

Chapter 2

Dynamics of a Macromolecule in a Viscous Liquid

Abstract In this chapter, the dynamics of the macromolecule moving in the uniform flow of a viscous liquid will be considered. To be accurate, one ought to consider a system consisting of a macromolecule and molecules of solvent (microscopic approach). However, since we are interested in large-scale or low-frequency dynamics of a macromolecular coil, a bead-spring model of a macromolecule can be used and molecules of solvent can be considered to constitute a continuum – a viscous liquid. This is a mesoscopic approach to the dynamics of dilute solutions of polymers. The approach provides the simplest model that appears to be rather complex, if the effects of excluded volume, hydrodynamic interaction, and internal viscosity are taken into account. Due to these effects, all the Brownian particles of the chain ought to be considered to interact with each other in a non-linear way. There is no intention to collect all the available results and methods concerning the dynamics of a macromolecule in viscous liquid in this chapter. We need to consider the results for dilute solutions mainly as a background and a preliminary step to the discussion of the dynamics of a macromolecule in very concentrated solutions and melts of polymers.

2.1 Equation of Macromolecular Dynamics

The theory of relaxation processes for a macromolecular coil is based, mainly, on the phenomenological approach to the Brownian motion of particles. Each bead of the chain is likened to a spherical Brownian particle, so that a set of the equation for motion of the macromolecule can be written as a set of coupled stochastic equations for coupled Brownian particles

$$m \frac{d^2 \mathbf{r}^\alpha}{dt^2} = \mathbf{F}^\alpha + \mathbf{G}^\alpha + \mathbf{K}^\alpha + \phi^\alpha, \quad \alpha = 0, 1, \dots, N \quad (2.1)$$

where m is the mass of a Brownian particle associated with a piece of the macromolecule of length $M/(N+1)$, \mathbf{r}^α are the co-ordinates of the Brownian

particles. Every Brownian particle is involved in thermal motion, which, as usual (Chandrasekhar 1943; Gardiner 1983; Doi and Edwards 1986), can be described by putting a stochastic force ϕ^α (for a particle labelled α) into an equation of motion of a macromolecule. The essential features of the stochastic force are connected with properties of the dissipative forces \mathbf{F}^α and \mathbf{G}^α (the fluctuation-dissipation theorem). For the linear case, the relation will be discussed in Section 2.6.

According to relations (1.10) and (1.28), the elastic forces acting on the particle are taken in the form

$$\mathbf{K}^\alpha = -\frac{\partial F}{\partial \mathbf{r}^\alpha} = -2T\mu A_{\alpha\gamma} \mathbf{r}^\gamma - \frac{\partial U}{\partial \mathbf{r}^\alpha}, \quad (2.2)$$

whereas the dissipative forces \mathbf{F}^α and \mathbf{G}^α are needed in special discussion.

To say nothing about the different equivalent forms of the theory of the Brownian motion that has been discussed by many authors (Chandrasekhar 1943; Gardiner 1983), there exist different approaches (Rouse 1953; Zimm 1956; Cerf 1958; Peterlin 1967) to the dynamics of a bead-spring chain in the flow of viscous liquid.¹ In this chapter, we shall try to formulate the theory in a unified way, embracing all the above-mentioned approaches simultaneously. Some parameters are used to characterise the motion of the particles and interaction inside the coil. This phenomenological (or, better to say, mesoscopic) approach permits the formulation of overall results regardless to the extent to which the mechanism of a particular effect is understood.

2.2 Intramacromolecular Hydrodynamic Interactions

In the study of the dynamics of the macromolecule in the subchains approximation, each particle of the chain is considered, to a first approximation, to be spherical with a radius a , so that the coefficient of resistance of the particle in a viscous liquid, according to Stokes, can be written as follows

$$\zeta_0 = 6\pi\eta_s a, \quad (2.3)$$

where η_s is viscosity coefficient of the liquid.

Each particle, moving at a velocity \mathbf{u}^γ , is acted upon by the hydrodynamic drag force, which has the form

$$\mathbf{F}^\gamma = -\zeta_0(\mathbf{u}^\gamma - \mathbf{v}^\gamma), \quad (2.4)$$

where \mathbf{v}^γ is the velocity of the liquid of the point, at which the given particle is present, the velocity corresponding to the situation where no account is taken of the particle. When an assembly of particles is considered, the velocity \mathbf{v}^γ

¹ See Ferry (1990) for a short history of development.

is, generally speaking, determined by the motion of all the particles. As can be seen from formulae for forces applied to points (see Appendix C), we have

$$v_j^\gamma = \nu_{jl} r_l^\gamma - \sum_{\beta=0}^N H_{jl}^{\gamma\beta} F_l^\beta, \quad (2.5)$$

where $\nu_{jl} r_l^\gamma$ is velocity of the flow in the point r_l^γ in absence of the particles in the liquid, and $\nu_{ij} = \frac{\partial v_i}{\partial x_j}$ is a tensor of velocity gradients² of the uniform flow.³ The components of the hydrodynamic interaction tensor $H_{jl}^{\gamma\beta}$ for $\gamma = \beta$ are zero, while, in the case $\gamma \neq \beta$, they are determined by the relation

$$H_{ik}^{\gamma\beta} = \frac{1}{8\pi\eta_s |\mathbf{r}^\gamma - \mathbf{r}^\beta|} \left(\delta_{ik} + e_i^{\gamma\beta} e_k^{\gamma\beta} \right) \quad (2.6)$$

where $e_i^{\gamma\beta} = (r_i^\gamma - r_i^\beta) / |\mathbf{r}^\gamma - \mathbf{r}^\beta|$.

