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Generalized Rouse Theory for Entangled Polymeric Liquids

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ABSTRACT: Starting from a microscopic description for interacting chains, generalized Rouse equations for the motion of segments of a test chain are derived. The effects of interaction of other chains on the test chain are present in the form of a dynamic friction function $\Delta\zeta(t)$. The translational invariance of the interaction law against curvilinear displacements is used to factorize the time evolution of $\Delta\zeta(t)$ in terms of lateral and curvilinear motion of the chains. In a self-consistent way it is shown that lateral motion freezes in at a critical chain length. This is interpreted as a reptation transition and holds for $\tau^{\perp} \ll t \ll \tau^{\parallel}$, $\tau^{\perp}$ and $\tau^{\parallel}$ being collision times for lateral and curvilinear motion. The relaxation time of $\Delta\zeta(t)$ is proportional to the chain length. This leads to a splitting of the normal modes in a short-wavelength Rouse-like spectrum and a long-wavelength terminal spectrum.

1. Introduction

The entanglement concept for dense polymeric liquids of high molecular weight grew out of the necessity to explain the unusual viscoelastic properties of these materials.[1,2] At intermediate frequencies, such a polymeric liquid behaves as elastically as a rubber, and only at very small frequencies does it show viscous flow like an ordinary liquid. Since the elastic properties of a rubber are attributed to its network structure, it was suggested to understand the polymeric liquid as a temporary network. But, in contrast to temporary networks that are produced by weak chemical forces between the molecules, for the kind of polymeric liquids that we have in mind, the temporary network character is only due to the topological structure of the long-chain molecules. Each polymer forms a large random coil, and in a concentrated solution (up from the so-called semidilute regime) or a melt, these coils will be strongly "interwoven". Since two chains cannot penetrate each other, it was natural to assume that there exists a kind of knots or entanglements between the chains. Such topological bonds between two linear chains are not permanent. Motion of the chains involved will lead to a disentanglement—in the same way as a knot between two ropes can be untied by an appropriate motion of the ropes. However, for the polymer chains this motion is a purely random one, and since it affords a large-scale motion of the polymers, the typical lifetime of an entanglement will be strongly molecular-weight dependent. The strong molecular-weight dependence of viscoelastic properties is indeed characteristic for topological networks.

Despite the undisputed success of the entanglement concept, a serious drawback was that the precise nature of an entanglement was never clarified, and also the expressions used for the characteristic relaxation times of the topological network were purely empirical. The latter point was partially overcome by the tube model, which was proposed first by Edwards[3] in connection with rubber theory but then applied to polymeric liquids by de Gennes.[4-7] In the tube model, the combined topological constraints that one test chain feels because of its interaction with other polymers are summarily described as a tube, which is open only at the ends. In this tube the test chain is forced to perform a reptative motion. Only at the ends does the test chain have the complete freedom of motion. For this highly simplified model the characteristic times can be calculated. A novel prediction of this theory was a calculation of the self-diffusion coefficient, $D_s \sim M^{-2}$, M being the molecular weight, which has been confirmed in the mean time by a large number of experiments.[8] The tube model has clearly dominated polymer liquid theory and the interpretation of experimental results for the past decade. Doi and Edwards have expressed these ideas in a mathematically well-defined form,[9,10] which allowed a calculation of all dynamical properties of interest.

But, in the end, the tube model also has a number of unsatisfactory features. It clearly oversimplifies the true structure of the system; it concentrates on the dynamics of one test chain and, in its simplest version, completely disregards the influence of the motion of other chains on the dynamics of the test chain. Although in more refined treatments the tube itself becomes a dynamic quantity, by effects that are named tube length fluctuations, constraint release, etc.,[11] these attempts to amend the tube model are not really convincing. In this way the model becomes more and more complicated, and it loses the main virtue of the original model, simplicity.

Therefore, at this point is seems better to come back to the originally posed problem, the dynamics of a system of interacting linear chains. This is the subject of this work. When I use the word entanglement in the following, this does not mean any specific assumption about the precise form of an entanglement. Such a specification is simply not necessary. Here the word entanglement means the hindrance of the large-scale motions of the chains due to their mutual inpenetrability, i.e., due to excluded volume interactions. Another word to describe this effect would be "topological interaction", which has been introduced by Edwards. Mainly because of traditional aspects I prefer the notion entanglement.

The following section gives the derivation of generalized Rouse equations for a system of entangled chains, starting from microscopic equations by using the projection operator formalism. The novel aspect of this derivation is not the form of the equations, which also could be obtained by intuitive reasoning,[12] but the precise definition of an entanglement friction function, as the autocorrelation function of excluded volume forces.

The actual calculation of the entanglement friction function is given in sections 3–5. It is stimulated to a large extent by the way of thinking of the tube model, i.e., the idea of unhindered curvilinear motion. But a tube concept itself is never used in this theory. Instead it is shown that reptative motion can be understood as a consequence of the invariance of the interaction potential of two chains against curvilinear displacements of the segments.

In an earlier publication[13] it was already shown that in this way the result of the tube model for the self-diffusion coefficient can be rederived in a self-consistent way. The quantitative agreement of this theory with the experiments of Leger et al. was recently shown by Shiwa.[14] An extension of the theory to the problem of the diffusion of a tracer molecule in a matrix with different molecular weight was

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also given.[15] This is important for a correct assessment of the above-mentioned attempts to incorporate constraint release processes into the tube model. It is found that such lateral motions of the test chain are of much greater importance than has been thought before.

This article concentrates on the dynamics of internal modes of a chain, and in section 6 the spectrum of the generalized Rouse modes is discussed. It is shown that the molecular-weight dependence of the entanglement friction function leads to a natural splitting of the relaxation spectrum, into a Rouse-like high-frequency branch and a strongly molecular-weight dependent low-frequency branch.

2. Generalized Langevin Equations

The statistical mechanics of polymeric liquids is distinct from those of simple liquids because polymers are long, connected structures. Compared to these global properties, the exact microscopic structure of a polymer is irrelevant. Therefore we assume that the configuration of the polymers can be characterized by coarse-grained segment coordinates, $r(s_i)$. s_i is the segment index, $s_i = 1, 2, ..., n$, and i numbers the chains, $i = 1, 2, ..., N$. Alternatively we may also use a continuous chain model. Then s_i is considered as a continuous parameter, $-L^0/2 \le s_i \le L^0/2$, where L^0 is the equilibrium length of a chain, $L^0 = nb$. b is the bond length of the discrete chain. b may be seen as the Kuhn step length. For formal reasons it will be useful to characterize those coordinates that describe the precise local structure of a polymer and that are eliminated by the coarse graining procedure, as a set of $\{\mathbf{r}_\mu\}$. Such a $\mathbf{r}_\mu$ may be the relative distance vector between an atom in the polymer and the nearest coarse-grained coordinate, for example. We will not discuss here how this coarse graining has to be performed. One might do this either by the intuitive approach of Kuhn[16] or, more rigorously, by means of renormalization group methods.[7] For our purpose it is sufficient to assume that on the length scale of the coarse-grained coordinates the microscopic details of the chains are smeared out. The set of "microscopic" coordinates $\{\mathbf{r}_\mu\}$ is also assumed to include the coordinates of solvent molecules, in the case where we consider solutions.

An appropriate ansatz for the potential energy of a system of continuous chains is the Edwards Hamiltonian:[10]

$$H_E = \frac{3k_BT}{2b}\sum_{i=1}^{N}\int_{-L^0/2}^{L^0/2} ds_i \left(\frac{d\mathbf{r}(s_i)}{ds_i}\right)^2 + \frac{v_0 k_B T}{2b^2}\sum_{i,j=1}^{N}\int_{-L^0/2}^{L^0/2} ds_i \int_{-L^0/2}^{L^0/2} ds_j\, \delta(\mathbf{r}(s_i) - \mathbf{r}(s_j)) \quad (2.1a)$$

The first term describes elastic forces along the backbone of a polymer, which keep the segments together, with the result that the segments form a linear object with a well-defined equilibrium length L^0. The second term describes repulsive forces between segments; v_0 is called the excluded volume parameter, which characterizes the strength of repulsive interactions. We restrict our treatment to the case $v_0 > 0$. The special case of Θ systems, where $v_0 = 0$, is not considered here. Describing the form of the interaction forces by the δ function is a strong simplification. But it is sufficient for our purpose, where we only want to describe phenomena that occur on a length scale much larger than the range of these interaction forces. The usefulness of such a simplified ansatz for the interaction law is typical for systems of chains, and the ultimate justification for it comes from the large anisotropy of the shape of a macromolecule, because the length of a macromolecule is so tremendously larger than its diameter.

The Edwards Hamiltonian (2.1a) describes the entanglement effect in the following sense: the excluded volume term will cause a hindrance in the motion of the segments when they collide. But the first term in (2.1a) guarantees that this hindrance is transmitted to the neighboring segments of the chains involved in such an encounter. Because of this term, a collision between two segments can inflict major parts of the chains and therefore not only is a local event but has global consequences for the system. This is the essence of the entanglement effect.

Entanglements can truly be described only by a continuous chain model. But the algebra that we have to use is more concise for a discrete set of variables, and discrete notations are more familiar to most polymer scientists. Therefore I prefer here to use the discrete chain model. One should always keep in mind that this is only a simplification of the mathematical language but that the true physical problem is the problem of continuous chains. In discrete form, H_E is

$$H_E = \frac{3k_BT}{2b^2}\sum_{i=1}^{N}\sum_{s_i=1}^{n-1}(\mathbf{r}(s_i+1) - \mathbf{r}(s_i))^2 + \frac{v_0 k_B T}{2}\sum_{i,j=1}^{N}\sum_{s_i,s_j=1}^{n}\delta(\mathbf{r}(s_i) - \mathbf{r}(s_j)) \quad (2.1b)$$

The complete Hamiltonian would be formally given as

$$H = H_E + U_{mic} + T$$

where U_{mic} is the potential energy for interactions between microscopic coordinates and between microscopic and coarse-grained coordinates. T is the kinetic energy. The phase space function for our system is given by the Liouville equation

$$\frac{\partial}{\partial t} f(t) = \hat{L} f(t) \quad (2.2)$$

$$\hat{L} = -\sum_{i=1}^{N}\sum_{s_i=1}^{n}\left[\mathbf{v}(s_i)\cdot\frac{\partial}{\partial \mathbf{r}(s_i)} + \mathbf{F}(s_i)/m\cdot\frac{\partial}{\partial \mathbf{v}(s_i)}\right] - \sum_{\mu}\left[\mathbf{v}_\mu\cdot\frac{\partial}{\partial \mathbf{r}_\mu} - \frac{1}{m_\mu}\frac{\partial U}{\partial \mathbf{r}_\mu}\cdot\frac{\partial}{\partial \mathbf{v}_\mu}\right] \quad (2.3)$$

$\mathbf{v}(s_i)$ and $\mathbf{v}_\mu$ are velocities of segments and of "microscopic constituents". m and m_μ are the corresponding masses. $\mathbf{F}(s_i)$ is the force on segment s_i:

$$\mathbf{F}(s_i) = -\frac{\partial H}{\partial \mathbf{r}(s_i)} = -\frac{\partial H_E}{\partial \mathbf{r}(s_i)} - \frac{\partial U_{mic}}{\partial \mathbf{r}(s_i)} \quad (2.4)$$

It consists of an intramolecular elastic force, of intra- and intermolecular excluded volume forces, and of forces that solvent particles and microscopic degrees of freedom of the chains exert on the coarse-grained segments.

To obtain a tractable equation of motion for the segments of a chain, we use the projection operator method. The projection operator method is an exact way to derive equations of motion for a reduced set of variables of a system. Since the method is presented in a number of textbooks and review articles,[17] the details will not be explained here.

