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Projection of the Rouse model onto macroscopic equations of motion for polymers under shear

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Abstract. — A projection operator technique is used to show how the Onsager coefficients among collective polymer variables can be expressed in terms of correlation and response functions. For a collection of noninteracting Rouse polymers, and with no external shear imposed, the matrix of Onsager coefficients is calculated for the collective variables of concentration and stress. By including appropriate convective terms, these Onsager coefficients are used to systematically formulate Langevin equations for concentration and stress variables. Due to memory effects, these equations are non-local in both space and time. Moreover, they can be used to compute the dynamical response functions and the Green functions in the presence of shear flow. The resulting coupled equations for concentration and stress variables turn out to be appropriate generalizations of those obtained from simple phenomenological constitutive equations, such as the upper convected Maxwell model and the second order fluid model.

Introduction.

In recent years a dynamical theory for concentration fluctuations within sheared polymer solutions has been developed by several authors. Helfand and Fredrickson [1] formulated a phenomenological theory where coupled equations of motion for monomer concentration, the velocity field of the solvent, and the deviatoric polymeric stress tensor field were presented. They showed that the coupling between the concentration fluctuations and the stress tensor field is essential in order to explain the anisotropic growth of concentration fluctuations. For this purpose, they added a type of elastic stress-induced diffusion term to the equation of motion for the concentration fluctuations and utilized the so-called second order fluid model [2] as a constitutive equation. A key feature leading to the predicted enhancement of concentration

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fluctuations was the assumed concentration dependence of the viscosity and normal stress coefficients in the constitutive equation. Simultaneously, Onuki [3] presented a theory that could be used to describe polymer dynamics in solution, assuming either Rouse or reptation dynamics depending on the polymer concentration. In this context, he used Marrucci’s constitutive model [4] in which a long lived strain variable is used as an alternative to stress in the second order fluid model. Finally, Milner [5, 6] developed a dynamical theory for entangled polymer solutions. Included among the basic ingredients of his theory was the “two fluid model” put forward by Brochard and de Gennes [7] and discussed later on by Onuki [8] and by Doi and Onuki [17]. By an appropriate generalization of the two mode picture [7], Milner was able to calculate a non equilibrium steady state structure factor in excellent agreement with results obtained by Wu et al. [9] via light scattering experiments.

Common to all these theoretical formulations is a set of coupled equations of motion for slow variables including the concentration fluctuations and the fluctuations of the elastic stress variable. These equations have generally been guessed at, although it was recognized early on [1, 5] that, in principle, they could be projected out from the semi-microscopic Rouse or reptation models. While such a projection technique has the great advantage of yielding the Onsager coefficients unambiguously [5], the procedure was only partially carried out [1, 5]. In particular, previous authors have sidestepped the derivation of the equation of motion for the stress variable, instead utilizing a strictly phenomenological constitutive equation. This is unsatisfying in that the concentration fluctuations and the fluctuations of the stress variable are not treated on the same footing. Hence, the resulting description of polymer solution dynamics does not result from a systematic and consistent chain of approximations. A more satisfying approach would be to project the Rouse model in one step onto coupled Langevin equations for both concentration and stress, and then show in a second step how various phenomenological constitutive equations can be obtained from there. This is the approach adopted in the present paper. Moreover, in the simplified approach used here, we neglect hydrodynamic interactions and treat a polymer solution as a binary polymer blend where the two components have a high and a very low degree of polymerisation. For simplicity, we also neglect interactions between chains, other than their effect on establishing the values of the monomeric friction coefficient and statistical segment length, thus allowing us to focus on the dynamics of a single chain of the high molecular weight species. Random phase approximation techniques, which facilitate corrections for interchain interactions, are discussed briefly at the end of our analysis.

In order to deduce macroscopic equations of motion from the Rouse model, it is necessary to have a method available for calculating the matrix of Onsager coefficients in a systematic fashion. This can be achieved by applying the projection operator technique [11-14] in an unusual way. Originally, the projection operator technique was developed in order to deduce equations of motion for a given set of collective variables, where the microscopic dynamics was assumed to be deterministic (i.e. satisfying the Liouville equation). The quantities characterizing the projected Langevin equations are a frequency matrix and a matrix of memory kernels. The latter quantities have the peculiarity that their dynamical evolution is not governed by the Liouville operator $L$ itself, but by the projected Liouville operator $L_P = (1 - P)L(1 - P)$, where $P$ denotes the projection operator. Since $L_P$ is difficult to handle, it is not easy to derive explicit expressions for the memory kernels. In spite of this traditional perspective on the projection operator technique, one can view the technique differently. As is well known, [13, 14], the Langevin equations (for the collective variables) that arise from the projection operator technique imply certain equations of motion for the dynamical correlation functions, governed again by the frequency matrix and the matrix of memory kernels. If all the collective variables are invariant under time reversal, then the frequency matrix strictly vanishes. In this case, the equations of motion for the dynamical correlation functions can be used to express
the matrix of memory kernels as the matrix of dynamical linear response functions multiplied by the inverse of the matrix of dynamical correlation functions. Furthermore, there is a close connection between the memory kernels and the Onsager coefficients. Since the projection operator technique is traditionally based on a free energy bilinear in the collective variables, the matrix of Onsager coefficients is given by the matrix of memory kernels times the matrix of static correlation functions. Thus, the projection operator technique is a suitable tool for calculating Onsager coefficients. Phrased somewhat differently, the projection operator technique can be applied as a method to determine Onsager coefficients, provided that the static and dynamical correlation functions can be calculated by other means. These statements are strictly valid only if the microscopic dynamics are deterministic and for situations in which the frequency matrix vanishes.