A system of equations for the drag forces follows from equations (2.4) and (2.5)

$$F_j^\alpha = -\zeta_0 (u_j^\alpha - \nu_{jl} r_l^\alpha) - \zeta_0 \sum_{\gamma} H_{jl}^{\alpha\gamma} F_l^\gamma. \quad (2.7)$$

A solution of equations (2.7) can be written in the form

$$F_j^\alpha = -\zeta_0 B_{jl}^{\alpha\gamma} (u_l^\gamma - \nu_{li} r_i^\gamma) \quad (2.8)$$

where the matrix of hydrodynamic resistance $B_{jl}^{\alpha\gamma}$ is introduced as the matrix inverse to the matrix

$$\delta_{jl} \delta_{\alpha\gamma} + \zeta_0 H_{jl}^{\alpha\gamma}.$$

For small perturbations, the solution of equations (2.7) assumes the following form, to the first approximation

$$F_j^\alpha = -\zeta_0 \sum_{\gamma} \left[\left(\delta_{\alpha\gamma} \delta_{jl} - \zeta_0 H_{jl}^{\alpha\gamma} \right) (u_l^\gamma - \nu_{li} r_i^\gamma) \right]. \quad (2.9)$$

This equation shows that the resistance-drag force for a certain particle depends on the relative velocities of all the particles of the macromolecule and also on the relative distance between the particles. This expression determines an approximate matrix of hydrodynamic resistance

² Note that henceforth it will be convenient to use the following notation for the symmetric and antisymmetric tensors of velocity gradients

$$\gamma_{ij} = \frac{1}{2} (\nu_{ij} + \nu_{ji}), \quad \omega_{ij} = \frac{1}{2} (\nu_{ij} - \nu_{ji}).$$

³ The dependence of the velocity gradients on the co-ordinates leads to possible migration of macromolecules in a flow (Aubert and Tirell 1980; Brunn 1984) – the effect, which is not discussed in this monograph.

$$B_{jl}^{\alpha\gamma} = \delta_{\alpha\gamma}\delta_{jl} - \zeta_0 H_{jl}^{\alpha\gamma}. \quad (2.10)$$

The exact components of the matrix of hydrodynamic resistance for a two-particle chain are shown in Appendix F.

We note that the values of the hydrodynamic interaction tensor (2.6) averaged beforehand with the aid of some kind of distribution function, are frequently used to estimate the influence of the hydrodynamic interaction, as was suggested by Kirkwood and Riseman (1948).⁴ For example, after averaging with respect to the equilibrium distribution function for the ideal coil and taking the relation (1.23) into account, the hydrodynamic interaction tensor (2.6) assumes the following form

$$\langle \zeta_0 H_{ij}^{\alpha\gamma} \rangle = 2h|\alpha - \gamma|^{-1/2}\delta_{ij}.$$

The non-dimensional hydrodynamic interaction parameter appears here

$$h = \frac{\zeta_0 \sqrt{6/\pi}}{12\pi\eta_s b} \approx \frac{a}{b} \quad (2.11)$$

where a is the radius of a fictitious particle associated with a subchain of length M/N and b is the mean square distance between neighbouring particles along the chain.

One can expect that the parameter of hydrodynamic interaction (2.11) behaves universally for subsequent division of the chain. One can reasonably guess that the quantity (2.11) does not depend on the length of the macromolecule and on the number of subchains. In this case, the hydrodynamic radius of the particle for the Gaussian chain

$$a \sim \left(\frac{M}{N} \right)^{1/2}.$$

The dependence of the friction coefficient of the particle is similar. If the excluded-volume effect is taken into account, the more general relation (2.19) is valid.

2.3 Resistance-Drag Coefficient of a Macromolecular Coil

To calculate the resistance coefficient for the macromolecular coil, we have to determine, first of all, the velocity of the coil, which is the velocity of the mass centre of the macromolecular coil

$$\mathbf{v} = \frac{1}{1+N} \sum_{\alpha=0}^N \mathbf{u}^\alpha$$

⁴ A more general approach can be found in paper of Bixon and Zwanzig (1978).

and the force acting on the coil, which is the sum of forces acting on every particle of the coil

$$\mathbf{F} = \sum_{\alpha=0}^N \mathbf{F}^{\alpha}$$

where the force \mathbf{F}^{α} is determined by equation (2.9).