Let us consider a set of variables $X_i(t)$ of a system, which is described by a Liouvillean $\hat{L}$. Then the equation of motion for $X_i(t)$ is

$$\frac{d}{dt} X_i(t) = -\hat{L} X_i(t) \quad (2.5)$$

The projection operator formalism shows that this equation of motion can be brought into the form of a generalized Langevin equation:

$$\frac{d}{dt} X_i(t) = -\sum_{j,k}\left[X_k(t)\Gamma_{kj}L_{ji} + \int_0^t dt' X_k(t-t')\,\Gamma_{kj}\,M_{ji}(t')\right] + F_i(t) \tag{2.6}$$

where

$$L_{ji} = \langle X_j^*(0)\,\hat{L}\,X_i(0)\rangle \tag{2.7}$$

$$M_{ji}(t) = \langle F_j^*(0)\,F_i(t)\rangle \tag{2.8}$$

and

$$F_i(t) = -e^{-\hat{Q}\hat{L}t}\hat{Q}\hat{L}X_i(0) \tag{2.9}$$

$$\hat{Q} \equiv 1 - \hat{P}$$

and $\hat{P}$ is the projection operator

$$\hat{P}Y = \sum_{ij} X_i(0)\,\Gamma_{ij}\,\langle X_j^*(0)Y\rangle \tag{2.10}$$

Y being an arbitrary phase space variable. The Γ matrix is defined by the matrix equation

$$\sum_j \Gamma_{ij}\langle X_j^*(0)\,X_k(0)\rangle = \delta_{ik} \tag{2.11}$$

and the angular brackets denote an equilibrium average in the complete phase space.

The variables $X_i(t)$, for which we want to evaluate eq 2.6–2.11, are the coarse-grained coordinates and the corresponding velocities of one of the chains

$$X_s(t) = \mathbf{r}(s,t) \tag{2.12a}$$

$$X_{n+s}(t) = \mathbf{v}(s,t) \tag{2.12b}$$

for $s = 1, ..., n$. Since in the following we will treat only the properties of one test chain, we can delete here the chain index i. The Γ matrix is easily found to be block diagonal:

$$(\Gamma_{ij}) = \begin{bmatrix} (\gamma_{s,s'}) & (0) \\ (0) & (m\beta 1\delta_{s,s'}) \end{bmatrix} \tag{2.13}$$

Here the $\gamma_{s,s'}$ are defined by

$$\sum_{s'}\gamma_{s,s''}\langle \mathbf{r}(s')\,\mathbf{r}(s'')\rangle = 1\delta_{s,s'} \tag{2.14}$$

and can be obtained in a way, proposed by Zwanzig,[18] that yields

$$\gamma_{s,s'} = \underline{\phi}_{s,s'} + \underline{\phi}_{s-1,s'-1} - \underline{\phi}_{s,s'-1} - \underline{\phi}_{s-1,s'} \tag{2.15}$$

Here we have to set $\underline{\phi}_{s,s'} = 0$ if either index is 0 or n. The ϕ are defined as the inverse of the bond correlation function:

$$\sum_{s'=1}^{n-1} \underline{\phi}_{s,s'}\langle(\mathbf{r}(s'+1) - \mathbf{r}(s))(\mathbf{r}(s''+1) - \mathbf{r}(s''))\rangle = 1\delta_{s,s''} \tag{2.16}$$

Independent of the specific form of the $\underline{\phi}$ matrix, eq 2.15 yields for the γ matrix the property

$$\sum_{s=1}^{n}\gamma_{s,s'} = \sum_{s'=1}^{n}\gamma_{s,s'} = 0 \tag{2.17}$$

If we would neglect the excluded volume potential, according to (2.1b), we have a Markov chain, where the bond correlation function is diagonal. Then[18]

$$\gamma^0{}_{s,s'} = \frac{3}{b^2}1A_{s,s'} \tag{2.18}$$

where $A_{s,s'}$ are the elements of the usual nearest-neighbor matrix for an open chain. If the Liouville operator (2.3) acts on the X_i chosen in (2.12), then

$$-\hat{L}X_s = \mathbf{v}(s), \qquad -\hat{L}X_{n+s} = \mathbf{F}(s)/m \tag{2.19}$$

Then the L matrix is readily evaluated as

$$(L_{ij}) = \frac{k_BT}{m}1\begin{bmatrix} (0) & (\delta_{s,s'}) \\ (-\delta_{s,s'}) & (0) \end{bmatrix} \tag{2.20}$$

Here we have used Yvon's identity, $\langle Y\mathbf{F}(s)\rangle = -k_BT \times \langle \partial Y/\partial \mathbf{r}(s)\rangle$. By eq 2.19 the random forces $\mathbf{F}_i(t)$ are

$$\mathbf{F}_s(t) = 0, \quad \mathbf{F}_{n+s}(t) = \mathbf{f}(s,t)/m \tag{2.21}$$

with

$$\mathbf{f}(s,t) = e^{-\hat{Q}\hat{L}t}(\mathbf{F}(s) - \hat{P}\,\mathbf{F}(s)) = e^{-\hat{Q}\hat{L}t}(\mathbf{F}(s) + k_BT\sum_{s'=1}^{n}\gamma_{s,s'}\mathbf{r}(s')) \tag{2.22}$$

We have again used the Yvon identity and eq 2.17. As explained before, the force on a segment has three contributions: intrachain elastic forces, excluded volume (ev) forces between segments, and forces from the microscopic (mic) degrees of freedom. With eq 2.1 we can write

$$\mathbf{F}(s) = -\frac{3k_BT}{b^2}\sum_{s'=1}^{n} A_{s,s'}\,\mathbf{r}(s') + \mathbf{F}_{ev}(s) + \mathbf{F}_{mic}(s) \tag{2.23}$$

Then

$$\mathbf{f}(s,t) = e^{-\hat{Q}\hat{L}t}\left[k_BT\sum_{s'=1}^{n}\left(\gamma_{s,s'} - \frac{3}{b^2}1A_{s,s'}\right)\cdot\mathbf{r}(s) + \mathbf{F}_{ev}(s)\right] + \mathbf{f}_{mic}(s,t) \tag{2.24}$$

where

$$\mathbf{f}_{mic}(s,t) = e^{-\hat{Q}\hat{L}t}\mathbf{F}_{mic}(s) \tag{2.25}$$

Finally, the M matrix is

$$(M_{ij}) = \begin{bmatrix} (0) & (0) \\ (0) & \left(\frac{k_BT}{m^2}\zeta_{s,s'}(t)\right) \end{bmatrix} \tag{2.26}$$

where a friction function is defined in terms of the random force autocorrelation function

$$\zeta_{s,s'}(t) = \beta\langle \mathbf{f}(s,t)\,\mathbf{f}(s',0)\rangle \tag{2.27}$$

So far we did not make use of the distinction between coarse-grained variables and microscopic variables. The latter ones enter the equations of motion only in form of a contribution $\mathbf{f}_{mic}(s,t)$, in the random force term $\mathbf{f}(s,t)$. Otherwise eq 2.6 yields closed equations for the coarse-grained variables. The reason behind this separation in two sets of degrees of freedom is the idea that the microscopic degrees of freedom fluctuate on a much smaller time scale, compared with the time scale of the coarse-grained segments, and that they are uncorrelated to the latter ones. Then

$$\zeta_{s,s'}(t) = 2\zeta^0{}_{s,s'}\delta(t) + \Delta\zeta_{s,s'}(t) \tag{2.28}$$

where

$$\zeta^0{}_{s,s'} = \beta\int_0^\infty dt\,\langle \mathbf{f}_{mic}(s,t)\,\mathbf{f}_{mic}(s',0)\rangle \tag{2.29}$$

$$\Delta\zeta_{s,s'}(t) = \beta\langle(\mathbf{f}(s,t) - \mathbf{f}_{mic}(s,t))(\mathbf{f}(s',0) - \mathbf{f}_{mic}(s',0))\rangle \tag{2.30}$$

The Markov approximation for the microscopic variables,

which we here introduce simple as an ad hoc ansatz, could in principle be performed in a precise way, if a small parameter exists that characterizes the separation of time scales. In the microscopic description of Brownian motion, e.g., the mass ratio of solvent particles and Brownian particles, is this smallness parameter.[19]

Summing up (2.13), (2.20), (2.21), (2.26) and (2.28), the generalized Langevin equation (2.6) takes the form

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathbf{r}(s,t) = \mathbf{v}(s,t) \tag{2.31}$$

$$m\,\frac{\mathrm{d}}{\mathrm{d}t}\,\mathbf{v}(s,t) = -\sum_{s'=1}^{n}\gamma_{s,s'}\mathbf{r}(s',t) - \sum_{s'=1}^{n}\zeta^0_{s,s'}\mathbf{v}(s',t) - \sum_{s'=1}^{n}\int_0^t \mathrm{d}t'\,\Delta\zeta_{s,s'}(t-t')\cdot\mathbf{v}(s',t') + \mathbf{f}(s,t) \tag{2.32}$$

In polymeric liquids damping is always very strong. In dilute solution it is caused by the solvent. In concentrated solutions and melts the damping will primarily be due to the forces among the polymers. There are always local forces of the microscopic degrees of freedom, represented in $\zeta^0_{s,s'}$, and long-range force correlations between the coarse-grained segments create a dynamic friction $\Delta\zeta_{s,s'}(t)$. Therefore, on all time scales of interest, we can neglect the acceleration term in (2.32). We define now dynamic mobilities as

$$\sum_{s'=1}^{n}\left[\mu_{s,s'}(t)\cdot\zeta^0_{s',s''} + \int_0^t \mathrm{d}t'\,\mu_{s,s'}(t-t')\cdot\Delta\zeta_{s',s''}(t')\right] = 2\delta_{s,s''}\,\delta(t)\,\mathbf{1} \tag{2.33}$$

Then we can solve the right-hand side of eq 2.32 for $\mathbf{v}(s,t)$ and obtain a Langevin equation for the segment coordinates:

$$\frac{\mathrm{d}}{\mathrm{d}t}\,\mathbf{r}(s,t) = -k_\mathrm{B}T\sum_{s',s''=1}^{n}\int_0^t \mathrm{d}t'\,\mu_{s,s'}(t-t')\cdot\gamma_{s',s''}\mathbf{r}(s'',t') + \mathbf{g}(s,t) \tag{2.34}$$

With use of eq 2.27 and 2.33, the $\mathbf{g}(s,t)$ fullfil the fluctuation dissipation theorem:

$$\langle\mathbf{g}(s,t)\;\mathbf{g}(s',t')\rangle = k_\mathrm{B}T\,\mu_{s,s'}(t-t') \tag{2.35}$$

So far our approach was quite general; we used only time scale arguments to obtain the stochastic equations (2.36) for the segment coordinates. All the specific properties of a polymeric liquid are contained in the dynamic mobility function and in the matrix γ, which is directly expressed in terms of the bond correlation matrix ϕ. For a dilute system, e.g., we could now easily reproduce the Rouse–Zimm equation. But this has been done in a more direct way by Bixon[20] and by Zwanzig[18] and is not the purpose of this paper.