We now discuss the above in the context of the system of interest here, namely a solution of non-interacting polymers, viewed as a binary polymer blend where the two components have a high and very low degree of polymerisation. Assuming at first that the full microscopic dynamics of all the chemical monomers would be taken into account the dynamics would be deterministic characterized by a Liouville operator. At this level of deterministic description one can conclude that the frequency matrix must vanish because both collective fields, the concentration field and the stress tensor field are invariant with respect to time reversal. The Onsager coefficients can then be expressed as mentioned above in terms of static and dynamic correlation functions. These quantities, however, are most conveniently calculated within the semi-microscopical Rouse model. It should be emphasized that the Rouse model is itself a coarse-grained model, where each Kuhnian segment represents 10 to 20 chemical repeat units. The dynamics of the Kuhnian segments are modeled by a Langevin equation describing an overdamped Brownian particle harmonically coupled to next neighbours along the chain in a viscous background, experiencing stochastical forces. Consequently the time evolution is no longer governed by a Liouville operator but by a Fokker-Planck operator. Although Rouse originally assumed that the viscous background is provided by solvent molecules the Rouse model can also be used to describe individual components of a polymer blend assuming that the polymers are not entangled. In this case an individual polymer is than embedded in a viscous background provided by the neighboring polymers. Adopting this point of view the Onsager coefficients of a component of a polymer blend can be calculated in the framework of the Rouse model. And this will be done for the high molecular weight species of the binary blend, which is used by us to mimick for the sake of simplicity the non-interacting polymers in solution. Finally it shall be mentioned that Bixon [15] was the first to use the projection operator technique in the context of polymers. Starting from Kirkwood’s generalized diffusion equation, he explored the theoretical foundation of the Rouse-Zimm model. Zwanzig [16] subsequently generalized Bixon’s approach. In both cases, the goal was to obtain equations of motions for semi-microscopic variables, namely the Rouse modes or the position vectors of Kuhnian segments. The approach that will be taken here is somewhat different. Our starting point is the semi-microscopic Rouse model from which single-chain correlation and response functions can be calculated. Projection operator techniques are then used to deduce larger scale equations for the macroscopic fields of interest. It should be noted that a discussion of the appropriate dynamical operator in the context of the projection operator technique for polymers can be found in Zwanzig’s paper [16]. Finally, we comment that an alternative description of how to calculate Onsager coefficients in polymeric systems was given by Kawasaki and Sekimoto [18, 19]. These authors made a local equilibrium approximation and projected a semi-microscopic Fokker-Planck equation onto a Fokker-Planck equation for the collective density fields. As shall be discussed below, the Kawasaki-Sekimoto approximation recovers a subset of the results obtained for the Rouse model by our more general approach, but fails for
certain collective variables such as the deviatoric stress.

A principal outcome of the present study is a set of explicit expressions for Onsager coefficients in the framework of the Rouse model, where both concentration and stress fluctuations are included as collective variables. Having these transport coefficients in hand, we then construct linear Langevin equations for the concentration and stress dynamics of non-interacting polymer assemblies in the presence of external fields conjugate to the collective variables. A peculiarity of the stress variable, however, is that there is no single relaxation time, but rather a set of relaxation times corresponding to the different Rouse modes. As a result, the stress Langevin equation is not local in time, but contains a memory kernel reflecting the Rouse spectrum. Following this approach, we show explicitly how the semi-microscopic Rouse model in the absence of imposed shear can be mapped onto a coupled set of hydrodynamic equations. All the transport coefficients entering these equations can be obtained in the framework of the Rouse model. While the static correlation functions can be calculated exactly in closed form, the dynamical correlation and response functions of the Rouse model can only be expressed in terms of quadratures for arbitrary wavevectors and frequencies. However, for small wavevectors (i.e., the hydrodynamic regime), simple projected equations result for the collective variables. Our next step is to generalize these equations to incorporate the effects of an externally imposed shear flow. As is well known, shear flow convects as well as rotates Kuhnian segments. By including both effects, we deduce coupled equations of motion for the concentration and stress fluctuations of Rouse polymers under shear. This set of equations can be viewed as a generalization (to arbitrary frequencies and to include spatial inhomogeneities) of certain phenomenological constitutive equations [2]. Explicitly, we show how the upper convected Maxwell model [2], Marrucci's model [4], the Lodge equation [20, 21] equation and the second order fluid model [22] can be deduced on the basis of microscopic calculations.

The present paper is organized as follows: in section 1 we set up the notation and define the collective variables of interest. Section 2 is dedicated to developing the projection operator technique. Explicit expressions for the bare transport coefficients can be found in section 3, while alternative derivations of these coefficients and the local equilibrium approximation are discussed in section 4. Projected hydrodynamic equations in the absence of shear flow can be found in section 5. In section 6, the necessary changes resulting from the imposition of a flow are introduced. Finally, the phenomenological constitutive equations are discussed in section 7. For completeness, we have also included two appendices that describe details of our calculations: Appendix A outlines the calculation of the correlation and response functions in the Rouse model, while Appendix B summarizes a perturbative calculation for small shear rates.

1. Rouse model and collective variables.

In the framework of the Rouse model the dynamics of the position \( r(s, t) \) of a Kuhnian segment at contour position \( s \) is governed by the following Langevin equation:

\[
\partial_t r(s, t) = -\frac{1}{\zeta} \frac{\delta H}{\delta r(s, t)} + \theta_r(s, t) \tag{1}
\]

with the effective Hamiltonian

\[
H = \frac{3k_B T}{2b^2} \int_0^N ds \frac{dr(s, t)}{ds} \frac{dr(s, t)}{ds} \tag{2}
\]

and where \( b, N \) and \( \zeta \) are the segment size, the number of Kuhnian segments per chain, and the friction coefficient. The stochastic velocity \( \theta_r(s, t) \) is modeled as a Gaussian white noise.
with zero mean and characterized by the covariance

\[ < \theta_r(s, t) \theta_r(s', t') > = 2k_B T \zeta^{-1} \delta(s - s') \delta(t - t') \]  

(3)