We assume that the macromolecular coil moves in a non-flowing liquid and each particle has the mean velocity of the macromolecular coil as a whole. So, we can write down Stokes law for the coil

$$F_j = -\zeta_0(1+N) \left(\delta_{jl} - \frac{\zeta_0}{8\pi\eta_s} \frac{1}{N+1} \sum_{\alpha=0}^N \sum_{\gamma=0}^N \frac{\delta_{jl} + e_j^{\alpha\gamma} e_l^{\alpha\gamma}}{|\mathbf{r}^{\alpha} - \mathbf{r}^{\gamma}|} \right) v_l. \quad (2.12)$$

After the preliminary averaging of the right-hand side of relation (2.12) with respect to the equilibrium distribution function has been done (see relations (1.23)), we have

$$\mathbf{F} = -\zeta_M \mathbf{v}, \quad \zeta_M = \zeta_0(1+N) \left(1 - \frac{2h}{N+1} \sum_{\alpha=0}^N \sum_{\gamma=0}^N \frac{1}{|\alpha - \gamma|^{1/2}} \right).$$

One can easily estimate the asymptotic behaviour of the sum as

$$\frac{1}{N+1} \sum_{\alpha=0}^N \sum_{\gamma=0}^N \frac{1}{|\alpha - \gamma|^{1/2}} \approx 2.47 N^{1/2},$$

so that the above equations are followed the asymptotic expression for the friction coefficient

$$\zeta_M = \zeta_0 N \left(1 - 4.94 h N^{1/2} \right). \quad (2.13)$$

This expression, with accuracy up to the first-order terms in the power of h , practically coincides with expression derived by Kirkwood and Riseman (1948); they have the numerical coefficient 5.33 instead of 4.94, though their way of calculation was more accurate.

It is understandable that the resistance coefficient decreases as the hydrodynamic interaction increases. However, if one uses the bead-spring model of a macromolecule, the resistance coefficient of the whole macromolecule cannot depend on the arbitrary number of subchains N .⁵ To ensure this, one has to consider that the product $hN^{1/2}$ does not depend on N which implies that the coefficient of hydrodynamic interaction changes with N as $h \sim N^{-1/2}$ which means, in this situation, that coefficient of resistance of a particle always remains to be proportional to the length of the subchain. All this is valid,

⁵ Kirkwood and Riseman (1948) did not encounter this problem, because they used the bead-rod or, in other words, pearl-necklace model of macromolecule (Kramers 1946), in which N is a number of Kuhn's stiff segments, so that N present the length of the macromolecule.

when the hydrodynamic interaction is weak and we consider the first-order corrections to the resistance coefficient.⁶

In the general case of arbitrary values of h , simple speculations appeared to be useful to determine the dependence of the resistance coefficient on the length of the macromolecule (Gennes 1979). The excluded-volume effects (see Section 1.5) can also be taken into account and one considers the resistance coefficient to be a function of two non-dimensional parameters h and v/b^3 . For a macromolecule, consisting of N smaller subchains, the friction coefficient can be written as

$$\zeta_M = \zeta Z \left(N, \frac{v}{b^3}, h \right),$$

where ζ is the friction coefficient of a particle of the chain. To obtain the dependence of the resistance coefficient on the length of the macromolecule, we compare the resistance coefficients for the two different presentations of a macromolecule. One can assume, as was done in Section 1.5 for a similar consideration, that, at $N \rightarrow \infty$, the quantities v/b^3 and h do not depend on the number of divisions of the macromolecule into subchains. The requirement of the universality of the representation of the resistance coefficient is followed by the asymptotic (long macromolecules) expression for the dependence of the resistance coefficient on the length of the macromolecule.

$$\zeta_M \sim M^{(z-2)\nu}, \quad 0 < (z-2)\nu \leq 1. \quad (2.14)$$

Here ν is the index introduced in relation (1.31), whereas z is a new index, so-called dynamic index. To calculate the index in the power function, it is necessary to use special methods (Al-Naomi et al. 1978; Baldwin and Helfand 1990; Öttinger 1989b, 1990), which gives values from 3 to 4 for the parameter z .

2.4 Effective Resistance-Drag Coefficient of a Particle

One may note that, in linear approximation with respect to the velocity of a particle (see, for example, equations (2.4) and (2.9)), the expression for forces are determined by small velocities of the particles and of the flow. The force, acting on a particle in the flow, does not depend on the specific choice of hydrodynamic interaction and can be written in the following general form

$$F_j^\alpha = -\zeta_0 B_{ji}^{\alpha\gamma} (u_i^\gamma - \nu_{il} r_l^\gamma). \quad (2.15)$$

The resistance matrix depends on co-ordinates of all particles, in non-linear manner. The situation is illustrated in Appendix F for the case of two particles. To avoid the non-linear problem, one uses the preliminary averaging of the hydrodynamic resistance matrix (Kirkwood and Riseman 1948; Zimm

⁶ The development of the theory of translational mobility of a macromolecule can be found in papers of Dünweg et al. (2002) and Liu and Dünweg (2003).

1956). If one averages with respect to the equilibrium distribution function, the matrix takes the form

$$B_{ji}^{\alpha\gamma} = B_{\alpha\gamma}\delta_{ji} \quad (2.16)$$

where matrix $B_{\alpha\gamma}$ does not depend on the co-ordinates and assumes, under the conditions of weak hydrodynamic interaction, the following form, according to equations (2.10) and (2.11),

$$B_{\alpha\gamma} = \delta_{\alpha\gamma} - 2h|\alpha - \gamma|^{-1/2}. \quad (2.17)$$

This is the first term of expansion in powers of the parameter of hydrodynamic interaction.