3. Generalized Rouse Equations

Our interest lies in the effect of entanglements on the dynamic modes of a polymer or, if one wants to avoid the word entanglement, the effect of mutual inpenetrability of such long-chain structures on their dynamics. To keep the theory as concise as possible and to make the problem solvable, let us simplify those features that are not essential to the entanglement problem. It is empirically known that in dense polymeric liquids with relatively low molecular weights a simple Rouse model gives a good description of the dynamic properties. This may be understood as an indication that (a) the bond autocorrelation matrix ϕ is diagonal and eq 2.18 can be used for the γ matrix and (b) hydrodynamic interaction is screened and the ζ^0 matrix can be approximated by its diagonal elements:

$$\zeta^0_{s,s'} \simeq \zeta^0\delta_{s,s'}\mathbf{1} \tag{3.1}$$

Because of (a), the dynamic friction function is now the autocorrelation function of excluded volume forces alone

$$\Delta\zeta_{s,s'}(t) = \beta\langle\mathbf{F}_\mathrm{ev}(s)\;e^{-\hat{Q}\hat{L}t}\;\mathbf{F}_\mathrm{ev}(s')\rangle \tag{3.2}$$

and will be called the entanglement friction function. From a Fourier transform of the excluded volume potential in (2.1), $F_\mathrm{ev}(s)$ is

$$\mathbf{F}_\mathrm{ev}(s) = k_\mathrm{B}T\frac{v_0}{(2\pi)^3}\int' \mathrm{d}^3q\; i\mathbf{q}e^{-i\mathbf{q}\cdot\mathbf{r}(s)}\,c(-\mathbf{q}) \tag{3.3}$$

where $c(\mathbf{q})$ are the collective segment density fluctuations

$$c(\mathbf{q}) = \sum_{i=1}^{N}\sum_{s_i=1}^{n} e^{-i\mathbf{q}\cdot\mathbf{r}(s_i)} \tag{3.4a}$$

for the discrete chain model and

$$c(\mathbf{q}) = \sum_{i=1}^{N}\frac{1}{b}\int_0^{L^0}\mathrm{d}s_i\;e^{-i\mathbf{q}\cdot\mathbf{r}(s_i)} \tag{3.4b}$$

In eq 3.3, integration is restricted to $|\mathbf{q}| \le q_c^{-1}$, where q_c^{-1} is of the order of the range of the true interaction potential. q_c can be determined as[13]

$$\frac{v_0}{(2\pi)^3}\int^{q_c}\mathrm{d}^3q = \frac{v_0 q_c^{\,3}}{6\pi^2} = 1 \tag{3.5}$$

We insert the Fourier representation of the excluded volume force in the entanglement friction function, which yields

$$\Delta\zeta_{s,s'}(t) = -k_\mathrm{B}T\left(\frac{v_0}{(2\pi)^3}\right)^2\int'\mathrm{d}^3q\int'\mathrm{d}^3q'\;\mathbf{q}\mathbf{q}'\times\langle e^{-i\mathbf{q}\cdot\mathbf{r}(s)}c(-\mathbf{q})e^{-\hat{Q}\hat{L}t}e^{-i\mathbf{q}'\cdot\mathbf{r}(s')}c(-\mathbf{q}')\rangle \tag{3.6}$$

Of course, a rigorous calculation of the dynamic four-point correlation function is impossible. A perturbation expansion in terms of the excluded volume potential would be possible, but this would not help to calculate entanglement effects, since entanglements certainly are not a small perturbation. Therefore, as the simplest nontrivial approximation we make a factorization:

$$\langle e^{-i\mathbf{q}\cdot\mathbf{r}(s_1)}c(-\mathbf{q})e^{-\hat{Q}\hat{L}t}e^{-i\mathbf{q}'\cdot\mathbf{r}(s'_1)}c(-\mathbf{q}')\rangle \cong R_{s'_1,s_1}(q',t)\times\sum_{i=2}^{N}\sum_{s_i,s'_i=1}^{n}R_{s'_i,s_i}(q',t)\langle\exp[-i(\mathbf{q}+\mathbf{q}')\cdot(\mathbf{r}(s_1)-\mathbf{r}(s_i))]\rangle \tag{3.7}$$

The relaxation functions $R_{s'_i,s_i}(\mathbf{q},t)$ are defined by

$$\langle e^{-i\mathbf{q}\cdot(\mathbf{r}(s_i,t)-\mathbf{r}(s'_i,0))}\rangle = \sum_{s''_i=1}^{n}R_{s_i,s''_i}(\mathbf{q},t)\langle e^{-i\mathbf{q}\cdot(\mathbf{r}(s''_i,0)-\mathbf{r}(s'_i,0))}\rangle \tag{3.8}$$

Details of approximation 3.7 are explained in the Appendix. Here we want only to give some physical arguments for its motivation. The factorization assumes that the two segments of the two chains are uncorrelated at t, similar to what is done in the "molecular chaos assumption" of the Boltzmann equation for a gas. For a gas, this assumption is good only in the dilute case. In dense gases repeated collisions lead to dynamic correlations, which forbid a factorization of the four-point correlation function. But for a polymeric liquid the situation should be different. In a highly entangled state a chain has many collisions with different chains; all of these are random events which are transmitted along the chain. So a segment feels not only its own collisions but also collisions of other segments of its chain in a random way. So, information about a specific collision should be forgotten in a short time. With (3.7) in (3.6) we obtain

$$\Delta\zeta_{s_1,s'_1}(t) = -k_BT\frac{v_0}{(2\pi)^3}\int' d^3q\ R_{s'_1,s_1}(q,t) \times \sum_{i=2}^{N}\sum_{s_i,s'_i=1}^{n} R_{s'_i,s_i}(q,t)\frac{v_0}{(2\pi)^3}\int' d^3q'\ \mathbf{qq}' \times \langle \exp[-i(\mathbf{q}+\mathbf{q}')\cdot(\mathbf{r}(s_1) - \mathbf{r}(s_i))]\rangle \quad (3.9)$$

Since the remaining correlation function for the segments s_1 and s_i has to be an even function of $\mathbf{q} + \mathbf{q}'$, the $\mathbf{q}'$ integral is readily evaluated as

$$\frac{v_0}{(2\pi)^3}\int' d^3q\ \mathbf{qq}'\langle \exp[-i(\mathbf{q}+\mathbf{q}')\cdot(\mathbf{r}(s_1) - \mathbf{r}(s_i))]\rangle = -\mathbf{qq}v_0\langle\delta(\mathbf{r}(s_1) - \mathbf{r}(s_i))\rangle + 0(v_0^2) \quad (3.10)$$

This expression is just proportional to the mean energy of excluded volume interactions between two segments. An entanglement parameter ψ has been introduced[13] as

$$\psi(c,n) = \tfrac{1}{4}n^2Nv_0\langle\delta(\mathbf{r}(s_1) - \mathbf{r}(s_i))\rangle \quad (3.11)$$

where it is assumed that the segments can be treated as statistically equivalent. We will see later on that this definition is convenient. ψ is just one-half of the mean interaction energy of one chain, in units of k_BT. It can be related to the free energy density or to the osmotic pressure of the system. For semidilute solutions in the long-chain limit,[21] $\psi(c,n) \sim nc^{5/4}$. Scaling arguments tell[7] that the mean number of segments between two entanglements of a chain is $g(c) \sim c^{-5/4}$ for semidilute systems. Then our entanglement parameter is $\psi(c,n) \sim n/g(c)$, i.e., ψ is proportional to the number of entanglements of a chain. Recently, Shiwa has calculated this entanglement parameter for dilute and semidilute solutions,[14] using the result of the renormalization group method for the osmotic pressure. With eq 3.10 and 3.11 we obtain

$$\Delta\zeta_{s_1,s'_1}(t) = \frac{4}{3}\frac{k_BT\psi}{n^2N}1\sum_{i=2}^{N}\sum_{s_i,s'_i=1}^{n}\frac{v_0}{(2\pi)^3}\int' d^3q\ q^2\ R_{s'_1,s_1}(q,t)\ R_{s'_i,s_i}(q,t) \quad (3.12)$$

All Fourier modes up to q_c, defined in eq 3.5, contribute to the relaxation of the entanglement friction function. But, because of the weight q^2, we can assume that the integral above is dominated by the large-q modes. At large q only correlations between small numbers of particles contribute, and in the limit $q \to \infty$, only self-correlations are effective. We might formulate this remark as an expansion in v_0, in the following form:

$$\frac{v_0}{(2\pi)^3}\int' d^3q\ q^2\ R_{s'_1,s_1}(q,t)\ R_{s'_i,s_i}(q,t) = q_c^2\int_0^1 dx\ x^4\ R_{s'_1,s_1}(xq_c,t)\ R_{s'_i,s_i}(xq_c,t) \quad (3.13)$$

Then we assume that in the limit of large Fourier vectors the correlation function between different segments vanishes, and only the self-correlation function of a segment survives:

$$R_{s'_i,s_i}(xq_c,t) = G(xq_c,t), \quad \text{for large } q_c \quad (3.14)$$

$G(q,t)$ is the single segment propagator

$$G(q,t) = \langle e^{-i\mathbf{q}\cdot(\mathbf{r}(s_i,t)-\mathbf{r}(s_i,0))}\rangle \quad (3.15)$$

for arbitrary s_i. Again we assume statistical equivalence of the segments. The validity of assumption 3.14 can be shown explicitely for the Rouse and Rouse–Zimm models.[22] Indeed, if we now use eq 3.13 and 3.14, the entanglement friction function is

$$\Delta\zeta_{s,s'}(t) = \Delta\zeta(t)1\delta_{s,s'} \quad (3.16)$$

with

$$\Delta\zeta(t) = \frac{4}{3}k_BT\frac{\psi}{n}\frac{v_0}{(2\pi)^3}\int' d^3q\ q^2\ G(q,t)^2 \quad (3.17)$$

which brings eq 2.34 finally in the form of a generalized Rouse equation:

$$\frac{d}{dt}\mathbf{r}(s,t) = -\frac{3k_BT}{b^2}\int_0^t dt'\,\mu(t-t')\sum_{s'=1}^{n}A_{s,s'}\,\mathbf{r}(s',t') + \mathbf{g}(s,t) \quad (3.18)$$

The dynamic mobility is obtained by an integral equation:

$$\mu(t) = \frac{2}{\zeta^0}\delta(t) - \frac{1}{\zeta^0}\int_0^t dt'\,\Delta\zeta(t-t')\,\mu(t') \quad (3.19)$$

If the entanglement friction function is zero, then the familiar result for the Rouse equations is obtained. The fluctuation–dissipation theorem for $\mathbf{g}(s,t)$ now has the form

$$\langle \mathbf{g}(s,t)\ \mathbf{g}(s',t')\rangle = k_BT\,\mu(t-t')\,\delta_{s,s'}1 \quad (3.20)$$

Because of the formal similarity with the original Rouse equations, the set of eq 3.18 is diagonalized by the Rouse eigenfunctions.

Equations 3.18–3.20 are the final result of this section. They deserve some comments. Of course such a generalization of the Rouse theory is obvious and has been proposed before (see, e.g., ref 12 or 23). But this is not the point. The actual progress, presented in this theory, lies in the precise definition of entanglement friction, eq 3.2, which subsequently has been expressed in a tractable form, eq 3.17. According to this result, entanglement friction is given by the mean strength of interaction between two segments times a Fourier integral over the modes that describe the separation of these two segments.

4. Curvilinear and Lateral Motion

The problem now is to obtain an expression for the single segment propagator $G(q,t)$ that allows a calculation of the entanglement friction function. Therefore we do not need the complete form of $G(q,t)$ for all times but only on the time scale where entanglements decay. During the past decade important progress in the understanding of entangled polymeric liquids has been made because of the introduction of the tube model. And although in this theory I will not make use of this model, one can learn quite a lot from it. If we reduce the tube model to its innermost kernel, it simply says the following: in entangled liquids lateral motion of polymer chains is strongly hindered, but curvilinear motion is nearly free. Therefore the chains will predominantly move curvilinearly, which is called reptation. Our task here is to see whether and how this simple picture can be transferred to a microscopic description.

In a microscopic theory any simplification of a complicated many-body problem will come from a symmetry property of the Hamiltonian. If we consider it in this way, the essential idea of the tube model may also be formulated as follows: the energy of interaction between the test chain and its environment (the tube in the tube model) is invariant against curvilinear displacements of the segments of the test chain.

The physical origin of this translational invariance is simple to understand. Let us consider the energy of interaction for two chains alone. For the model of short-ranged forces (on the length scale of coarse-grained-segment coordinates) interaction means that the chains are in contact. Then the energy of interaction is a constant times the number of contacts. Now, if segment s_i, which is in contact with segment s_j, moves curvilinearly, this does

not mean that the contact breaks but only that now another segment s_i' will be in contact with s_j. Thus the number of contacts is conserved and therefore also the energy of interaction. In contrast, a small lateral displacement of s_i will immediately interrupt the contact and therefore lead to a change in the interaction energy. The invariance of the interaction potential against curvilinear displacement is a consequence of the connectedness of the chain, and thus it is a property specific for polymeric liquids.

