymbol{\gamma} = 0$$

$$\vartheta' + \boldsymbol{\gamma}\cdot\boldsymbol{e} = 0$$

The first equation implies $e \cdot e' = 0$ i.e. $|e| = \text{const.}$ and with suitable initial condition $|e| = 1$.

Appendix D

In this Appendix we present a simple calculation of protein chain eigenfrequencies. Hydrogen bonds, absent in the main body of the paper, are introduced here. Collective electric modes will be investigated by looking at dipole-dipole interactions such that the dipole moment (distance between charges) is finite. We will look at coulomb interactions between chain.

In Figure 3, the middle arrow represents the dipole moment of a peptide unit. This is the sum of two dipole moments, that from O to C; and from N to H, both pointing in the same direction. In the α-helix protein there are three hydrogen bonded dipole chains (Figure 4). The resultant dipoles are assumed to be aligned along the α-helix axis, positive at the amino end (N), negative at the carboxy end (C). There are three chains. All dipole moments have the same polarity. Fig.3 Fig.4

Each dipole moment represents one peptide unit and negatively charged atoms have combined mass m_1 , charge Q_1 . Positively charged atoms have M_2 and q_2 respectively. The dipole moment is μ and the spacing of peptide units along hydrogen bonds is "a", a quantity absent in our main calculation.

Consider identical rotations of all μ around the centres of mass in a plane containing one of the hydrogen bonded chains in Figure 4. Here interactions with nearest neighbours along the chain are taken into account. Oscillations are through angles θ , limited by the bonds to small values.

The oscillation described here is the simplest collective mode of the system. The kinetic energy per dipole (peptide unit) is

$$K = \frac{1}{2} m_1 \mu_1^2 \dot{\theta}^2 + \frac{1}{2} m_2 \mu_2^2 \dot{\theta}^2 \,, \tag{D.1}$$

where $\mu_1 = m_2 \mu / m$, $\mu_2 = m_1 \mu / m$, $m = m_1 + m_2$. The potential energy per dipole is

$$\phi = \frac{1}{2} \sum_{i=1,2 j=1,\ldots 4} q_i q_j / r_{ij} \tag{D.2}$$

where r_{ij} are the eight distance involved. When we calculate these distance, we find that four of them are just "a" (when $q_i = q_j$). Two are given by

$$(a^2 + \mu^2 + 2a\mu cos\theta)^{1/2}$$

and two by

$$(a^2 + \mu^2 - 2a\mu cos\theta)^{1/2}$$

(when $q_i = -q_j$). We now insert these values into (D.2), expand in θ up to θ^2 , assumed small, and obtain

$$\phi = \text{const} + \frac{q^2 a\mu(\mu^3 + 3a^2\mu)\theta^2}{(a^2 - \mu^2)^3} .$$

Using energy conservation, $K + \phi = E$, we obtain harmonic oscillator behaviour of θ such that

$$\theta = \theta_{\max} cos(\omega t) \tag{D.3}$$

$$\omega^2 = \frac{2q^2(3 + \mu^2/a^2)^3}{a^3(1 - \mu^2/a^2)} (1/m_1 + 1/m_2) \tag{D.4}$$

In contradistinction to most similar calculations, this one takes finite dipole moments into account. However, we can look at the $\mu/a - 0$ limit, corresponding to the main calculation, to obtain

$$\omega^2 = (6q^2/a^3)(1/m_1 + 1/m_2) . \tag{D.5}$$

Plasma physicists will recognize the similarity between this and the plasma frequency corresponding to oscillations of a two component, completely ionized electron-proton plasma (hydrogen plasma). This frequency is

$$\omega_p^2 = 4\pi n e^2 (1/m_e + 1/m_p)$$

Here m_p is the proton mass and $n = 1/a^3$ in a cubic box. This plasma frequency was first calculated by Tonks and Langmuir in 1929 and used to investigate plasma properties by Merill and Webb in 1939. For reference see e.g. Krall and Trivelpiece (1973).

The plasma frequency constitutes one of the basic quantities of plasma physics. It is used to learn the plasma density. Similarly, our result (D.5) could perhaps be used to recognize specific proteins by exciting collective electrical oscillations and then measuring their angular frequencies.