In order to go from the microscopic description as given by equations (1) and (2) in a systematic way to a macroscopic description, one has to assemble an appropriate set of collective variables. The first collective variable that comes to mind is the density field, which contains information regarding the spatial distribution of the Kuhnian segments. The density fluctuations for a polymeric system prove to be influenced by elastic forces, described by an elastic force field \( F(x, t) \). In the framework of the Rouse model, this field is given by

\[ F(x, t) = \int_0^N ds \delta(x - r(s, t)) \frac{-\delta H}{\delta r(s, t)} \equiv \nabla \cdot \sigma(x, t) \]

where the collective field \( \sigma(x, t) \) denotes the elastic stress tensor

\[ \sigma(x, t) = \int_0^N ds \delta(x - r(s, t)) \frac{3k_B T}{b^2} \frac{dr(s, t)}{ds} \frac{dr(s, t)}{ds} \]  

(4)

associated with an individual polymer. This collective field contains not only information about the position but also concerning the orientation of the Kuhnian segments. The dynamics of the density field and the stress tensor field are not independent from one another. In particular, we shall later show that the equation of motion for the density field contains a term proportional to the divergence of the elastic force field \( F(x, t) \), hence proportional to \( \nabla \nabla : \sigma(x, t) \). One can take advantage of this specific sort of coupling by decomposing the Fourier transform \( \sigma(q, t) \) of the stress tensor into longitudinal and transverse components, \( \sigma^\parallel(q, t) = \hat{q}_\alpha \hat{q}_\beta \sigma_{\alpha\beta}(q, t) \) and \( \sigma^\perp(q, t) = (\delta_{\alpha\beta} - \hat{q}_\alpha \hat{q}_\beta) \sigma_{\alpha\beta}(q, t) \), with \( \hat{q}_\alpha = q_\alpha/q \).

Up to this point, only a single polymer was considered for the sake of simplicity. However, for the case of non-interacting polymers in solution or in melts, the single polymer picture is retained and the collective fields gain a factor of the average polymer concentration:

\[ c(q, t) = \frac{c_0}{N} \int_0^N ds e^{-iq \cdot r(s, t)} - c_0 \delta_{q_0, 0} \]  

(5)

\[ \bar{Q}(q, t) = \frac{c_0}{N} \int_0^N ds e^{-iq \cdot r(s, t)} \left( \frac{3}{b^2} \frac{dr(s, t)}{ds} \frac{dr(s, t)}{ds} - \delta \right) \]  

(6)

Here, \( c(q, t) \) is the fluctuation of the monomer concentration about its average value, \( c_0 \), and \( \bar{Q}(q, t) \) is the fluctuation of the stress tensor field measured in units of \( k_B T \) times the polymer concentration \( c_0/N \). Thus, we retain \( \{c, Q^\parallel, Q^\perp\} \) as a set of collective variables.

2. Projection operator technique.

The projection operator technique as developed by Zwanzig [11, 12] and Mori [13] will now be used to formulate the transport coefficients in terms of correlation and response functions for a melt of Rouse polymers without shear flow. Our starting point is the observation that a dynamical correlation function \( C^A_B(q, t) \) of the Rouse model\(^{(1)}\) among two collective variables \( A(q, t), B(q, t) \) can be interpreted as a Zwanzig-Mori product [23, 14]

\[ (A_q|e^{+iL_\alpha t}B_q) \equiv C^A_B(q, t) \]  

(7)

\(^{(1)}\) Here and in the following the subscript \( \circ \) will always be used to indicate that the shear flow is turned off.
In this context, \( L_0 \) is the Fokker-Planck operator associated with the dynamics of the Rouse model [24]. Although the projection operator technique was originally invented for the case of a deterministic dynamics [11-13] this technique was later on reformulated for the case of a stochastic dynamics [25-27] governed by a Fokker Planck operator. Such an operator is not necessarily self-adjoint as it is the case for a Liouville operator. However, as will become obvious below, it will not be necessary for the present purposes to explicitly invoke \( L_0 \). Our next step is to introduce the projection operator [14]

\[
P = \sum_{A_q, B_q} |A_q)C^{-1}_{oq}|^{AB} (B_q|
\]

where \( A_q, B_q \in \{c_q, Q^\|, Q^\perp \} \) and with, e.g., \( c_q \equiv c(q, t = 0) \). \( C^{-1}_{oq} \) denotes in this context the inverse of the matrix of static correlation functions in the Rouse model. From the work of Zwanzig and Mori, the Onsager coefficient \( \Lambda^{AB}_o(q, t) \) is defined in terms of \( Q \equiv 1 - P \) and \( L_0 \) as [14]

\[
\Lambda^{AB}_o(q, t) = (iQL_oA_q|e^{iQL_o}|QL_oB_q)
\]

(8)

It is also important to recall that the projection operator technique provides not only a Langevin-type equation of motion for the collective variables, but also an equation for the Mori products or correlation functions [13, 14]:

\[
\frac{d}{dt}C^{AB}_o(q, t) = i\Omega^{AC}_{eq}C^{CB}_o(q, t) - \int_0^t dt' \Gamma^{AC}_o(q, t - t')C^{CB}_o(q, t')
\]

(9)

Here and in the following the Einstein summation convention has been adopted. As discussed in the introduction, the frequency matrix \( i\Omega^{AC}_{eq} \) vanishes for the system under consideration due to our particular choice of collective variables, provided that no shear flow is taken into account. By making use of equation (8), the memory kernel \( \Gamma^{AC}_o \) is given by

\[
\Gamma^{AC}_o(q, t) = \Lambda^{AB}_o(q, t)C^{-1}_{oq}|^{BC}
\]

(10)

To facilitate the following discussion, it proves more convenient to work with the Laplace transforms of the above relations. We define the Laplace transform of an arbitrary function \( f(q, t) \) by

\[
f(q, \omega) = \int_0^\infty dt \, e^{-i\omega t} f(q, t)
\]

Since the dynamical linear response function \( \chi^{AB}_o(q, t) \) is related to the correlation function \( C^{AB}_o(q, t) \) by the dissipation fluctuation theorem

\[
\chi^{AB}_o(q, t) = -\frac{\Theta(t)}{k_BT} \partial_t C^{AB}_o(q, t)
\]