When normal co-ordinates, defined by equations (1.13), are employed, it is possible to make use of the arbitrariness of the transform matrix to define matrix Q in such a way that matrix B in the right-hand side of equation (2.16) assumes a diagonal form after transformation. The problem of the simultaneous adjustment of the symmetrical matrices A and B to a diagonal form does have a solution. Since matrix A is defined non-negatively and B is defined positively, it is possible to find a transformation such that B is transformed into a unit matrix (with accuracy to constant multiplier), and A into a diagonal matrix. Therefore, one can write simultaneously the equations

$$\begin{aligned} Q_{\alpha\lambda}A_{\alpha\gamma}Q_{\gamma\nu} &= \lambda_\nu\delta_{\lambda\nu}, \\ \zeta_0Q_{\alpha\lambda}B_{\alpha\gamma}Q_{\gamma\nu} &= \zeta\delta_{\lambda\nu}. \end{aligned} \quad (2.18)$$

One ought to introduce the effective coefficient of friction of the particle ζ into relation (2.18) to ensure the physical dimensionality of the friction coefficient. Eigenvalues λ_μ are now defined not by equations (1.16), but by more general expression that will be discussed in Section 2.6.

The dependence of the effective friction coefficient on the length of the macromolecule is of special interest. In a case when the hydrodynamic interaction of the particles of the macromolecule may be neglected, i.e. when the coil is, as it were, free-draining, the coefficient of resistance of the latter is proportional to the length of the macromolecule and the coefficient of friction of the particle associated with length M/N is proportional to this length

$$\zeta \sim \frac{M}{N}.$$

The mutual influence of the particles leads to their shielding within the coil and the overall coefficient of the resistance of the coil proves to be smaller than that for a free-draining coil. The requirement of covariance in relation to successive subdivisions of the macromolecule into subchains gives rise, according to formula (2.14), to the following power dependence for large values of N

$$\zeta \sim \left(\frac{M}{N}\right)^{(z-2)\nu}. \quad (2.19)$$

In order to calculate the power exponents, a calculation based on specific representations, similar the case, when volume-effects are taken into account, is necessary. One notes that these results are valid for infinitely long chains.

2.5 Intramolecular Friction

On the deformation of the macromolecule, i.e. when the particles constituting the chain are involved in relative motion, an additional dissipation of energy takes place and intramolecular friction forces appear. In the simplest case of a chain with two particles (a dumbbell), the force associated with the internal viscosity depends on the relative velocity of the ends of the dumbbell $\mathbf{u}^1 - \mathbf{u}^0$ and is proportional, according to Kuhn and Kuhn (1945) to

$$-(u_j^1 - u_j^0)e_j e_i \quad (2.20)$$

where \mathbf{e} is a unit vector in the direction of the vector connecting the particles of the dumbbell and κ is the phenomenological internal friction coefficient.

When a multi-particle model of the macromolecule (Slonimskii-Kargin-Rouse model) is considered, one must assume that the force acting on each particle is determined by the difference between the velocities of all the particles $\mathbf{u}^\gamma - \mathbf{u}^\beta$. These quantities must be introduced in such a way that dissipative forces do not appear on the rotation of the macromolecular coil as a whole, whereupon $u_j^\alpha = \Omega_{jl} r_l^\alpha$. Thus, in terms of a linear approximation with respect to velocities, the internal friction force must be formulated as follows

$$G_i^\alpha = - \sum_{\beta \neq \alpha} C_{\alpha\beta} (u_j^\alpha - u_j^\beta) e_j^{\alpha\beta} e_i^{\alpha\beta}, \quad (2.21)$$

where $e_j^{\alpha\beta} = (r_j^\alpha - r_j^\beta)/|\mathbf{r}^\alpha - \mathbf{r}^\beta|$. Matrix $C_{\alpha\beta}$ is symmetrical, the components of the matrix are non-negative and may depend on the distance between the particles. The diagonal components of the matrix are equal to zero.

The internal friction force can also be written in the form

$$G_i^\alpha = -G_{ij}^{\alpha\gamma} u_j^\gamma, \quad (2.22)$$

where the matrix

$$G_{ij}^{\alpha\beta} = \delta_{\alpha\beta} \sum_{\gamma \neq \alpha} C_{\alpha\gamma} e_i^{\alpha\gamma} e_j^{\alpha\gamma} - C_{\alpha\beta} e_i^{\alpha\beta} e_j^{\alpha\beta} \quad (2.23)$$

has been introduced.

The written matrix is symmetrical with respect to the upper and lower indices. Expression (2.23) defines the general form of a matrix of internal friction, which allows the force to remain unchanged on the rotation of the macromolecular coil as a whole. In contrast to matrix $C_{\alpha\beta}$, matrix (2.23) has

non-zero diagonal components, which are depicted by the first term in (2.23). Since the components of matrix $C_{\alpha\beta}$ are non-negative, the diagonal components of matrix $G_{\alpha\beta}$ exceed the non-diagonal ones and can be considered to be approximately diagonal to the indices α and β .