When numerical values are introduced into D.5 (Branden and Tooze 1991), say

$$q = 0.4e$$

$$a = 5\mathring{A}$$

$$m_1 = m(O) + m(N)$$

$$m_2 = m(H) + m(C)$$

$$\mu/a = 1/3 \ ,$$

the value for ω comes out as just under $10^{13}s^{-1}$, as indeed found in experiments, see Fröhlich (1973) and Tu (1982). However, a detailed calculation for various proteins is indicated.

The formula for the basic eigenfrequency (D.5) could be refined so as to include chemical energy and also the resistance of hydrogen and peptide bonds. This last improvement, incidentally, would bring the calculation more in line with the main body of our paper.

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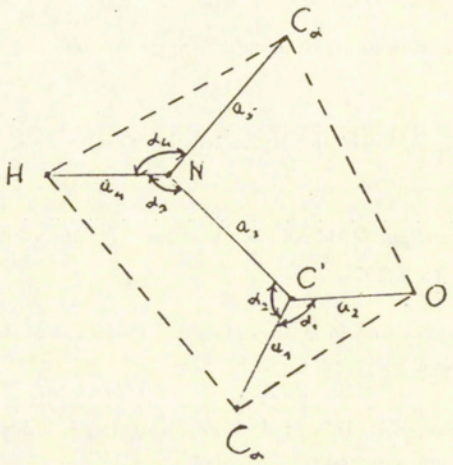

Fig.1. Bond distances (in Å) and angles (in degrees) in a peptide unit. a_1=1,51; a_2=1,24; a_3=1,33; a_4= 1,47 ; a_5=1,46. α_1=121, α_2=117, α_3=120, α_4=120.

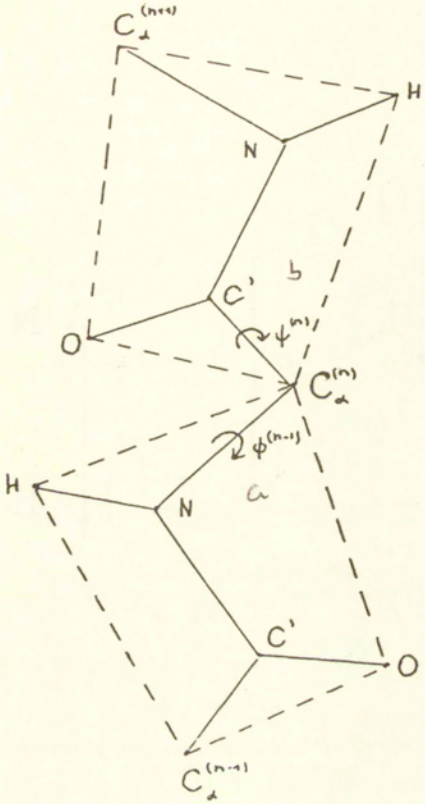

Fig.2. The dihedral angles in (n-1)-th and n-th peptide units.

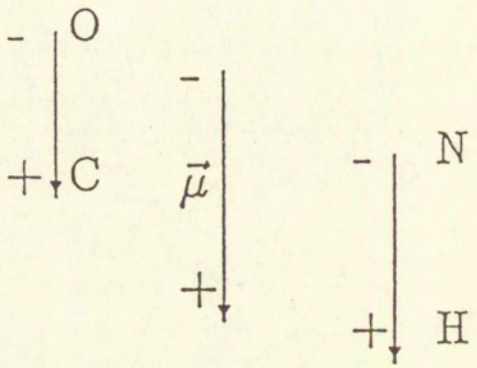

Figure 3. Dipole moment of a peptide unit (middle arrow).

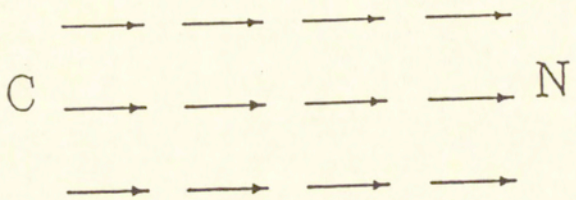

Figure 4. In an α-helix, resultant dipole moments of peptide units are taken to be aligned along the axis. There are three chains. The winding of the hydrogen bonded chains around the helix is not shown in this simplified picture. (From Branden & Tooze 1991)