(11)

where \( \Theta(t) \) denotes the Heaviside step function due to causality. A Laplace transform of equation (9) for \( i\Omega^{AB}_{eq} \equiv 0 \) yields immediately

\[
\Gamma^{AC}_o(q, \omega) = k_BT\chi^{AB}_o(q, \omega)C^{-1}_{oq}(q, \omega)|^{BC}
\]

(12)

Combining equations (10) and (12) allows one to express the Onsager coefficients entirely in terms of correlation and response functions of the Rouse model:

\[
\Lambda^{AB}_o(q, \omega) = k_BT\chi^{AC}_o(q, \omega)C^{-1}_{oq}(q, \omega)|^{CD}C^{DB}_{eq}
\]

(13)
This is a very simple and interesting result, because it indicates that tedious calculations with projected Fokker-Planck operator $QL_nQ$ appearing in equation (8) can be avoided if one has access to the correlation and response functions. This result can also be understood in the following way: in the Langevin equations for the collective variables, the product of the decay rate times a collective variable can be interpreted in canonical form as an Onsager coefficient times the derivative of a free energy for the collective variables with respect to an appropriate collective variable. For small departures from equilibrium, the free energy can be expressed as a bilinear form in the collective variables, weighted by the inverse matrix of static correlation functions. Consequently one has the following chain of identities ($\beta = 1/k_B T$, $F$ is the free energy):

$$\Gamma^A_B(q, \omega)B(q, \omega) = \Lambda^A_\omega(q, \omega)\frac{\delta F}{\delta C(q, \omega)} = \Lambda^A_\omega(q, \omega)C^{-1}_\omega CB(q, \omega)$$

(14)

which reproduces equation (10). Next, if we temporarily assume that there is only one collective variable $A$ and that the dynamical correlation function is given by $C^{AA}_\omega(q, t) = e^{-\Gamma^{AA}_\omega t}C^{AA}_\omega$, i.e. there exists a single relaxation time, then it follows from equation (11) that: $k_B T \chi^{AA}_\omega(q, \omega) = \Gamma^{AA}C^{AA}_\omega(q, \omega)$. Thus, equation (12) can be viewed as an appropriate generalization of the above arguments for the case that more than one collective variable is retained and the dynamical correlation functions cannot be described by a simple exponential decay.

In the following analysis, it will be convenient to extend the above to situations in which the chains remain non-interacting with each other, but each polymer interacts with prescribed external fields. These interactions will be taken to have the form of a product of a collective field variable with a corresponding conjugate field. For such situations, the projection operator technique yields the following macroscopic Langevin equation [14] for a collective variable $A(q, \omega)$:

$$i\omega A(q, \omega) = -\Gamma^A_B(q, \omega)B(q, \omega) - \Lambda^A_B(q, \omega)\beta h^B(q, \omega) + \theta^A(q, \omega)$$

(15)

where the frequency matrix has again been assumed to vanish. Here, $h^B(q, \omega)$ denotes the external field conjugate to the collective variable $B(q, \omega)$. $\theta^A$ is a random force with zero mean, $<\theta^A(q, \omega)> = 0$, and covariance

$$<\theta^A(q, \omega)\theta^B(-q, -\omega)> = 2\text{Re}\{\Lambda^A_B(q, \omega)\}$$

(16)

This relationship is also known as the second fluctuation dissipation theorem [14]. The above Langevin equations are linear stochastic differential equations that can at least formally be solved without difficulty. For this purpose, it is convenient to introduce a bare matrix of Green functions

$$G^{AB}_\omega(q, \omega) = [i\omega \delta + \Gamma^A_B(q, \omega)]^{-1}$$

(17)

where $\delta$ denotes the unit matrix. In terms of these Green functions, the fluctuation-dissipation theorem can be rewritten as

$$k_B T \chi^{AB}_\omega(q, \omega) = G^{AC}_\omega(q, \omega)\Lambda^C_B(q, \omega)$$

(18)

This relationship is indeed identical to equation (11), because equation (10) permits one to write: $\Lambda^B_C(q, \omega) = G^{-1}_\omega(q, \omega)[C^{CD}C^{DB}_\omega - i\omega C^{CB}_\omega]$. By subsequent use of

$$G^{AC}_\omega(q, \omega) = C^{AD}_\omega(q, \omega)C^{-1}_\omega|D^C$$

(19)

which is just another way of writing equation (9) for $i\Omega^{AC}_\omega \equiv 0$, equation (11) is recovered. Combining equations (15), (17) and (18) one finds immediately:

$$A(q, \omega) = -\chi^{AB}_\omega(q, \omega)h^B(q, \omega) + G^{AB}_\omega(q, \omega)\theta^B(q, \omega)$$

(20)
which represents the formal solution of the macroscopic Langevin equations. This equation indicates that the instantaneous value of the fluctuating collective variable \( A(q, \omega) \) is partly determined in a linear theory by the noise terms \( \theta^B \) and partly by the conjugate fields \( h^B \). Note that due to equations (11) and (19), both the response functions and the Green functions can be calculated easily if one has access to the static and dynamic correlation functions. The same statement clearly holds for the Onsager coefficients given in equation (13) which determine the strength of the noise terms equation (16).

The procedure for obtaining the dynamical response functions in the presence of a shear flow is now already apparent: first, equations (12) and (13) can be used to calculate the bare (i.e. no-flow) transport coefficients appearing in equation (15). While in general it is very difficult to calculate the static and dynamic correlation functions for interacting polymers, these calculations can be easily performed for non-interacting polymers due to the Gaussian nature of the Rouse model. Such calculations are summarized in appendix A. Next, shear is taken into account by adding appropriate convective terms to equation (15), assuming sufficiently weak flows that the dissipative coefficients are unchanged by the flow. The resulting equation can then be transformed into an equation of the form of equation (20) and the dynamical response functions and Green functions under shear can be read off directly.

Finally, it should be mentioned that the equations of linear response theory are recovered if equation (20) is thermally averaged. This suggests that equation (20) in combination with the random phase approximation can be used to incorporate weak interactions between chains derived from a potential. In the present paper, however, interactions between chains will be neglected in order to highlight concentration-stress couplings and shear flow induced effects.