Expression (2.22) for an internal friction force is non-linear with respect to the co-ordinates. To avoid the non-linearity, some simpler forms for internal friction force were used (Cerf 1958). One can introduce a preliminary-averaged matrix of internal viscosity

$$\langle G_{ik}^{\alpha\gamma} \rangle = G_{\alpha\gamma} \delta_{ik},$$

where $G_{\alpha\gamma}$ is now a symmetrical numerical matrix which retains the main features of matrix (2.23), so that, instead of equation (2.22), we obtain the following expression for the force

$$G_i^\alpha = -G_{\alpha\gamma} u_i^\gamma.$$

The equation clearly does not satisfy the requirement that the internal viscosity force disappears when the coil is rotated as a whole. By ensuring linearisation of the internal friction force according to Cerf's procedure, equation (2.22) may be modified and written thus

$$G_j^\alpha = -G_{\alpha\gamma} (u_j^\gamma - \Omega_{jl} r_l^\gamma). \quad (2.24)$$

The speed of rotation of the macromolecular coil in a flow Ω_{jl} is determined by the velocity gradients

$$\Omega_{jl} = \omega_{jl} + A_{jlsk} \gamma_{sk}.$$

When linear effects are considered, matrix A_{jlsk} can be determined by considering the average rotation of the coil subjected to equilibrium averaging. Since the coil is spherical at equilibrium, it follows from symmetry conditions that

$$\Omega_{jl} = \omega_{jl}$$

to within first-order terms, so that the internal friction force can be written as

$$G_j^\alpha = -G_{\alpha\gamma} (u_j^\gamma - \omega_{jl} r_l^\gamma). \quad (2.25)$$

In terms of the normal co-ordinates introduced by equation (1.13), the matrix of the internal friction can be written as follows

$$Q_{\alpha\lambda} G_{\alpha\gamma} Q_{\gamma\mu} = -\zeta \varphi_\alpha \delta_{\lambda\mu}$$

and for the internal friction force, we have

$$G_j^\alpha = -\zeta \varphi_\alpha (\dot{\rho}_j^\alpha - \omega_{jl} \rho_l^\alpha) \quad (2.26)$$

where ζ is the effective coefficient of friction, φ_α is an internal viscosity coefficient of mode α . It is noteworthy that the representation of the force in

the form of equation (2.26) is possible only for weak intramolecular friction, $\varphi_\alpha \ll 1$.

The characteristics $\varphi_\alpha = \varphi_\alpha(M, \alpha)$ of the intramolecular friction forces in equations (2.26), introduced here as phenomenological quantities, should not depend on the method of subdivision of the macromolecule into subchains and, by virtue of the nature of the transformation, should be a function of the ratio α/M . One may expect that φ_α is a monotonically increasing function of the number of the mode α . This dependence can be fitted by

$$\varphi_\alpha = \varphi_1 \alpha^\theta \sim \left(\frac{\alpha}{M}\right)^\theta, \quad \varphi_1 \sim M^{-\theta}, \quad (2.27)$$

where θ is a positive number and φ_1 is a measure of the internal viscosity.⁷ For the considered subchain model, the internal rigidity cannot reach infinity, so it is better to use the following approximation

$$\varphi_\alpha = \frac{\varphi_1 \varphi_\infty \alpha^\theta}{\varphi_\infty + \varphi_1 \alpha^\theta}.$$

The internal viscosity force is defined phenomenologically by equations (2.26) formulated above. Various internal-friction mechanisms, discussed in a number of studies (Adelman and Freed 1977; Dasbach et al. 1992; Gennes 1977; Kuhn and Kuhn 1945; MacInnes 1977a, 1977b; Peterlin 1972; Rabin and Öttinger 1990) are possible. Investigation of various models should lead to the determination of matrices $C_{\alpha\beta}$ and $G_{\alpha\beta}$ and the dependence of the internal friction coefficients on the chain length and on the parameters of the macromolecule.

The significance and importance of the internal viscosity can be elucidated by comparing the consequences of the theory with experimental data, which will be discussed further on. However, here one should note that the phenomenological characteristics of the intramolecular friction prove to depend not only on the characteristics of the macromolecule, as might have been expected, but also on the properties of the liquid in which the macromolecule is present (Schrag 1991).

The internal viscosity of the macromolecule is a consequence of the intramolecular relaxation processes occurring on the deformation of the macromolecule at a finite rate. The very introduction of the internal viscosity is possible only insofar as the deformation times are large, compared with the relaxation times of the intramolecular processes. If the deformation frequencies are of the same order of magnitude as the reciprocal of the relaxation time, these relaxation processes must be taken explicitly into account and the internal viscosity force have to be written, instead of (2.26) as

$$G_j^\alpha = -\zeta \int_0^\infty \varphi_\alpha(s) (\dot{\rho}_j^\alpha - \omega_{jl} \rho_l^\alpha)_{t-s} ds. \quad (2.28)$$

⁷ To satisfy empirical relations in viscoelasticity and optical anisotropy of dilute solutions of polymers (see Sections 6.2.3 and 10.4.1), one has to assume that $\theta = z\nu - 1$.

This relation, at $\varphi_\alpha(s) \sim \delta(s)$, is equivalent to relation (2.26).