There are only two effects by which this translational invariance is disturbed, as we will also see below, end effects and curvilinear density fluctuations. If the end segment of chain i moves curvilinearly, there comes no other segment behind, and the contact between i and j may break. Curvilinear density fluctuations mean that there might be more than one segment of chain i at a specific contact point. Then this contact has to be counted as two. If one of these segments moves curvilinearly, the contact is preserved, but the strength of contact and therefore the interaction energy may change. But these two effects may be considered as of minor importance and neglected or treated as perturbations. We now want to make these ideas concrete. Since the connectedness of the chains is essential for these considerations, it is here appropriate to work with the continuous chain model.

By definition, curvilinear motion means displacement of segments parallel to the local tangent vector of the chain. The tangent vector of a space curve $\mathbf{r}(s_i)$ is

$$\hat{\mathbf{t}}(s_i) = \frac{\mathrm{d}\mathbf{r}(s_i)}{\mathrm{d}l(s_i)}, \quad |\hat{\mathbf{t}}(s_i)| = 1 \tag{4.1}$$

where $l(s_i)$ is the contour length of segment s_i, measured from $\mathbf{r}_i^0 = \mathbf{r}(s_i=0)$, e.g.

$$l(s_i) = \int_0^{s_i} \mathrm{d}s_i' \left|\frac{\mathrm{d}\mathbf{r}(s_i')}{\mathrm{d}s_i'}\right| \tag{4.2}$$

In terms of contour length and tangent vectors, the chain configuration may also be specified as

$$\mathbf{r}(s_i) = \mathbf{r}_i^0 + \int_0^{l(s_i)} \mathrm{d}l_i' \, \hat{\mathbf{t}}(l_i') \tag{4.3}$$

or

$$\mathbf{r}(s_i) = \int_{L_i^1}^{L_i^2} \mathrm{d}l_i \, \delta(l_i - l(s_i)) \, \mathbf{r}(l_i) \tag{4.4}$$

where $L_i^1 = l(-L^0/2)$ and $L_i^2 = l(L^0/2)$ are contour lengths of the two end segments measured from the mid of the chain, and

$$\mathbf{r}(l_i) = \mathbf{r}_i^0 + \int_0^{l_i} \mathrm{d}l_i' \, \hat{\mathbf{t}}(l_i') \tag{4.5}$$

There is an essential difference between the coordinates $\mathbf{r}(s_i)$ and $\mathbf{r}(l_i)$. $\mathbf{r}(s_i)$ still keeps track of the individual segments. In contrast, $\mathbf{r}(l_i)$ just describes the location of a certain length element of the space curve, irrespective of which segment occupies this length element at a certain moment. Since our discussion above shows that the interaction of two chains should be independent of the question of which specific segments are in interaction, we suppose that $\mathbf{r}(l_i)$ is the appropriate variable to formulate the law of interaction. In Fourier representation the interaction term in (2.1a) is

$$U_{ij}^{\mathrm{ev}} = \frac{v_0 k_B T}{(2\pi)^3} \int' \mathrm{d}^3q \, \frac{1}{b^2} \int_{-L^0/2}^{L^0/2} \mathrm{d}s_i \int_{-L^0/2}^{L^0/2} \mathrm{d}s_j \times \exp[-i\mathbf{q}\cdot(\mathbf{r}(s_i) - \mathbf{r}(s_j))] \tag{4.6}$$

Now, instead of s_i, we may consider $l(s_i)$ as the integration variable. Then the potential is written as

$$U_{ij}^{\mathrm{ev}} = \frac{v_0 k_B T}{(2\pi)^3} \int' \mathrm{d}^3q \, \frac{1}{b^2} \int_{L_i^1}^{L_i^2} \mathrm{d}l_i \int_{L_j^1}^{L_j^2} \mathrm{d}l_j \, \dot{s}(l_i) \, \dot{s}(l_j) \times \exp[-i\mathbf{q}\cdot(\mathbf{r}(l_i) - \mathbf{r}(l_j))] \tag{4.7}$$

The $\dot{s}_i(l_i)$ are curvilinear segment densities:

$$\dot{s}(l_i) = \mathrm{d}s(l_i)/\mathrm{d}l_i \tag{4.8}$$

where $s(l_i)$ is the inverse of $l(s_i)$. From eq 4.7 we see explicitly that the interaction potential depends on (a) the contour length of the end segments, L_i^1 and L_i^2, (b) curvilinear density fluctuations $\dot{s}(l_i)$, and (c) the space curve $\mathbf{r}(l_i)$, which describes the topological structure of the chain. The essential difference between these types of degrees of freedom is that contour length fluctuations and curvilinear density fluctuations can be expanded around their average values, whereas for the topological structure of the chains there exists no average configuration.

With use of the transformation rules (4.3)–(4.5), the tangential component of the excluded volume force on a segment is

$$-\hat{\mathbf{t}}(s_i)\cdot\frac{\delta}{\delta\mathbf{r}(s_i)} U^{\mathrm{ev}} = -\frac{\delta}{\delta l(s_i)} U^{\mathrm{ev}} \tag{4.9}$$

If we neglect the modification of the interaction law (4.7) by curvilinear density fluctuations, the excluded volume potential depends on the contour length only via the dependence of the integrals in (4.7) on L_i^1 and L_i^2, i.e., via interactions at the end segments of the chains. Only here does the excluded volume force have parallel components. In the long-chain limit such interactions will seldom occur, compared to the probability of interactions of the inner segments. If we neglect such end effects, the tangential component of the excluded volume force would be zero:

$$-\hat{\mathbf{t}}(s_i)\cdot\frac{\delta}{\delta\mathbf{r}(s_i)} U^{\mathrm{ev}} = 0 \tag{4.10}$$

In this approximation only intramolecular elastic forces and forces from the microscopic degrees of freedom act on the curvilinear motion of the chain segments. For the continuous chain model the elastic force ($\mathbf{F}_{\mathrm{el}}$) on a segment is

$$\mathbf{F}_{\mathrm{el}}(s_i) = 3k_B T \frac{\mathrm{d}^2\mathbf{r}(s_i)}{\mathrm{d}s_i^2} \tag{4.11}$$

which can be decomposed as

$$\mathbf{F}_{\mathrm{el}}(s_i) = 3k_B T \frac{\mathrm{d}^2 l(s_i)}{\mathrm{d}s_i^2} \hat{\mathbf{t}}(s_i) + 3k_B T(\dot{s}(l_i))^{-2} \frac{\mathrm{d}^2\mathbf{r}(l_i)}{\mathrm{d}l_i^2}\bigg|_{l_i=l(s_i)} \tag{4.12}$$

The second term here is perpendicular to the chain axis, since

$$\hat{\mathbf{t}}(l_i)\cdot\frac{\mathrm{d}^2\mathbf{r}(l_i)}{\mathrm{d}l_i^2} = \hat{\mathbf{t}}(l_i)\cdot\frac{\mathrm{d}\hat{\mathbf{t}}(l_i)}{\mathrm{d}l_i} = \frac{1}{2}\frac{\mathrm{d}}{\mathrm{d}l_i}\hat{\mathbf{t}}(l_i)^2 = 0$$

Then the tangential component of the equation of motion is

$$\frac{m}{b}\hat{\mathbf{t}}(s_i,t)\cdot\frac{\mathrm{d}\mathbf{v}(s_i,t)}{\mathrm{d}t} = 3k_B T \frac{\mathrm{d}^2 l(s_i,t)}{\mathrm{d}s_i^2} + \hat{\mathbf{t}}(s_i,t)\cdot\mathbf{F}_{\mathrm{mic}}(s_i,t) \tag{4.13}$$

Applying the projection operator technique, explained in the last section, the term in (4.13) that results from the microscopic degrees of freedom is easily decomposed in a

friction term and a random force term. Here we project only on curvilinear velocities

$$v^{\parallel}(s_i) = \hat{\mathbf{t}}(s_i)\cdot\mathbf{v}(s_i) \tag{4.14}$$

and obtain the obvious result

$$m\hat{\mathbf{t}}(s_i,t)\cdot\frac{\mathrm{d}}{\mathrm{d}t}\,\mathbf{v}(s_i,t) = \frac{3k_BT}{b}\,\frac{\mathrm{d}^2l(s_i,t)}{\mathrm{d}s_i^2} - \zeta^0 v^{\parallel}(s_i,t) + f_0^{\parallel}(s_i,t) \tag{4.15}$$

where

$$\langle f_0^{\parallel}(s_i,t)\, f_0^{\parallel}(s'_j,t')\rangle = 2k_BT\zeta^0\delta_{s_i,s'_j}\,\delta(t-t') \tag{4.16}$$

If we neglect the acceleration term, the equation for curvilineat motion is

$$v^{\parallel}(s_i,t) = \frac{1}{\zeta^0}\left[\,3k_BT\,\frac{\mathrm{d}^2l(s_i,t)}{\mathrm{d}s_i^2} + f_0^{\parallel}(s_i,t)\,\right] \tag{4.17}$$

Unfortunately, $v^{\parallel}(s_i,t)$ is not just $\mathrm{d}l(s_i,t)/\mathrm{d}t$, and it is not possible to write a closed equation for curvilinear motion of the individual segments. $l(s_i,t)$ couples to $\mathbf{r}(l_i,t)$ and by this to the lateral velocity

$$\mathbf{v}^{\perp}(s_i,t) = (1 - \hat{\mathbf{t}}(s_i,t)\,\hat{\mathbf{t}}(s_i,t))\cdot\mathbf{v}(s_i,t) \tag{4.18}$$

But if we consider the total curvilinear velocity of the chain, defined as

$$v_i^{\parallel}(t) = \frac{1}{L^0}\int_{-L^0/2}^{L^0/2}\mathrm{d}s_i\; v^{\parallel}(s_i) \tag{4.19}$$

we find that it is not influenced by such a coupling to lateral degrees of freedom. From eq 4.17 and 4.18

$$v_i^{\parallel}(t) = \frac{1}{\zeta^0}\,f_{i0}^{\parallel}(t) \tag{4.20}$$

where

$$\langle f_{i0}^{\parallel}(t)\, f_{j0}^{\parallel}(t')\rangle = \frac{2k_BT\,\zeta^0}{n}\,\delta_{ij}\,\delta(t-t') \tag{4.21}$$

Neglecting excluded volume interactions at the ends and curvilinear density fluctuations, $v_i^{\parallel}(t)$ depends only on the stochastic forces of the microscopic degrees of freedom!

Now let us consider the lateral component of the equation of motion. With eq 4.12

$$m(1 - \hat{\mathbf{t}}(s_i,t)\,\hat{\mathbf{t}}(s_i,t))\cdot\frac{\mathrm{d}}{\mathrm{d}t}\,\mathbf{v}(s_i,t) = \frac{3k_BT}{b}(\dot{s}(l_i))^{-2}\left.\frac{\mathrm{d}^2\mathbf{r}(l_i,t)}{\mathrm{d}l_i^2}\right|_{l_i=l(s_i)} + \mathbf{F}^{\perp}{}_{\mathrm{ev}}(s_i,t) + \mathbf{F}^{\perp}{}_{\mathrm{mic}}(s_i,t) \tag{4.22}$$

In analogy to eq 4.19, we define the total lateral velocity of a chain as

$$\mathbf{v}_i^{\perp}(t) = \frac{1}{L^0}\int_{-L^0/2}^{L^0/2}\mathrm{d}s_i\;\mathbf{v}^{\perp}(s_i,t) \tag{4.23}$$

Integrating the equation of motion (4.22) over all chain elements, this becomes

$$\frac{m}{L^0}\int_{-L^0/2}^{L^0/2}\mathrm{d}s_i\;(1 - \hat{\mathbf{t}}(s_i,t)\,\hat{\mathbf{t}}(s_i,t))\cdot\frac{\mathrm{d}}{\mathrm{d}t}\,\mathbf{v}(s_i,t) = \frac{3k_BT}{b}\int_{L_i^1}^{L_i^2}\mathrm{d}l_i\;(\dot{s}_i(l_i))^{-1}\,\frac{\mathrm{d}^2\mathbf{r}(l_i,t)}{\mathrm{d}l_i^2} + \frac{1}{L^0}\int_{-L^0/2}^{L^0/2}\mathrm{d}s_i\;(\mathbf{F}^{\perp}{}_{\mathrm{ev}}(s_i,t) + \mathbf{F}^{\perp}{}_{\mathrm{mic}}(s_i,t)) \tag{4.24}$$