3. Bare transport coefficients.

By taking the variables \( A, B \) of the Mori equation (15) from the set of collective variables \( \{c, Q^\parallel, Q^\perp\} \), one obtains the appropriate macroscopic Langevin equations for describing Rouse polymers. Equations (12) and (13) provide a precise description of how to calculate the transport coefficients. We summarize the required calculations of correlation and response functions of the Rouse model in appendix A. In the present section, only the resulting memory kernels and Onsager coefficients are given. In terms of the center of mass diffusion constant \( D = k_B T/\zeta N \) and the squared radius of gyration \( R^2 = N b^2/6 \), one finds the following non-vanishing memory kernels to leading order in \( q R \):

\[
\begin{align*}
\Gamma_0^c &= Dq^2(1 - R^2 q^2/6) + O(q^6) \\
\Gamma_0^{Q^\parallel} &= -(k_B T/\zeta)q^2 + O(q^4) \\
\Gamma_0^{Q^\parallel c} &= -2Dq^2\left[1 + (3/2)i\omega\left(1 - \frac{k_B T \sigma_0}{G^\ast(\omega)}\right)\frac{\eta}{k_B T \sigma_0}\right] + O(q^4) \\
\Gamma_0^{Q^\parallel Q^\parallel} &= -i\omega\left(1 - \frac{k_B T \sigma_0}{G^\ast(\omega)}\right) + O(q^2) \\
\Gamma_0^{Q^\perp Q^\perp} &= -i\omega\left(1 - \frac{k_B T \sigma_0}{G^\ast(\omega)}\right) + O(q^2)
\end{align*}
\]

(21)

These results can be understood in the following way: \( \Gamma_0^c \) is the decay rate of concentration fluctuations. The actual value of \( \Gamma_0^c \) depends on the set of collective variables that were chosen; for the present choice we have \( \Gamma_0^c = \Gamma_0^{cc}\{c, Q^\parallel, Q^\perp\} \). If instead \( c \) was taken as the only collective variable, then one would obtain

\[
\Gamma_0^c\{c\} = Dq^2(1 + \frac{1}{3}R^2 q^2) > \Gamma_0^{cc}\{c, Q^\parallel, Q^\perp\}
\]
This inequality is natural because in changing the set of collective variables from \{c\} to \{c, Q^\parallel, Q^\perp\}, the memory kernel \(\Gamma^c_0\{c\}\) is split into \(\Gamma^c_0\{c, Q^\parallel, Q^\perp\}\) and \(\Gamma^{Q^\parallel\perp}_0\{c, Q^\parallel, Q^\perp\}\). The enlarged set of collective variables accounts by diffusion driven by elastic forces, described by the force density \(\nabla \cdot k_B T \vec{Q}(x,t)\). Multiplying this quantity by the mobility \(1/\zeta\), one obtains a contribution to the concentration current. The divergence of this current enters the equation of motion for \(c\). This leads naturally to \(-k_B T/\zeta q^2\) as the leading term of \(\Gamma^c_0\). Since concentration is a conserved quantity, \(\Gamma^c_0\) and \(\Gamma^{Q^\parallel\perp}_0\) are both of order \(q^2\). The stress tensor, however, is not conserved and thus \(\Gamma^{Q^\parallel\perp}_0\) has an order \(q^0\) contribution. Since the stress of a Rouse polymer relaxes not with a single relaxation time, but rather with a set of relaxation times given by the Rouse spectrum \(\{\tau_p\}\), \(\Gamma^{Q^\parallel\perp}_0\) has the peculiar structure displayed above. In this context, \(G^*(\omega)\) denotes the complex shear modulus

\[
G^*(\omega) = G'(\omega) + iG''(\omega) = k_B T c_0 \sum_{p \geq 1} \frac{i\omega}{i\omega + 2/\tau_p}
\]

On extremely long timescales (low frequencies) there seems to be only one relaxation rate

\[
(N^{-1} \sum_{p \geq 1} \tau_p/2)^{-1} \equiv \lim_{\omega \to 0} \Gamma^{Q^\parallel\perp}_0
\]

On finite timescales the stress relaxation rate is a frequency-dependent memory kernel. Both collective fields \(Q^\parallel\) and \(c\) contain a delta function \(\delta(x - r(s,t))\) that picks up the monomer positions. Therefore, it is not surprising that the leading order term in \(\Gamma^{Q^\parallel\perp}_0\) is proportional to \(Dq^2\), the leading order term in the decay of concentration fluctuations. Finally, it should be mentioned that the zero-shear viscosity is obtained from the relation \(\eta = \lim_{\omega \to 0} G''(\omega)/\omega = c_0 N\zeta b^2/36\).

The non-vanishing Onsager coefficients are similarly derived:

\[
\begin{align*}
\Lambda^c_0 &= +c_0 N Dq^2 \\
\Lambda^{Q^\parallel}_0 &= -2c_0 N Dq^2 \\
\Lambda^{Q^\perp}_0 &= -2c_0 N Dq^2 \\
\Lambda^{Q^\parallel\perp}_0 &= -2c_0 i\omega \left(1 - \frac{k_B T c_0}{G^*(\omega)}\right) + O(q^2) \\
\Lambda^{Q^\perp\perp}_0 &= -2c_0 i\omega \left(1 - \frac{k_B T c_0}{G^*(\omega)}\right) + O(q^2)
\end{align*}
\]

For the case that the concentration field would be the only collective variable the equation of motion would simply read: \(\partial_t c(q,t) = -\Lambda^c_0 \delta \beta F/\delta c(q,t) + \Theta(q,t)\). As it can be seen from equations (14) and (54) of appendix A that the result for the Onsager coefficient \(\Lambda^c_0\) implies: \(\partial_t c(q,t) = -Dq^2 c(q,t) + \Theta(q,t)\), which is just Fick’s law. Due to the second fluctuation dissipation theorem given by equation (16) the real part of the Onsager coefficients determines the strength of the noise. Especially for the stress variables the noise is not white but colored, determined in leading order in \(q^2\) by the storage modulus \(G'(\omega)\) and the loss modulus \(G''(\omega)\) where \(G^*(\omega) = G'(\omega) + G''(\omega)\):

\[
2 \text{Re} \{\Lambda^{Q^\parallel\perp}_0(q,\omega)\} = 4k_B T c_0^2 \frac{\omega G''(\omega)}{G'(\omega)^2 + G''(\omega)^2}
\]

All these kinetic coefficients were calculated in the spirit of equation (13). In the next section, we show that the same result for the Onsager coefficient \(\Lambda^c_0\) can be obtained by direct application of equation (8). The discussion surrounding the derivation of this coefficient will highlight
the advantages and disadvantages of the two representations for the Onsager coefficients; i.e., equations (8) and (13).