2.6 The Cerf-Zimm-Rouse Modes

Now one can return to the equation (2.1) for the dynamics of the macromolecule in the flow of a viscous liquid. The dissipative forces acting on the particles of the chain have generally non-linear forms, but the assumptions, when these force can be written in linear approximation, were discussed in the previous sections, so that we are able to write, in terms of the normal co-ordinates introduced previously and by taking into account all the considerations described above, the dynamic equation

$$\begin{aligned}
 Q_{\gamma\alpha} Q_{\gamma\mu} m \frac{d^2 \rho_i^\mu}{dt^2} &= -\zeta(\rho_i^\alpha - \nu_{ij} \rho_j^\alpha) - \zeta \varphi_\alpha (\rho_i^\alpha - \omega_{ij} \rho_j^\alpha) - 2\mu T \lambda_\alpha \rho_i^\alpha + \xi_i^\alpha, \\
 \xi_i^\alpha &= Q_{\gamma\alpha} \phi_i^\gamma, \quad \alpha = 0, 1, 2, \dots, N
 \end{aligned} \tag{2.29}$$

The transformation matrix $Q_{\alpha\nu}$ is not, generally speaking, orthogonal and the left-hand side of the equation formulated therefore includes the derivatives of all the co-ordinates, but we shall not dwell on this factor, bearing in mind, that in the limit $m \rightarrow 0$ in which we are interested, the left-hand side of the equation vanishes.

At the above limit, equation (2.29) at $\alpha = 0$ is the equation of motion for the centre of the mass of the macromolecule – a diffusion mode. At $\alpha = 1, 2, \dots \ll N$, equation (2.29) defines the independent relaxation modes of the macromolecule.

It is convenient here to introduce two sets of relaxation times

$$\tau_\alpha^\perp = \frac{\zeta}{4T\mu\lambda_\alpha}, \quad \tau_\alpha^\parallel = (1 + \varphi_\alpha) \tau_\alpha^\perp, \quad \alpha = 1, 2, \dots, \ll N \tag{2.30}$$

as relaxation times of the mean dimensions of the macromolecular coil (see Section 2.7.2), whereas every mode is characterised by two relaxation times: orientational and deformational. These terms are justified, when one considers the dynamics of dumbbells with arbitrary big internal viscosity (see Appendix F).

The behaviour of modes with small numbers should be independent on the arbitrary number of subdivisions N . This means that the relaxation times should not depend on N . Since the dependence of quantities μ and ζ on the number of subdivisions was elucidated previously (equations (1.32) and (2.19)), the above requirement immediately leads to the expression

$$\lambda_\alpha \sim \left(\frac{\alpha}{N} \right)^{z\nu}, \quad \alpha = 1, 2, \dots, \ll N,$$

so that for the relaxation times one has

$$\tau_{\alpha}^{\perp} \sim \left(\frac{\alpha}{M} \right)^{-z\nu}.$$

The situation of a freely-draining macromolecule without excluded-volume effects and internal viscosity, when $z\nu = 2$, and the above eigenvalues reduce to (1.17), is especially simple. In this case, equation (2.29) describes Rouse modes, and it is convenient to use the largest orientation relaxation time

$$\tau_1 = \frac{\zeta N \langle R^2 \rangle}{6\pi^2 T} = \frac{\zeta N^2}{4\pi^2 \mu T} \sim M^2, \quad (2.31)$$

where $\langle R^2 \rangle$ is the end-to-end distance, as a characteristic (Rouse) relaxation time of a macromolecule.

The random force ξ_i^{γ} in the dynamic equations (2.29) is determined by its average moments and is specified from the condition that the equilibrium moments of the co-ordinates and velocities are known beforehand (Chandrasekhar 1943). In the linearised version, with $\varphi_{\alpha} \ll 1$, this requirement determines the relation

$$\langle \xi_i^{\alpha}(t) \xi_j^{\gamma}(t') \rangle = 2T\zeta(1 + \varphi_{\alpha})\delta_{\alpha\gamma}\delta_{ij}\delta(t - t') \quad (2.32)$$

which is valid to within first-order terms in the velocity gradients. Here and henceforth the angular brackets indicate averaging with respect to the assembly of realisations of the random force.

Let us notice that the eigenvalues λ_{α} in equation (2.29) are considered constant here and henceforth. The same applies to φ_{α} . However, the introduced dissipative matrices are, generally speaking, functions of invariants $\rho^{\alpha}\rho^{\alpha}$ or of mean values $\langle \rho^{\alpha}\rho^{\alpha} \rangle$. The latter are functions of the velocity gradients, the expansion of which begins with a second-order term. It will be necessary to take this into account when discussing the non-linear results of the calculations.

2.7 The Moments of Linear Modes

In this section we refer to the stochastic equation (2.29) to calculate the mode moments, that is, the averaged values of the products of the normal co-ordinates and their velocities. It is convenient in this section to omit the label of mode and to rewrite the dynamic equation for the relaxation mode in the form of two linear equations

$$\begin{aligned} \frac{d\rho_i}{dt} &= \psi_i, \\ m \frac{d\psi_i}{dt} &= -\zeta(\psi_i - \nu_{ij}\rho_j) - \zeta\varphi(\psi_i - \omega_{ij}\rho_j) - 2T\mu\lambda\rho_i + \xi_i. \end{aligned} \quad (2.33)$$