Neglecting again curvilinear density fluctuations, i.e., setting $\dot{s}(l_i) = 1$, the elastic force term in (4.24) vanishes. To decompose the remaining force terms in a systematic and a random part, again the projection operator method is used. Here a projector on $\mathbf{v}_i^{\perp}$ is sufficient:

$$\hat{P}Y = \frac{3}{2}\,\frac{nm}{k_BT}\,\mathbf{v}_i^{\perp}\cdot\langle\mathbf{v}_i^{\perp}Y\rangle \tag{4.25}$$

Then, following the procedure outlined in section 2:

$$\frac{1}{L^0}\int_{-L^0/2}^{L^0/2}\mathrm{d}s_i\;(\mathbf{F}^{\perp}{}_{\mathrm{ev}}(s_i,t) + \mathbf{F}^{\perp}{}_{\mathrm{mic}}(s_i,t)) = \mathbf{f}_i^{\perp}(t) - \frac{3}{2}\,\frac{nm}{k_BT}\int_0^t\mathrm{d}t'\;\mathbf{v}_i^{\perp}(t-t')\cdot\langle\mathbf{v}_i^{\perp}(0)\;\hat{L}\;\mathbf{f}_i^{\perp}(t')\rangle \tag{4.26}$$

where

$$\mathbf{f}_i^{\perp}(t) = e^{-\hat{Q}\hat{L}t}\frac{1}{L^0}\int_{-L^0/2}^{L^0/2}\mathrm{d}s_i\;(\mathbf{F}^{\perp}{}_{\mathrm{ev}}(s_i) + \mathbf{F}^{\perp}{}_{\mathrm{mic}}(s_i)) \tag{4.27}$$

Because of the hermitean properties of the scalar product

$$\langle\mathbf{v}_i^{\perp}(0)\;\hat{L}\;\mathbf{f}_i^{\perp}(t')\rangle = -\langle\mathbf{f}_i^{\perp}(t')\;\hat{L}\;\mathbf{v}_i^{\perp}(0)\rangle$$

and with use of the Liouvillean (2.3)

$$\hat{L}\mathbf{v}_i^{\perp} = \frac{1}{mL^0}\int_{-L^0/2}^{L^0/2}\mathrm{d}s_i\;(3k_BT(\dot{s}(l_i))^{-2}\left.\frac{\mathrm{d}^2\mathbf{r}(l_i)}{\mathrm{d}l_i^2}\right|_{l_i=l(s_i)} + \mathbf{F}^{\perp}{}_{\mathrm{ev}}(s_i) + \mathbf{F}^{\perp}{}_{\mathrm{mic}}(s_i) + \mathbf{v}^{\perp}(s_i)\cdot\hat{\mathbf{L}}(\hat{\mathbf{t}}(s_i)\,\hat{\mathbf{t}}(s_i)) \tag{4.28}$$

If we set $\dot{s}(l_i) = 1$, the elastic force term is again zero. The last term on the right-hand side is an inertial force that results from the time-dependent coordinate system. Since we assume that the system is overdampled, we neglect this inertial term. By the same reasoning, we also neglect the acceleration term, and we invoke the time scale separation hypothesis with respect to microscopic and coarse-grained degrees of freedom. Then

$$\zeta_0\,\mathbf{v}_i^{\perp}(t) + {}^3\!/_2\int_0^t\mathrm{d}t'\;\Delta\zeta^{\perp}(t-t')\;\mathbf{v}_i^{\perp}(t') = \mathbf{f}_i^{\perp}(t) \tag{4.29}$$

where

$$\langle\mathbf{f}_i^{\perp}(t)\;\mathbf{f}_j^{\perp}(0)\rangle = \frac{2}{3}\,\frac{2k_BT\,\zeta_0}{n}\,\delta(t)\,\delta_{ij}\mathbf{1} + \frac{k_BT}{n}\,\Delta\zeta^{\perp}(t)\,\mathbf{1} \tag{4.30}$$

$$\Delta\zeta^{\perp}(t) = {}^1\!/_3\beta\langle\mathbf{F}^{\perp}{}_{\mathrm{ev}}(s_i)\cdot e^{-\hat{Q}\hat{L}t}\,\mathbf{F}^{\perp}{}_{\mathrm{ev}}(s_i)\rangle \tag{4.31}$$

for arbitrary s_i. The explicit expression for $\Delta\zeta^{\perp}(t)$ will be explained in the next section.

The velocity of a segment s_i is now decomposed as

$$\mathbf{v}(s_i,t) = v_i^{\parallel}(t)\;\hat{\mathbf{t}}(s_i,t) + \mathbf{v}_i^{\perp}(t) + \Delta\mathbf{v}_i(s_i,t) \tag{4.32}$$

where $\Delta\mathbf{v}(s_i,t)$ is the deviation of the velocity of the segment from the total curvilinear and lateral velocity of the chain.

The velocity autocorrelation function is now factorized as

$$\langle\mathbf{v}(s_i,t)\cdot\mathbf{v}(s_i,0)\rangle = \langle\mathbf{v}_i^{\parallel}(t)\;\mathbf{v}_i^{\parallel}(0)\rangle + \langle\mathbf{v}_i^{\perp}(t)\cdot\mathbf{v}_i^{\perp}(0)\rangle + \langle\Delta\mathbf{v}_i(s_i,t)\cdot\Delta\mathbf{v}(s_i,0)\rangle \tag{4.33}$$

Whereas the separation of the curvilinear velocity component is a consequence of eq 4.20 and 4.21, the factorization of the lateral component and of $\Delta\mathbf{v}(s_i,t)$ is less stringent, since here similar terms like the inertial force term in eq 4.28 in principle lead to nonvanishing cross terms. The discussion of such coupling terms is out of the scope of this article, and therefore we will take eq 4.33 simply as an approximation. Then the mean-square displacement of a segment has three contributions:

$$W(t) = \frac{1}{6}\langle(\mathbf{r}(s_i,t) - \mathbf{r}(s_i,0))^2\rangle = \frac{1}{3}\int_0^t dt'\,(t-t') \times \langle \mathbf{v}(s_i,t')\cdot\mathbf{v}(s_i,0)\rangle \cong W^{\parallel}(t) + W^{\perp}(t) + W^{\mathrm{int}}(t) \quad (4.34)$$

where

$$W^{\parallel}(t) = \frac{1}{3}\int_0^t dt'\,(t-t')\langle \mathbf{v}_i^{\parallel}(t')\,\mathbf{v}_i^{\parallel}(0)\rangle = \frac{1}{3}\frac{k_BT}{n\zeta^0}t = \frac{1}{3}D^{\mathrm{R}}t = D^{\parallel}t \quad (4.35)$$

$D^{\mathrm{R}} = k_BT/(n\zeta^0)$ being a generalized Rouse diffusion coefficient, which is independent of long-range topological effects but may depend on concentration via the effective segment friction coefficient ζ^0. $W^{\perp}(t)$ and $W^{\mathrm{int}}(t)$ are defined by similar Kubo formulas corresponding to those for $W(t)$ or $W^{\parallel}(t)$, respectively.

Although the decomposition (4.35) in general is only an approximation, it seems worthwhile to note that this becomes correct at least for the Rouse model, where from eq 4.29 we obtain $W^{\perp}(t) = {}^2/_3D^{\mathrm{R}}t$ and $W(t) = D^{\mathrm{R}}t + W^{\mathrm{int}}(t)$. Equations 4.34 and 4.35 seem to suggest the inequality

$$W(t) \geq \frac{1}{3}D^{\mathrm{R}}t \quad (4.36)$$

which cannot be correct since it is well-known that in entangled polymeric liquids for long times $W(t) \sim D^{\mathrm{R}}/nt \ll {}^1/_3D^{\mathrm{R}}t$! The explanation of this apparent discrepancy lies in the total neglect of tangential excluded volume forces, eq 4.10. The equation of motion 4.20 and eq 4.35 are consequences of this. The justification for this step was the observation that for long chains interactions at the ends of the chain, which are mainly responsible for tangential force components, are seldom compared to interactions of the inner segments. If we characterize this by two collision times $\tau^{\parallel}$ and $\tau^{\perp}$, the assumption reads $\tau^{\parallel} \gg \tau^{\perp}$. But even if such end interactions seldom occur, for times larger than $\tau^{\parallel}$ they will happen, and this will lead to a reduction of $W^{\parallel}(t)$, compared to $D^{\parallel}t$, and then also to a further reduction of $W(t)$. The results of this section should be considered as valid only for $t \lesssim \tau^{\parallel}$!

For times larger than the lateral collision time we can expect that $W^{\perp}(t)$ follows a diffusion law, which defines a lateral diffusion coefficient $D^{\perp}$:

$$W^{\perp}(t) = D^{\perp}t, \quad \tau^{\perp} \lesssim t \lesssim \tau^{\parallel} \quad (4.37)$$

In a Gaussian approximation the segment propagator (3.15) becomes

$$G(q,t) = \exp(-W(t)q^2t) \quad (4.38)$$

For the time regime under discussion this is

$$G(q,t) = e^{-(D^{\parallel}+D^{\perp})q^2t}e^{-W^{\mathrm{int}}(t)q^2}, \quad \tau^{\perp} \lesssim t \lesssim \tau^{\parallel} \quad (4.39)$$

We assume that this time regime brings the main contribution to the relaxation of the entanglement friction function. Then $\Delta\zeta(t)$ is also decomposed as

$$\Delta\zeta(t) = \Delta\zeta^{\mathrm{int}}(t) + \Delta\zeta^{\mathrm{com}}(t) \quad (4.40)$$

where

$$\Delta\zeta^{\mathrm{com}}(t) = \frac{4k_BT\psi}{3n}\frac{v_0}{(2\pi)^3}\int' d^3q\; q^2 \exp(-2(D^{\parallel}+D^{\perp})q^2t) \quad (4.41)$$

$$\Delta\zeta^{\mathrm{int}}(t) = \frac{4k_BT\psi}{3n}\frac{v_0}{(2\pi)^3}\int' d^3q\; q^2 \exp(-2(D^{\parallel}+D^{\perp})q^2t) \times (e^{-2W^{\mathrm{int}}(t)q^2} - 1) \quad (4.42)$$

$\Delta\zeta^{\mathrm{com}}(t)$ gives the relaxation of the entanglement effect solely by center of mass motion; $\Delta\zeta^{\mathrm{int}}(t)$ depends also on relaxation by internal motions of the chains. One can suppose that the latter mechanism is less effective than the first one since, if the centers of mass of two interacting chains would be pinned down, the two segments interacting at $t = 0$ could never separate completely and the force autocorrelation function could not decay to zero. Also the molecular weight dependence of $\Delta\zeta^{\mathrm{int}}(t)$ should be much weaker, compared to the center of mass term $\Delta\zeta^{\mathrm{com}}(t)$. This assumption can be supported by inserting the results of the Rouse model for noninteracting chains in eq 4.42. Here $D^{\parallel} \sim D^{\perp} \sim n^{-1}$. For intermediate times $W^{\mathrm{int}}(t) \sim (t)^{1/2}$, independent of n,[24] whereas for large times $W^{\mathrm{int}}(t)$ becomes constant, $\lim^{t\to\infty} W^{\mathrm{int}}(t) \sim n$. This may be described by a scaling ansatz:

$$W^{\mathrm{int}}(t) = nh(t/n^2) \quad (4.43)$$

with $h(\tau) \sim \tau$ for small τ and $h(\tau)$ is constant for large τ. Then we obtain

$$\Delta\zeta^{\mathrm{int}}(t) \sim n^{-5/2}\tau^{-5/2}\int_0^{(\alpha\tau n)^{1/2}q_c} dx\; x^4\, e^{-2x^2}\left(1 - \exp\left(-\frac{2}{\alpha}x^2\,\frac{h(\tau)}{\tau}\right)\right) \quad (4.44)$$

where $\alpha = k_BT/\zeta^0$ and $\tau = t/n^2$. For not too small times we can set the upper limit of the integral to infinity (nq_c^2 will always be large!), and therefore

$$\Delta\zeta^{\mathrm{int}}(t) \sim n^{-5/2}\tau^{-5/2}\,I(\tau) \quad (4.45)$$

If we take the time integral of the friction function, which alone will be needed for the long-wavelength modes, then

$$\int_0^{\infty} dt\;\Delta\zeta^{\mathrm{int}}(t) \sim n^{-1/2} \quad (4.46)$$

for large n. In contrast, the time integral of $\Delta\zeta^{\mathrm{com}}(t)$ will be found to be $\sim n$ for large n. Of course, this is only an estimate of $\Delta\zeta^{\mathrm{int}}(t)$ since for an actual calculation we would need $W^{\mathrm{int}}(t)$ for the system of interacting chains. But we take the result of (4.46) as a justification to neglect $\Delta\zeta^{\mathrm{int}}$ in the following. Then the entanglement friction function is finally

$$\Delta\zeta(t) = \frac{4k_BT\psi}{3n}\frac{v_0}{(2\pi)^3}\int' d^3q\; q^2 \exp(-2(D^{\parallel}+D^{\perp})q^2t) \quad (4.47)$$