4. Bare Onsager coefficients revisited.

The objective of the present section is to present an alternate derivation of the Onsager coefficient \( \Lambda^K_0 \) by application of equation (8). For this purpose, it is convenient to consider the time derivative of a generic collective variable \( K(q,t) \), which will later be taken as the concentration \( c(q,t) \) or the stress tensor \( \tilde{Q}(q,t) \), defined by equation (5) or (6), respectively. \( K(q,t) \) can clearly be regarded as a functional of \( r(s,t) \). Construction of the time derivative of \( K(q,t) \) therefore requires knowledge of \( \partial_t r(s,t) \). Consequently, if the microscopic Langevin equation (1) is taken into account, one can always write

\[
\partial_t K(q,t) = V^K(q,t) + \tilde{\theta}^K(q,t)
\]  

(24)

The right hand side of this expression represents a decomposition in a deterministic part \( V^K \) and a noise term \( \tilde{\theta}^K \), given explicitly by:

\[
V^K(q,t) = \int_0^N ds \frac{\delta K(q,t)}{\delta r(s,t)} \left[ -\frac{1}{\zeta} \frac{\delta H_0}{\delta r(s,t)} \right]
\]

(25)

\[
\tilde{\theta}^K(q,t) = \int_0^N ds \frac{\delta K(q,t)}{\delta r(s,t)} : \theta_r(s,t)
\]

(26)

We note that \( \tilde{\theta}^K(q,t) \) differs in general from the collective noise term \( \theta^K(q,t) \), which is defined in the framework of the Zwanzig-Mori projection operator technique as

\[
\theta^K(q,t) = e^{iQ L_q t} Q L_o K_q
\]

(27)

In order to clarify the difference between the two noise terms, we recall the origin of \( \tilde{\theta}^K \). The Rouse model is a highly simplified description of the dynamics of a polymer in which successive segments, described as overdamped Brownian particles, are harmonically coupled by "entropic springs". Because of the assumption of strong frictional coupling to the solvent, the momenta of the segments are no longer retained as phase space variables, leading to the semi-microscopic Langevin equation (1). The noise \( \theta_r(s,t) \) (and subsequently \( \tilde{\theta}^K(q,t) \)) arises from collisions with the solvent "bath" and from neglected shorter-scale degrees of freedom, and thus serves as a reminder of the underlying many-body problem. It is important to emphasize that the term \( V^K(q,t) \) is not necessarily closed in the set of collective variables represented by \( K(q,t) \).

On the other hand, the projection operator technique is a systematic method for obtaining a closed set of equations for a set of variables that can in principle be chosen arbitrarily. The price to be paid for the enforcement of closure is the Zwanzig-Mori noise \( \theta^K \). Since \( iL_o K_q = K_q = \partial_t K(q,t) \left|_{t=0} \right. \), the two different noise terms are actually related to each other for \( t = 0 \) through

\[
\theta^K_q = iQ L_o K_q = Q[V^K_q + \tilde{\theta}^K_q]
\]

This relationship can be inserted into the definition of the Onsager coefficients as given by equation (8) leading to

\[
\Lambda^K_0(q,t) = (Q[V^K_q + \tilde{\theta}^K_q]|e^{iQ L_o Q^t}|Q[V^K_q + \tilde{\theta}^K_q])
\]

(28)
Because a static correlation function between a collective variable and the noise term $\tilde{\theta}_q^K$ vanishes, one finds immediately $P\tilde{\theta}_q^K = 0$ or $Q\tilde{\theta}_q^K \equiv \tilde{\theta}_q^K$. This allows one to write:

$$\Lambda_0^{KL}(q, t) = (Q\tilde{\theta}_q^K + \tilde{\theta}_q^K |e^{tL}\tilde{\theta}_q^K|Q\tilde{\theta}_q^K + \tilde{\theta}_q^K)$$

For the special case that in addition $Q\tilde{\theta}_q^K = 0$ and $Q\tilde{\theta}_q^K \equiv \tilde{\theta}_q^K$ one can see immediately that this expression collapses to

$$\tilde{\Lambda}_0^{KL}(q, t) = (\tilde{\theta}_q^K |e^{tL}|\tilde{\theta}_q^K) \equiv \langle \dot{\theta}_q^K(-q, 0)\tilde{\theta}_q^K(q, t) > 0$$

Moreover, in taking advantage of $P\tilde{\theta}_q^K = 0$ and $Q\tilde{\theta}_q^K \equiv \tilde{\theta}_q^K$ one can see immediately that this expression collapses to

$$\tilde{\Lambda}_0^{KL}(q, t) = \frac{c_0}{N} < \int_0^N ds \frac{\delta K(-q, 0) k_B T \delta L(q, 0)}{\delta r(s, 0)} > 0 \delta(t)$$

(29)

With these preliminaries, $\Lambda_0^{cc}$ can now be easily calculated. Applying the procedure leading to equations (24-26) for the concentration $c(q, t)$ defined by equation (16), one finds:

$$V_q^c = -\frac{k_B T}{\zeta} q^2 [c_q + Q_q^\parallel]$$

(30)