2.7.1 Equations for the Moments of Co-ordinates

To calculate second-order moments of co-ordinates and velocities, one can start with the rates of change of quantities that can be written as follows

$$\begin{aligned}\frac{d\langle\rho_i\rho_k\rangle}{dt} &= \left\langle\rho_i\frac{d\rho_k}{dt}\right\rangle + \left\langle\rho_k\frac{d\rho_i}{dt}\right\rangle, \\ \frac{d\langle\psi_i\psi_k\rangle}{dt} &= \left\langle\psi_i\frac{d\psi_k}{dt}\right\rangle + \left\langle\psi_k\frac{d\psi_i}{dt}\right\rangle, \\ \frac{d\langle\rho_i\psi_k\rangle}{dt} &= \left\langle\rho_i\frac{d\psi_k}{dt}\right\rangle + \left\langle\psi_k\frac{d\rho_i}{dt}\right\rangle,\end{aligned}$$

while it is assumed that the equilibrium values of the moments are given by

$$\langle\rho_i\rho_k\rangle_0 = \frac{1}{2\mu\lambda}\delta_{ik}, \quad \langle\psi_i\psi_k\rangle_0 = \frac{T}{m}\delta_{ik}, \quad \langle\rho_i\psi_k\rangle_0 = 0.$$

Then, one can use equations (2.33) to obtain equations for the moments. After one has determined the averaged values of the products of the variables and the random force, the equations for the moments take the form

$$\frac{d\langle\rho_i\rho_k\rangle}{dt} = \langle\rho_i\psi_k\rangle + \langle\rho_k\psi_i\rangle, \quad (2.34)$$

$$\begin{aligned}\frac{d\langle\psi_i\psi_k\rangle}{dt} &= \frac{2T\mu\lambda}{m}(\langle\rho_i\psi_k\rangle + \langle\rho_k\psi_i\rangle) \\ &+ \frac{\zeta}{m}\left[2\frac{T}{m}\delta_{ik} - 2\langle\psi_i\psi_k\rangle + \nu_{ij}\langle\rho_j\psi_k\rangle + \nu_{kj}\langle\rho_j\psi_i\rangle\right. \\ &\left. + \varphi\left(2\frac{T}{m}\delta_{ik} - 2\langle\psi_i\psi_k\rangle + \omega_{ij}\langle\rho_j\psi_k\rangle + \omega_{kj}\langle\rho_j\psi_i\rangle\right)\right], \quad (2.35)\end{aligned}$$

$$\begin{aligned}\frac{d\langle\rho_i\psi_k\rangle}{dt} &= \langle\psi_i\psi_k\rangle - \frac{2T\mu\lambda}{m}\langle\rho_i\rho_k\rangle \\ &- \frac{\zeta}{m}[\langle\rho_i\psi_k\rangle - \nu_{kj}\langle\rho_j\rho_i\rangle + \varphi(\langle\rho_i\psi_k\rangle - \omega_{kj}\langle\rho_j\rho_i\rangle)]. \quad (2.36)\end{aligned}$$

It is easy to see that, at zeroth velocity gradients, the right-hand sides of the above equations are identically equal to zero.

2.7.2 The Slowest Relaxation Processes

The set of equations (2.34)–(2.36) for the second-order moments of co-ordinates and velocities can be simplified, if we consider the situation when the distribution of velocities corresponds to equilibrium, that is, we put $m \rightarrow 0$. In this case, equation (2.35) is followed by relation

$$\langle\rho_i\psi_k\rangle = -\frac{1}{2\tau_{\parallel}}\left(\langle\rho_i\rho_k\rangle - \frac{1}{2\mu\lambda}\delta_{ik}\right) + \nu_{kj}\langle\rho_j\rho_i\rangle - \varphi\gamma_{kj}\langle\rho_j\rho_i\rangle \quad (2.37)$$

where the relaxation times are given by relations (also by formulae (2.30))

$$\tau^{\parallel} = (1 + \varphi)\tau^{\perp}, \quad \tau^{\perp} = \frac{\zeta}{4T\mu\lambda}. \quad (2.38)$$

Now, one can use equations (2.34) to obtain relaxation equations for the moments of co-ordinates

$$\begin{aligned} & \frac{d\langle\rho_i\rho_k\rangle}{dt} - \nu_{ij}\langle\rho_j\rho_k\rangle - \nu_{kj}\langle\rho_j\rho_i\rangle \\ &= -\frac{1}{\tau^{\parallel}} \left(\langle\rho_i\rho_k\rangle - \frac{1}{2\mu\lambda}\delta_{ik} \right) - \varphi(\gamma_{ij}\langle\rho_j\rho_k\rangle + \gamma_{kj}\langle\rho_j\rho_i\rangle). \end{aligned} \quad (2.39)$$

The relaxation time τ^{\parallel} refers to the deformation processes. Indeed, by carrying out a direct summation of equation (2.39) with identical indices, one finds

$$\frac{d\langle\rho^2\rangle}{dt} = -\frac{1}{\tau^{\parallel}} \left(\langle\rho^2\rangle - \frac{3}{2\mu\lambda} \right) + 2(1 - \varphi)\gamma_{ij}\langle\rho_j\rho_i\rangle. \quad (2.40)$$

This equation describes only the deformation of the macromolecular coil and therefore τ^{\parallel} is a relaxation time of the deformation process. It can be shown (see Appendix F) that the orientation relaxation process is characterised by the relaxation time τ^{\perp} .