Because of the q^2 factor in the integrand the short-wavelength modes are heavily weighted in this expression, and the characteristic time for the relaxation of the entanglement friction function is found to be $\tau^e = [(D^{\parallel}+D^{\perp})q_c^2]^{-1} \sim nv_0^{2/3}$. This is the time that the center of mass of a Rouse chain needs to diffuse over a distance of the range of the interaction potential. It is a short time, since the range of the interaction potential is assumed to be very small, but nevertheless a time that depends on global chain properties since it is governed by center of mass motion. The explicit appearance of the range of the interaction potential in τ^e might seem to be contrary to our basic assumption that this is an unimportant length—which only justifies the use of the Edwards Hamiltonian. But we will see that the time integral over the friction function is indeed independent of q_c, and only the time integral is needed for the long-wavelength modes, which determine the macroscopic properties of the system.

The only problem left now is the determination of the lateral diffusion coefficient.

5. Reptation Transition

The lateral diffusion coefficient, defined in eq 4.37, can be expressed formally by the Kubo relation

$$D^{\perp} = \frac{1}{3}\int_0^{\infty} dt\ \langle \mathbf{v}_i^{\perp}(t)\cdot\mathbf{v}_i^{\perp}(0)\rangle \tag{5.1}$$

The equation of motion for $\mathbf{v}_i^{\perp}(t)$, (4.29), can be transformed into an integral equation for the velocity autocorrelation function:

$$\zeta^0\langle \mathbf{v}_i^{\perp}(t)\cdot\mathbf{v}_i^{\perp}(0)\rangle + \frac{3}{2}\int_0^t dt'\ \Delta\zeta^{\perp}(t-t')\langle \mathbf{v}_i^{\perp}(t')\cdot\mathbf{v}_i^{\perp}(0)\rangle = \frac{4k_BT}{n}\,\delta(t)\,\Theta(t) \tag{5.2}$$

Then $D^{\perp}$ is

$$D^{\perp} = \frac{\frac{2}{3}k_BT}{n\left[\zeta^0 + \frac{3}{2}\int_0^{\infty} dt\ \Delta\zeta^{\perp}(t)\right]} \tag{5.3}$$

When we now evaluate the lateral friction function $\Delta\zeta^{\perp}(t)$, eq 4.31, we closely follow the steps that led us from eq 3.2 over to eq 3.17 and finally to eq 4.47 for the full entanglement friction function. An additional complication arises since the lateral force component, which in Fourier representation is

$$\mathbf{F}^{\perp}{}_{ev}(s_i) = k_BT\frac{v_0}{(2\pi)^3}\int' d^3q\ i\mathbf{q}\cdot(1 - \hat{\mathbf{t}}(s_i)\,\hat{\mathbf{t}}(s_i))e^{-i\mathbf{q}\cdot\mathbf{r}(s_i)}\,c(-\mathbf{q}) \tag{5.4}$$

depends also on the orientation of the segment s_i. This leads to an additional relaxation mechanism. To avoid this complication, we make the plausible assumptions that reorientation of the coarse-grained segments is much slower than relaxation by spatial separation of the two interacting segments. Also, there should be no correlation between a tangent vector $\hat{\mathbf{t}}(s_i)$ of segment s_i and the distance vector $\mathbf{r}(s_j) - \mathbf{r}(s_i)$ of the interacting segments s_i and s_j. $\Delta\zeta^{\perp}(t)$ then becomes in analogy to eq 3.17

$$\Delta\zeta^{\perp}(t) = \frac{4}{3}k_BT\frac{\psi}{n}\frac{v_0}{(2\pi)^3}\int' d^3q\ \langle[\mathbf{q}\cdot(1 - \hat{\mathbf{t}}(s_i)\,\hat{\mathbf{t}}(s_i))]^2\rangle \times G^{\perp}(q,t)^2 = \frac{8}{9}k_BT\frac{\psi}{n}\frac{v_0}{(2\pi)^3}\int' d^3q\ q^2\,G^{\perp}(q,t)^2 \tag{5.5}$$

Another difference to the full friction function $\Delta\zeta(t)$ is seen in the appearance of a lateral propagator, $G^{\perp}(q,t)$. The reason for this is that to be consistent with our treatment of the full $G(q,t)$ in the last section, $\Delta\zeta^{\perp}(t)$ should be calculated by neglecting interactions at the end segments of the chains, which leads to independent curvilinear and lateral motion. Then the time evolution operator that determines the dynamics of lateral motion does not contain the curvilinear degrees of freedom at all. In a more formal way this has been explained in ref 15. But the coupling to internal degrees of freedom complicates the matter. Neglecting here again such internal relaxation processes, the requirement of independence from curvilinear motion can be fulfilled by simply setting

$$G^{\perp}(q,t) = e^{-D^{\perp}q^2t}, \quad \tau^{\perp} \lesssim t \lesssim \tau^{\parallel} \tag{5.6}$$

This makes the problem to determine $D^{\perp}$ self-consistently. Performing now the time integral over $\Delta\zeta^{\perp}(t)$, with the help of eq 3.5, we obtain the equation

$$D^{\perp} = \frac{\frac{2}{3}k_BT}{n\left[\zeta^0 + \frac{2}{3}\frac{k_BT}{D^{\perp}}\frac{\psi}{n}\right]} \tag{5.7}$$

with solutions

$$D^{\perp} = \frac{2}{3}\frac{k_BT}{n\zeta^0}(1 - \psi) = \frac{2}{3}D^{R}(1 - \psi), \quad \text{for } \psi < 1$$
$$D^{\perp} = 0, \quad \text{for } \psi \geq 1 \tag{5.8}$$

For $\psi \geq 1$ lateral motion freezes in at times $t \gtrsim \tau^{\perp}$. Of course, for smaller times lateral motion is still possible. Since the parameter ψ is proportional to the mean energy of interaction of one chain, it is convenient to introduce another parameter that measures the mean interaction per segment:[15]

$$\psi = n\frac{\phi c}{4k_BT} \tag{5.9}$$

Then the microscopic definition of ϕ is

$$\phi = Vv_0k_BT\langle\delta(\mathbf{r}(s_i) - \mathbf{r}(s_j))\rangle \tag{5.10}$$

where V is the volume of the system and s_i and s_j are two arbitrary segments in the discrete chain model. Thus ϕ is the mean excluded volume energy between two segments. The result, (5.8), also suggests the introduction of a critical segment number n_c, where the lateral motion freezes in, as

$$\psi = n/n_c \tag{5.11}$$

or

$$n_c = \frac{4k_BT}{\psi c} \tag{5.12}$$

Introducing the parameters ϕ or n_c is a natural step, since one can expect that in the long-chain limit they will depend only on the mean segment concentrations and on temperature but not on molecular weight. Des Cloizeaux's calculations[21] as well as the renormalization group calculations[14] show that this is indeed the case. But the latter results show also explicitely that for shorter chains ϕ and n_c depend on the chain length.

In analogy to the phenomenological description of molecular motions in entangled systems, the vanishing of $D^{\perp}$ for $n = n_c$ was named the reptation transition. Reptation means that a chain moves predominantly by curvilinear motion, only small lateral displacements with a finite amplitude, corresponding to the tube radius, being possible. This is just the result of our equations: undisturbed curvilinear diffusion, eq 4.35, but a limited lateral motion with a vanishing $D^{\perp}$ for $n \geq n_c$, eq 5.8. The tube or reptation model has dominated the literature on the dynamics of polymeric liquids for 1 decade. For the first time it allowed a consistent although not complete understanding of what happens when long entangled polymeric chains move. But despite its wide acceptance and its undoubted success, the critique and the questions about the very existence of a reptative motion never ceased. A number of computer simulations have been performed to clarify this central point,[25-27] but so far no direct verification of reptationlike behavior was obtained. Of course, all these works were plagued by the typical problems of computer experiments: limited number of chains, limited number of segments per chain, limited time resolution due to the finiteness of the simulation box. But with the availability of larger and faster computers confidence in the results of the simulation has grown, and in recent time severe scepticism about the reality of tubes and reptation has been expressed. In fact, the simulations seem to show that the chains move quite as fast in lateral directions as they do in the curvilinear direction.[26,27] Since the theme of this section is reptation and our results indicate that the rep-

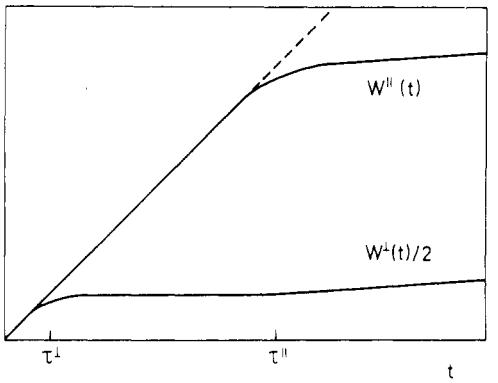

Figure 1. Schematic behavior of curvilinear mean-square displacement $W^{\parallel}(t)$ and lateral mean-square displacement $W^{\perp}(t)$ in the different time regimes defined by collision times $\tau^{\perp}$ and $\tau^{\parallel}$. The broken line indicates undisturbed Rouse evolution.

tation idea has a real basis, it seems necessary to discuss this seeming discrepancy.

Initially the tube model was meant as a simple qualitative description of the motion of chains under entanglement constraints. When the first success of this theory become noted, more and more details were added and the idea developed its own life.

Nowadays one gets the impression that many scientists working in this field consider (or at least they treat) the tube as a real entity with high stability. Such a stability was not attributed to the tube from the beginning. In the paper that initiated this whole field,[5] de Gennes wrote "reptation inside the tube and reorganization of the tube give comparable contributions to the relaxation of entanglements". This is indeed the result of the theory presented here, as can be seen best in eq 3.17. The entanglement friction function relaxes by motion of the test chain as well as by the motion of the chain with which it interacts. Therefore we have the factor $G(q,t)^2$. If the chains would have different degrees of polymerization, we could explicitely follow the different contributions. This has been done in ref 15, and it has shown that tube renewal or constraint release processes give a contribution to center of mass motion that is of the same importance as the reptation mechanism. The outcome of these results and the considerations and results presented here in the past two sections suggest that although a reptationlike behavior in the motion of the chains exists, it is a much weaker process than assumed in the tube model. First, reptation can only be clearly defined for what is called the total curvilinear displacement of the chain. On the level of segmental motions, curvilinear motion and lateral motion are always coupled. Second, even this total curvilinear displacement is only reptationlike for times smaller than the characteristic collision time of interactions of the end segments. For times larger than $\tau^{\parallel}$ total curvilinear motion and total lateral motion become coupled by such interactions. This leads to a drastic slowing down of curvilinear motion in the long-time evolution, but it also allows for a slow lateral motion in the form of constraint release processes. Figure 1 gives a schematic sketch of these conceptions about the behavior of curvilinear and lateral displacement on different time scales.