Since both $c_q$ and $Q_q^\parallel$ belong to the collective variables from which the projection operator was formulated, it follows that $QV_q^c = 0$. Therefore, equation (29) is applicable and reduces to

$$\Lambda_0^{cc}(q, \omega) \equiv \tilde{\Lambda}_0^{cc}(q, \omega) = c_0 NDq^2$$

in agreement with the result obtained earlier. However, equation (29) cannot be used to calculate a stress-stress Onsager coefficient such as $\Lambda_0^{\parallel\parallel}$. First of all, a calculation of $V_q^\parallel$ will reveal that $QV_q^\parallel \neq 0$, because the calculation of $\dot{\theta}\parallel$ yields new collective variables not contained in the set \{c_q, Q_q^\parallel, Q_q^L\}. Furthermore, $\tilde{\Lambda}_0^{KL}$ is delta-correlated in time. The stress relaxation, however, partially takes place via a relaxation of the shape of the polymer, which is an extended object. Thus, we expect a memory effect that cannot be described by white noise, but rather by some functional of the shear modulus as was found earlier.

Working within the context of the projection operator technique, Kawasaki and Sekimoto [18] used only the concentration fluctuations as collective variables. With such variables, there corresponds a set of modified projection operators $PKS$ and $QKS$. Consequently, due to equation (30), the Kawasaki-Sekimoto approach leads to $QKS V_q^c \neq 0$, because the stress is not contained in the set of collective variables. However, Kawasaki and Sekimoto argued that the small wavevector concentration fluctuations should be the slowest variables. Since the stress is not a conserved variable, one concludes that the stress fluctuations will decay more rapidly, leading to $QKS V_q^c \approx 0$ on long timescales. In essence, the local equilibrium approximation made by Kawasaki and Sekimoto thus amounts to the approximation $QKS V_q^c \approx 0$. For the case that the concentration fluctuations are considered to be the only collective variables, the local equilibrium approximation corresponds to $\Lambda_0^{cc}(q, t) \approx \tilde{\Lambda}_0^{cc}(q, t)$, while this becomes an exact equality only if the stress is included in the set of collective variables. The method described in the previous section for the calculation of Onsager coefficients can thus be understood as a means of going beyond the local equilibrium approximation.
5. Projected Rouse model without shear.

The differential equation (15) with transport coefficients $\Gamma_o^{AB}$ and $\Lambda_o^{AB}$ and its formal solution (20) with integral kernels $G_o^{AB}$ and $\chi_o^{AB}$ are in principle equivalent. Nevertheless, the nature of the collective variables often determines which is the more convenient representation. Since the stress variable does not have a single relaxation time, the stress relaxation rates $\Gamma_o^{Q^\perp Q^\parallel}$ and $\Gamma_o^{Q^\parallel Q^\perp}$ look rather peculiar. The integral representation is clearly more natural for such variables. In particular, $Q^\perp$, which is not coupled to either $C$ or $Q^\parallel$, the integral kernel $G_o^{Q^\perp Q^\perp}(q, \omega)$, the Green function, is given by:

$$G_o^{Q^\perp Q^\perp}(q, \omega) = (i\omega + \Gamma_o^{Q^\perp Q^\perp}(q, \omega))^{-1} = \frac{\eta^*(\omega)}{k_BT_0} + O(q^2) \quad (31)$$

In this expression, $\eta^*(\omega)$ denotes the complex viscosity, which is related to the shear modulus $G(t) = \frac{k_BT_0}{N} \sum_{p \geq 1} e^{-2t/\tau_p}$

via a Laplace transform: $\eta^*(\omega) = \int_0^\infty dt \, e^{-\omega t} G(t)$. Consequently, the Green function $G_o^{Q^\perp Q^\perp}(q, t)$ is to within a normalization constant (and at leading order in $q^2$) identical to the shear modulus. The remaining non-vanishing Green functions are given to leading order in $q^2$ by the following $2 \times 2$ matrix:

$$
\begin{pmatrix}
G_o^{c c} & G_o^{Q^\parallel c} \\
G_o^{Q^\parallel c} & G_o^{Q^\parallel Q^\parallel}
\end{pmatrix} = \begin{pmatrix}
\frac{1}{i\omega + Dq^2} & \frac{N Dq^2}{\omega + Dq^2} \frac{\eta^*(\omega)}{k_BT_0} \\
\frac{2 Dq^2}{\omega + Dq^2} \frac{\eta^*(\omega)}{k_BT_0} & \frac{\eta^*(\omega)}{k_BT_0}
\end{pmatrix}
\quad (32)
$$

With this information in hand, the semi-microscopic Rouse model, described by equations (1-3), can be projected onto macroscopic equations of motion valid in the hydrodynamic limit. By recalling that in the absence of external fields the equation of motion for a collective variable $A(q, \omega)$ reads $A(q, \omega) = G_o^{AB}(q, \omega)\Theta^B(q, \omega)$, the matrix of Green functions implies the following equations of motion to leading order in $q^2$:

$$
\partial_t c(q, t) = -Dq^2 c(q, t) + \frac{k_BT}{\zeta} \mathbf{q} : \bar{Q}(q, t) + \Theta^c(q, t)
$$

$$
\bar{Q}(q, t) = \int dt' \frac{G(t - t')}{k_BT_0} \Theta^\perp(q, t')
$$

While the first equation confirms the structure of the coupling of concentration and stress as proposed by Helfand and Fredrickson [1], the second equation indicates that the fluctuating stress tensor field $k_BT\bar{Q}(q, t)$ is driven by the tensorial noise term $\Theta^\perp(q, t)$, with the shear modulus acting as the linear response kernel. We have thus shown how the projection operator technique of Mori and Zwanzig can be used to project the semi-microscopic Rouse model onto equation of motions for the collective variables of concentration and stress. In the case of the Rouse model, the search for governing macroscopic equations of motion was seen to be facilitated by the direct calculation of appropriate correlation and response functions. Since these objects were calculated here only to lowest order in $q^2$, the projected equations of motion are only valid in the hydrodynamic regime.
The Green functions and Onsager coefficients can also be used to determine the dynamical structure factor of a non-interacting polymer solution