Explicit expressions for the moments will be necessary later to calculate the physical quantities. In the non-steady-state case, the second-order moments of co-ordinates are calculated as solutions of equations (2.39). To find the solutions, we multiply equation (2.39) by $\exp(\frac{t-s}{\tau^{\parallel}})$ and integrate over time from t to ∞ . After some transformation, we obtain

$$\begin{aligned} \langle\rho_i\rho_k\rangle &= \frac{1}{2\mu\lambda}\delta_{ik} + \int_0^{\infty} \exp\left(-\frac{s}{\tau^{\parallel}}\right) \\ &\quad \times [\nu_{ij}\langle\rho_j\rho_k\rangle + \nu_{kj}\langle\rho_j\rho_i\rangle - \varphi(\gamma_{ij}\langle\rho_j\rho_k\rangle + \gamma_{kj}\langle\rho_j\rho_i\rangle)]_{t-s} ds. \end{aligned}$$

The moments and velocity gradients in the integrand are taken at the point of time $t - s$.

Now we can use the equilibrium moments to find the first terms of the expansion of the moments as a series of repeated integrals

$$\langle\rho_i\rho_k\rangle = \frac{1}{2\mu\lambda} \left\{ \delta_{ik} + 2(1 - \varphi) \int_0^{\infty} \exp\left(-\frac{s}{\tau^{\parallel}}\right) \gamma_{ik}(t - s) ds \right\}. \quad (2.41)$$

The iteration procedure can be continued.

In the steady-state case, the expansion assumes the form

$$\begin{aligned} \langle\rho_i\rho_k\rangle &= \frac{1}{2\mu\lambda} \left\{ \delta_{ik} + 2\tau^{\perp}\gamma_{ik} \right. \\ &\quad \left. + 2(\tau^{\perp})^2 [2\gamma_{ij}\gamma_{jk} + (1 + \varphi)(\omega_{ij}\gamma_{jk} + \omega_{kj}\gamma_{ji})] \right\}. \end{aligned} \quad (2.42)$$

We may note that, in the approximation of the preliminary averaging, which was used, the expressions for the moments are valid only to within second-order terms with respect to the velocity gradients.

2.7.3 Fourier-Transforms of Moments

One can calculate the mode moments in different way. One can pass from equations (2.34)–(2.36) to the set of algebraic equations, introducing the Fourier-transforms of the unknown functions

$$\begin{aligned}\langle \rho_i \rho_k \rangle &= \int_{-\infty}^{\infty} R_{ik}(\omega) e^{-i\omega t} \frac{d\omega}{2\pi}, \\ \langle \rho_i \psi_k \rangle &= \int_{-\infty}^{\infty} Y_{ik}(\omega) e^{-i\omega t} \frac{d\omega}{2\pi}, \\ \langle \psi_i \psi_k \rangle &= \int_{-\infty}^{\infty} Z_{ik}(\omega) e^{-i\omega t} \frac{d\omega}{2\pi}.\end{aligned}$$

The solution of the resulting set of equations can be written accurately, within the first order terms with respect to the velocity gradients, as

$$\begin{aligned}R_{ik}(\omega) &= \frac{1}{2\mu\lambda} [\delta_{ik}\delta(\omega) + 2C\tau^\perp\gamma_{ik}(\omega)], \\ Y_{ik}(\omega) &= \frac{1}{2\mu\lambda} [-\omega_{ik}(\omega) - i\omega C\tau^\perp\gamma_{ik}(\omega)], \\ Z_{ik}(\omega) &= \frac{T}{m} \left[\delta_{ik}\delta(\omega) + \frac{2i\omega\tau_m C}{2(1+\varphi) - i\omega\tau_m} \tau^\perp\gamma_{ik}(\omega) \right], \\ C &= \frac{2(1+\varphi - i\omega\tau_m)}{[1 - i\omega\tau^\perp(1+\varphi) - \tau_m\tau^\perp\omega^2][2(1+\varphi) - i\omega\tau_m] - i\omega\tau_m}.\end{aligned}\tag{2.43}$$

The solution contains two characteristic relaxation times

$$\tau^\perp = \frac{\zeta}{4T\mu\lambda}, \quad \tau_m = \frac{m}{\zeta}.$$

The first relaxation time is much bigger than the second one within the limits of applicability of the subchain model. So, the terms multiplied by the quantity $\omega\tau_m$ in relations (2.43) can be neglected, and expressions can be written down in the simpler form

$$\begin{aligned}R_{ik}(\omega) &= \frac{1}{2\mu\lambda} \left[\delta_{ik}\delta(\omega) + \frac{2\tau^\perp}{1 - i\omega\tau^\perp} \gamma_{ik}(\omega) \right], \\ Y_{ik}(\omega) &= \frac{1}{2\mu\lambda} \left[-\omega_{ik}(\omega) + \frac{-i\omega\tau^\perp}{1 - i\omega\tau^\perp} \gamma_{ik}(\omega) \right], \\ Z_{ik}(\omega) &= \frac{T}{m} \delta_{ik}\delta(\omega).\end{aligned}\tag{2.44}$$

$$Z_{ik}(\omega) = \frac{T}{m} \delta_{ik}\delta(\omega).\tag{2.45}$$

It can easily be seen that the first expression from equations (2.44) corresponds to expressions (2.41) and (2.42).