Therefore is is unlikely that one can identify the reptation process by looking at the motion of single segments.[27] Therefore, also, I do not use this concept directly to describe the dynamics of segments or of normal modes of the chains, but only for the determination of the entanglement friction function. The entanglement friction function should be sensitive to center of mass motion, since this is the only truly global mode of the chains, and during the time span $\tau^{\perp} \ll t \ll \tau^{\parallel}$ center of mass motion is decoupled in curvilinear and lateral motion. So the main speculations in this theory are the assumption of widely separated collisions times, $\tau^{\perp} \ll \tau^{\parallel}$, and the assumption that the entanglement friction function relaxes on the time scale in between, $\tau^{\perp} \ll \tau^{e} \ll \tau^{\perp}$. To show that these ideas lead to consistent results let me present here shortly the result for the self-diffusion coefficient. This has been published before,[13] but it might also be obtained here directly from the generalized Rouse equation, (3.18), by summing first over all segments to obtain the center of mass mode and then using the result for $\Delta\zeta(t)$, eq 4.47 and 5.8. Then

$$D_s = D^R\left(1 - \frac{2}{3}\frac{n}{n_c}\right) = D^{\parallel} + D^{\perp}, \quad \text{for } n \le n_c$$

$$D_s = \frac{D^R}{1 + 2n/n_c}, \quad \text{for } n \ge n_c \tag{5.13}$$

This result can be understood in the following way. Before the reptation transition, the entanglement friction function relaxes fast by lateral motion. Then collisions of the end segments are unimportant, and curvilinear motion and lateral motion are uncoupled. Therefore for $n \le n_c$, center of mass diffusion is just the independent superposition of undisturbed curvilinear motion and strongly interaction dependent lateral motion. But when for $n \ge n_c$ lateral motion freezes in, the only relaxation mechanism left over for the entanglement friction function is by curvilinear motion. Since this is a very slow process (only the end segments are effective) entanglement friction becomes now very large with increasing chain length and leads to a drastic reduction in self-diffusion, $D_s \sim n^{-2}$.

6. Spectrum of the Generalized Rouse Modes

The generalized Rouse equations, (3.18), are easily transformed to normal modes by using standard techniques.[10,22,28] The result is

$$\dot{\mathbf{X}}_p(t) = -\nu_p^0 \zeta^0 \int_0^t dt' \, \mu(t - t') \, \mathbf{X}_p(t') + \mathbf{g}_p(t) \tag{6.1}$$

which may be formally solved as

$$\mathbf{X}_p(t) = R_p(t) \, \mathbf{X}_p(0) + \int_0^t dt' \, R_p(t - t') \, \mathbf{g}_p(t') \tag{6.2}$$

The relaxation function for the pth normal mode is obtained from

$$\dot{R}_p(t) = -\nu_p^0 \zeta^0 \int_0^t dt' \, \mu(t - t') \, R_p(t') \tag{6.3}$$

with $R_p(0) = 1$. ν_p^0 is the undisturbed relaxation frequency:

$$\nu_p^0 = \frac{3\pi^2 k_B T}{n^2 \zeta^0 b^2} p^2, \qquad p = 1, 2, \ldots, n \tag{6.4}$$

The dynamic mobility was related to the entanglement friction function by eq 3.19, and the latter can now be expressed as

$$\Delta\zeta(t) = 4\frac{k_B T}{n_c} q_c^2 \int_0^1 dy \, y^4 \exp(-ty^2/\tau^e) = 2\pi^{1/2} \frac{k_B T}{n_c} q_c^2 (\tau^e)^{5/2} \frac{d^2}{dt^2} t^{-1/2} \operatorname{erf}(t/\tau^e) \tag{6.5}$$

erf (x) is the error function.[29] The characteristic relaxation time of the entanglement friction function is

$$\tau^e = \frac{n\zeta^0}{2k_BTq_c^2}\left(1 - \frac{2}{3}\frac{n}{n_c}\right)^{-1}, \quad n < n_c$$

$$\tau^e = \frac{3}{2}\frac{n\zeta^0}{k_BTq_c^2}, \quad n \gtrsim n_c \tag{6.6}$$

Because of the molecular-weight dependence of τ^e, $\tau^e = O(n)$, the spectrum of normal modes splits into two branches. The high-frequency spectrum of short-wavelength modes is characterized by an initial exponential decay that ends in a finite plateau value:

$$R_p(t) = e^{-\nu_p t}(1 - R_p^0) + R_p^0, \quad p = n, n-1, \ldots \tag{6.7}$$

Both the renormalized relaxation frequency and the plateau value are determined by the initial value of the entanglement friction function:

$$\nu_p = \nu_p^0 + \Delta\zeta(0)/\zeta^0 \tag{6.8}$$

$$R_p^0 = \frac{1}{\nu_p}\frac{\Delta\zeta(0)}{\zeta^0} \tag{6.9}$$

From eq 6.5

$$\Delta\zeta(0) = \frac{4}{5}\frac{k_BTq_c^2}{n_c} \tag{6.10}$$

depends on temperature, concentration, and the specific nature of the polymer under consideration, but it is independent of the molecular weight. Of course, eq 6.7 can be valid only on a time scale $t \ll \tau^e$. For larger times all the modes will relax to equilibrium. Physically this means that for short times the short-wavelength modes see the entanglements with other chains as rigid constraints. For this time scale the behavior of the system could not be distinguished from that of a permanent network. But for times $\gtrsim\tau^e$ the entanglement constraint relaxes, the segment motion becomes "free", and the short-wavelength normal modes continue to relax. In principle this second stage of the relaxation process has to be determined by solving the integral equation (3.19). But since for the short-wavelength modes the dominant contribution to the relaxation is already obtained from the initial relaxation term, a reasonable representation of the entanglement effect is obtained by the first iteration of (3.19). Then

$$R_p(t) \simeq e^{-\nu_p t}(1 - R_p^0) + \frac{1}{\nu_p\zeta^0}\Delta\zeta(t), \quad p = n, n-1, \ldots \tag{6.11}$$

At the other end of the spectrum, the long-wavelength modes ($p = 1, 2, \ldots$) relax much slower than the entanglement friction function. For this part of the spectrum the generalized Rouse equations take the form of ordinary relaxation equations, with solution

$$R_p(t) = e^{-\nu_p t} \tag{6.12}$$

Here the renormalized relaxation frequencies are

$$\nu_p = \nu_p^0\left[1 + \int_0^\infty dt\ \Delta\zeta(t)/\zeta^0\right]^{-1} \tag{6.13}$$

In the strongly entangled case, where

$$\int_0^\infty dt\ \Delta\zeta(t)/\zeta^0 = 2n/n_c \gg 1$$

$$\nu_p = \nu_p^0\frac{n_c}{2n} \sim n^{-3} \tag{6.14}$$

since $\nu_p^0 \sim n^{-2}$ for the long-wavelength modes. This is the same spectrum that was obtained from Doi and Edwards[9,10] for their primitive chain model, if we would identify tentatively the critical segment number n_c with

$$n_c = \tfrac{2}{3}(a/b)^2 \tag{6.15}$$

Here a is the step length of the primitive chain in the Doi–Edwards model. Note that for a chain in a frozen matrix, which situation is the basis of the Doi–Edwards model, n_c would only be the half. The factor 2 in (6.15) stems from the self-consistent treatment of the motion of all chains in the system.

Both the Rouse-like spectrum at high frequencies as well as the form of the terminal spectrum at low frequencies are in agreement with expectations. It would be more interesting to see in detail how the intermediate modes behave. But here the analytical structure of the equations is complicated, and a numerical solution of the full integral equations (6.3) and (3.19) would be afforded. This will be the subject of following publications, where applications of this theory to diffusion, viscoelastic, and other relaxation problems will be considered. One can easily imagine that these intermediate modes of the spectrum, which produce the plateau in the shear relaxation modulus, should be especially important for systems close to the transition point from nonentangled to entangled behavior. Here they should have an important influence also on stationary transport properties, e.g., the shear viscosity.[30] This aspect is not taken into account by the Doi–Edwards theory.

7. Summary and Discussion

The subject of this work is a microscopic theory of relaxation and diffusion in dense high-molecular-weight polymeric liquids. The result may be characterized as an integration of the traditional entanglement and reptation concepts. The equations that describe the motion of the segments of a test chain are of the type of stochastic retarded Rouse equations, with a dynamic friction function. This friction function is identified as the autocorrelation function of forces, which other chains exert on the test chain, this corresponds to the phenomenological understanding of the entanglement effect. It is most important that entanglement friction is understood as a dynamic effect. This distinguishes the theory from other recent approaches to this subject, where entanglement friction is treated only as a contribution to a static friction coefficient.[31,32] It is also important that we have a clear definition of the dynamic friction function, so that there is no need for an ad hoc ansatz for the friction function, which may be misleading.[12]

The force autocorrelation function is simplified by a number of approximations, but the many-body character of the theory is never violated. An important simplification of the problem arises from the translational invariance of the interaction potential with respect to curvilinear displacements of the chains. This symmetry principle substitutes for the tube model. Disregarding curvilinear segment density fluctuations, only interactions at the ends of a chain violate the translational invariance. The consequences of this translational invariance are discussed in terms of two collision times, $\tau^\perp$ and $\tau^\parallel$. $\tau^\perp$ is the collision time for lateral motions of the chains, and $\tau^\parallel$ for curvilinear motion. In the idealized model of an infinitely long or an infinitely thin chain, $\tau^\parallel$ would be infinite. Then at sufficiently high concentration a complete freezing in of lateral motion would be observed, in agreement with the reptation concept. But for a real chain the ratio L/d is always finite, and therefore $\tau^\parallel$, although large, will also be finite. So the reptation concept cannot be used to describe directly the long-time motion of the polymers. But if we assume that

the characteristic relaxation time of the dynamic friction function τ^e is intermediate between $\tau^\perp$ and $\tau^\parallel$, the reptation concept can be used for the calculation of the entanglement friction function. So the main physical assumption of this theory is stated in the inequality

$$\tau^\perp \ll \tau^e \ll \tau^\parallel$$

Here the assumption $\tau^\perp \ll \tau^\parallel$ is a logical consequence of the interaction potential, but the assumption on τ^e is only a working hypothesis, to obtain a reptationlike theory.

The characterization of this theory as reptationlike does not mean that complete agreement with the results of the phenomenological tube model is obtained. If I use here the work reptation, it does not mean reptation in a frozen matrix but refers to curvilinear motion in a fluctuating surrounding. It is shown that this difference matters. Constraint release processes are found to be as important as curvilinear motion of the test chain. But this is not truly a contradiction to the reptation picture, since these constraint release processes of the test chain are made possible by curvilinear short-time motion of the constraining chains. This becomes explicit in the final form for the entanglement friction function, (4.47). If we set $D^\perp = 0$, one of the two $D^\parallel$ in the exponent of the integrand stems from curvilinear motion of a constraining chain. Constraint release processes would become even more important than reptation in mixtures, when the test chain has a much higher molecular weight than the other chains. A generalization of the theory to mixtures has been given recently for the discussion of center of mass motion.[15]

A convenient simplification of the structure of the force autocorrelation function has been obtained by use of the well-known pseudopotential for the two-segment interaction potential.[10] Since the excluded volume parameter ν_0, which characterizes the strength of the potential, is zero for a Θ system, it follows that the theory presented here cannot be applied to a Θ system. Often is is said that all concentrated solutions and especially melts are Θ systems. So the question might arise whether this theory is applicable at all to concentrated solutions and melts. But such a statement about the Θ-like behavior of concentrated solutions and melts should be formulated much more carefully. All that is observed experimentally is that quantities such as the radius of gyration of a chain behave as they do in a dilute Θ system. From this observation one cannot infer that the repulsive interaction between two segments is zero. Rather one should say that the Θ-like behavior of dense systems is a typical many-body effect. In fact, the vanishing of long-range intrachain excluded volume effects can be systematically derived as a screening effect in the framework of a theory[10,33] that starts from the Edwards Hamiltonian. This is a drastic proof of the suitability of H_E for concentrated solutions and melts.

Another approximation made in this work is much more questionable with respect to application of the theory to concentrated solutions and melts. This is the Rouse approximation for the dynamic friction matrix $\Delta\zeta_{s,s'}(t)$, introduced in section 3. This neglects dynamic force correlations between different pairs of segments of two chains and also correlations that involve more than two chains. The neglect of such highly cooperative correlation seems to be reasonable for semidilute solutions, but with increasing concentration it can not be precluded that such correlations might become more and more important. Especially in a melt close to a glass transition one might expect that such cooperative processes become even dominant. In principle it would be possible to go beyond this Rouse approximation, by using higher order terms of the series that is defined by eq A.15. But this would lead to complicated expressions for the friction matrix, and it would seriously inhibit the tractability of the generalized Langevin equations, (2.36). Therefore for pragmatic reasons it seems better first to use this simple version of the theory and to see how far one can proceed in this way.

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Appendix

Let us consider here first the meaning of the $\hat{Q}$ operator in the time evolution operator of the dynamic friction function $\Delta\zeta_{s,s'}(t)$, eq 3.2. With use of the operator identity

$$e^{-\hat{Q}\hat{L}t} = e^{-(\hat{L}-\hat{P}\hat{L})t} = e^{-\hat{L}t} + \int_0^t dt'\, e^{-\hat{L}(t-t')}\hat{P}\hat{L}e^{-\hat{Q}\hat{L}t'} \tag{A.1}$$

and the definition ((2.10), (2.12), (2.13)) of the projection operator $\hat{P}$, $\Delta\zeta_{s,s'}(t)$ is rewritten as

$$\begin{aligned}\Delta\zeta_{s,s'}(t) = \beta\langle \mathbf{F}_{ev}(s)\, e^{-\hat{L}t}\boldsymbol{F}_{ev}(s')\rangle + m\beta^2 \sum_{s''=1}^{n}\int_0^t dt' \times \\ \langle \mathbf{F}_{ev}(s)\, e^{-\hat{L}(t-t')}\mathbf{v}(s'')\rangle\langle \mathbf{v}(s'')\, \hat{L}e^{-\hat{Q}\hat{L}t'}\mathbf{F}_{ev}(s')\rangle + \\ \sum_{s'',s'''=1}^{n}\int_0^t dt' \times \\ \langle \mathbf{F}_{ev}(s)\, e^{-\hat{L}(t-t')}\mathbf{r}(s'')\rangle\gamma_{s'',s'''}\langle \mathbf{r}(s''')\, \hat{L}e^{-\hat{Q}\hat{L}t'}\mathbf{F}_{ev}(s')\rangle\end{aligned} \tag{A.2}$$

But

$$\langle \mathbf{r}(s'')\hat{L}... = \langle \mathbf{v}(s'')... \tag{A.3}$$

and since the $\hat{Q}$ operator is orthogonal to the velocities of the segments of the test chain and since $\langle \mathbf{v}(s'')\, \mathbf{F}_{ev}(s')\rangle = 0$, due to the statistical independence of the velocities and coordinates, the last term in (A.2) vanishes. With

$$\langle \mathbf{v}(s'')\hat{L}... = \frac{1}{m}\langle \mathbf{F}(s'')... \tag{A.4}$$

eq A.2 is

$$\begin{aligned}\Delta\zeta_{s,s'}(t) = \beta\langle \mathbf{F}_{ev}(s)\, e^{-\hat{L}t}\boldsymbol{F}_{ev}(s')\rangle + \\ \beta^2 \sum_{s''=1}^{n}\int_0^t dt'\, \langle \mathbf{F}_{ev}(s)\, e^{-\hat{L}(t-t')}\mathbf{v}(s'')\rangle\langle \mathbf{F}(s'')\, e^{-\hat{Q}\hat{L}t'}\mathbf{F}_{ev}(s')\rangle\end{aligned} \tag{A.5}$$

Here $\mathbf{F}(s'')$ is the total force on segment s''. This may be decomposed, as in eq 2.23, into an elastic force, an excluded volume force, and forces from microscopic degrees of freedom. In agreement with our previous assumptions we neglect correlations between $\mathbf{F}_{mic}(s'')$ and the excluded volume forces. Further, the elastic force contribution is proportional to the segment coordinates, to which variables the $\hat{Q}$ operator is orthogonal. Therefore

$$\begin{aligned}\langle \mathbf{F}(s'')\, e^{-\hat{Q}\hat{L}t'}\mathbf{F}_{ev}(s')\rangle = \\ \langle \mathbf{F}_{ev}(s'')\, e^{-\hat{Q}\hat{L}t'}\mathbf{F}_{ev}(s')\rangle - \frac{3k_BT}{b^2}\sum_{s'''=1}^{n} A_{s'',s'''}\langle \mathbf{r}(s''')\, \mathbf{F}_{ev}(s')\rangle\end{aligned} \tag{A.6}$$

The static correlation function is zero since we can always set the origin of the coordinate system at the position of segment s'''. So we find finally

$$\begin{aligned}\Delta\zeta_{s,s'}(t) = \beta\langle \mathbf{F}_{ev}(s)\, e^{-\hat{L}t}\boldsymbol{F}_{ev}(s')\rangle + \\ \beta\sum_{s''=1}^{n}\int_0^t dt'\, \langle \mathbf{F}_{ev}(s)\, e^{-\hat{L}(t-t')}\mathbf{v}(s'')\rangle\Delta\zeta_{s'',s'}(t')\end{aligned} \tag{A.7}$$

The advantage here is that the time evolution is defined

in terms of the original Liouville operator. If we insert eq 3.3 for the excluded volume force, we obtain the corresponding integral equation for the dynamic four-point correlation function of variables:

$$c_{s_i}(\mathbf{q}) = \exp[-i\mathbf{q}\cdot\mathbf{r}(s_i)] \tag{A.8}$$

Therefore the quantity that we have to consider next is

$$\langle 4\rangle = \langle c_{s_1}(\mathbf{q})\, c_{s_i}(-\mathbf{q})\, c_{s'_1}(\mathbf{q}',t)\, c_{s'_j}(-\mathbf{q}',t)\rangle \tag{A.9}$$

where

$$c_{s_i}(\mathbf{q},t) = e^{-\hat{L}t} \exp[-i\mathbf{q}\cdot\mathbf{r}(s_i)] \tag{A.10}$$

The time derivative is

$$\frac{\mathrm{d}}{\mathrm{d}t} c_{s_i}(\mathbf{q},t) = -i\mathbf{q}\cdot\mathbf{v}(s_i,t)\, c_{s_i}(\mathbf{q},t) \equiv -i\mathbf{q}\, j_{s_i}(\mathbf{q},t) \tag{A.11}$$

We can now proceed in exactly the same manner as in section 2, where we derived equations for $\mathbf{r}(s,t)$. We define a projection operator that projects on the $c_s(\mathbf{q})$ and $j_s(\mathbf{q})$ of one test chain. The generalized Langevin equations of the form of eq 2.31 and 2.32 result. We then assume that acceleration terms can be neglected and eliminate the $j_s(\mathbf{q},t)$ from the system of equations. The resulting equation for $c_s(\mathbf{q},t)$ can generally be written as

$$\frac{\mathrm{d}}{\mathrm{d}t} c_s(\mathbf{q},t) = -\sum_{s'=1}^{n} \int_0^t \mathrm{d}t'\, K_{s,s'}(\mathbf{q},t-t')c_{s'}(\mathbf{q},t') + d_s(\mathbf{q},t) \tag{A.12}$$

Only the expression for the random force term $d_s(\mathbf{q},t)$ is here interesting. This is

$$d_s(\mathbf{q},t) = -\frac{m}{\mathbf{q}^2 k_B T} \sum_{s',s''=1}^{n} \int_0^t \mathrm{d}t'\, K_{s,s'}(\mathbf{q},t-t')\, C_{s',s''}(\mathbf{q}) \times e^{-\hat{Q}\hat{L}t'}\hat{Q}\hat{L}(-i\mathbf{q}\cdot\mathbf{v}(s'') \exp[-i\mathbf{q}\cdot\mathbf{r}(s'')]) \tag{A.13}$$

where

$$C_{s,s'}(\mathbf{q}) = \langle \exp[-i\mathbf{q}\cdot(\mathbf{r}(s) - \mathbf{r}(s'))]\rangle \tag{A.14}$$

Now eq A.12 can be formally solved as

$$c_s(\mathbf{q},t) = \sum_{s'=1}^{n} R_{s,s'}(\mathbf{q},t)\, c_{s'}(\mathbf{q},0) + \sum_{s'=1}^{n} \int_0^t \mathrm{d}t'\, R_{s,s'}(\mathbf{q},t-t')\, d_{s'}(\mathbf{q},t') \tag{A.15}$$

where the relaxation function $R_{s,s'}(\mathbf{q},t)$ is determined by

$$\frac{\mathrm{d}}{\mathrm{d}t} R_{s,s'}(\mathbf{q},t) = -\sum_{s''=1}^{n} \int_0^t \mathrm{d}t'\, K_{s,s''}(\mathbf{q},t-t')\, R_{s'',s'}(\mathbf{q},t') \tag{A.16}$$

and $R_{s,s'}(\mathbf{q},0) = \delta_{s,s'}$.

Since $d_s(\mathbf{q},t)$ is orthogonal to all $c_{s'}(\mathbf{q},t)$, (A.15) yields also

$$C_{s,s'}(\mathbf{q},t) = \sum_{s''=1}^{n} R_{s,s''}(\mathbf{q},t)\, C_{s'',s'}(\mathbf{q}) \tag{A.17}$$

with

$$C_{s,s'}(\mathbf{q},t) = \langle \exp[-i\mathbf{q}\cdot(\mathbf{r}(s,t) - \mathbf{r}(s',0))]\rangle \tag{A.18}$$

If the operator expression at the right of (A.12) is evaluated (note that $\hat{Q}$ now is defined for variables $c_s(\mathbf{q})$ and $j_s(\mathbf{q})$ and not for $\mathbf{r}(s)$ and $\mathbf{v}(s)$ as in section 2 and at the beginning of this Appendix!), one obtains expressions that depend on random force terms from the microscopic degrees of freedom and again on excluded volume interaction. If inserted in the dynamic four-point correlation function, (A.9), this would yield dynamic six-point correlation functions, etc. So the lowest order mode-coupling approximation consists in neglecting the d term in (A.15):

$$c_s(\mathbf{q},t) \simeq \sum_{s'=1}^{n} R_{s,s'}(\mathbf{q},t)\, c_{s'}(\mathbf{q},0) \tag{A.19}$$

In this approximation the four-point correlation function is

$$\langle 4\rangle = \sum_{s''_1=s''_j=1}^{n} R_{s'_1,s''_1}(\mathbf{q}',t)\, R_{s'_j,s''_j}(\mathbf{q}',t) \times \langle c_{s_1}(\mathbf{q})\, c_{s_i}(-\mathbf{q})\, c_{s''_1}(\mathbf{q}')\, c_{s''_j}(-\mathbf{q}')\rangle \tag{A.20}$$

We have to remember that this expression is used in an integration over $\mathbf{q}$, which affords that the expression is only nonzero when segments s_1 and s_i are in contact. Assuming that such a pair of segments in contact is uncorrelated to the positions of any other segments, we take into account only the term $s_1 = s''_1$ and $s_i = s''_j$ in the sum above. Then

$$\langle 4\rangle = R_{s'_1,s_1}(\mathbf{q}',t)\, R_{s'_i,s_i}(\mathbf{q}',t)\, \delta_{i,j}\langle \exp[-i(\mathbf{q}+\mathbf{q}')\cdot(\mathbf{r}(s_1) - \mathbf{r}(s_i))]\rangle \tag{A.21}$$

(A.21) differs from the expression that we need for eq 3.7 still because of the different time evolution operator $\exp[-\hat{Q}\hat{L}t]$ in (3.7). But if we now insert the approximation (A.19) into the second term in (A.7), it vanishes since

$$\langle c_{s'_1}(\mathbf{q})\, c_{s'_i}(-\mathbf{q})\, \mathbf{v}(s''_1)\rangle = 0$$

So to the lowest order mode-coupling approximation it is allowed to use the full-time evolution operator instead of the projected one, and eq A.21 yields directly eq 3.7.

References and Notes

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