\[ S(q, \omega) = < c^*(q, \omega) c(q, \omega) > \]
\[ = |G^{cc}|^2 2 \text{Re} \{ \Lambda_0^{cc} \} + 2 \text{Re} \{ G^{cc} G^{Q^2} \} 2 \text{Re} \{ \Lambda_0^{Q^2} \} + |G^{Q^2 Q^2}|^2 2 \text{Re} \{ \Lambda_0^{Q^2 Q^2} \} \]

as can be seen from equation (20) for \( A(q, \omega) = c(q, \omega) \) and \( h^B(q, \omega) \equiv 0 \) in combination with equation (16). Thus, the calculation of the static structure factor \( S(q) = (2\pi)^{-1} \int d\omega S(q, \omega) \) can be used to check the consistency of the Green functions as given by equation (32). For this purpose, we approximate the complex viscosity by a Maxwell model, namely

\[ \eta^*(\omega) \sim \eta(1 + i\omega\tau_Q)^{-1} \]

where the stress relaxation time was chosen to be \( \tau_Q = N\eta/k_B T c_0 = (\pi^2/3)\tau_1 \), i.e. essentially the longest Rouse relaxation time \( \tau_1 \). In this approximation, equation (32) leads to \( S(q) = c_0 N (1 - R^2 q^2/3 + O(q^4)) \), which agrees to order \( q^2 \) with the well-known exact result \( S(q) = c_0 N f_D(R^2 q^2) \), \( f_D(x) \) denoting the Debye function.


As already mentioned above, the effect of an external shear flow on polymers is twofold: Kuhnian segments are both convected as well as oriented. Both effects influence the dynamical response of a polymeric material. Our intention is to gain both a qualitative and quantitative understanding of this response. If \( \partial r(s, t)/\partial t \) denotes the velocity of a Kuhnian segment at position \( r(s, t) \) due to Brownian motion, then the incremental effect of a steady shear flow \( u(x) = \dot{\gamma} ye_x \) with shear rate \( \dot{\gamma} \) is to add a drift velocity:

\[ \partial_t r_\gamma(s, t) = u(r(s, t)) + \partial_x r(s, t) \]  \hspace{1cm} (33)

This simple superposition of velocities on a microscopic lengthscale induces various convective terms in the macroscopic Langevin equations. A collective variable like the stress tensor \( \vec{\sigma} \) defined in equation (4) can, in the presence of a shear flow, be treated as a functional of \( r_\gamma(s, t) \). The convective terms for the stress tensor field are simply obtained by:

\[ \partial_t \vec{\sigma}(x, t) \big|_{\partial_t r_\gamma(s, t) = u(r(s, t))} = -u \cdot \nabla \vec{\sigma} + (\nabla u)^T \cdot \vec{\sigma} + \vec{\sigma} \cdot (\nabla u) \]  \hspace{1cm} (34)

The first term on the right hand side describes the convection of Kuhnian segments due to the flow field, whereas the second and third term describe the rotation of Kuhnian segments in the flow. The above is a well-known result giving rise to the so-called upper convected Maxwell derivative [2]. For the stress variables of interest here, \( Q^\parallel \) and \( Q^\perp \), the last relationship is specialized to

\[ \partial_t Q^\parallel(q, t) \big|_{\partial_t r_\gamma = u} = \dot{\gamma} q_x \frac{\partial}{\partial q_y} Q^\parallel(q, t) \pm 2\dot{\gamma} q_x \dot{q}_y [Q^\parallel(q, t) + c(q, t)] \] \hspace{1cm} (35)

where \( \diamond \in \{ \parallel, \perp \} \), and where \( \pm \) is taken to be \( + \) if \( \diamond \) equals \( \parallel \), and \( - \) if \( \diamond \) equals \( \perp \). The rotation of Kuhnian segments is now described by the second term on the right hand side. Note that a term involving \( c \) also appears in order to compensate for the fact that \( Q \) corresponds only to the anisotropic part of \( \vec{\sigma} \). For completeness, we note that the convective term of the concentration fluctuation \( c \) is the familiar \( \dot{\gamma} q_x (\partial/\partial q_y) c \).
An important effect of an external shear flow is to inject momentum into the system. Since the set of collective variables does not contain the momentum field, the frequency matrix without shear flow was argued to vanish: \( i\Omega^{AB}_{q} = 0 \). However, the rotation of Kuhnian segments induced by the shear flow leads to a frequency matrix \( i\Omega^{AB}_{\gamma} \) characterized by the following non vanishing matrix elements:

\[
 i\Omega^{A} = i\Omega^{A}_{y} = -i\Omega^{A}_{y} = 2\gamma q_{x} q_{y}
\]

By incorporating this frequency matrix and the convective terms given in equation (35), we thus obtain the following macroscopic Langevin equations in the presence of shear flow:

\[
 \left( \omega - \gamma q_{x} \frac{\partial}{\partial q_{y}} \right) A(q, \omega) = [\Omega^{B} - \Gamma^{B}(q, \omega)] B(q, \omega) - \chi^{AB}(q, \omega) \beta h^{B}(q, \omega) + \theta^{A}(q, \omega)
\]

Implicitly assuming weak flows, we neglect any changes in the dissipative coefficients caused by the shear. As is shown in appendix B, the method of characteristics allows one to rewrite equation (37) in the form of equation (20) as

\[
 A(q, \omega) = -\chi^{AB}(q, \omega) h^{B}(q, \omega) + G^{AB}(q, \omega) \delta^{B}(q, \omega)
\]

where the matrix of dynamical response functions and matrix of Green functions in the presence of an external shear flow are given by:

\[
 k_{B} T \chi^{AB}(q, \omega) = \int_{-\infty}^{\infty} dt' T^{AC}(q, \omega, t') \Lambda^{CB}(q(t'), \omega) \exp[-t' q_{x} \frac{\partial}{\partial q_{y}}]
\]

\[
 G^{AB}(q, \omega) = \int_{-\infty}^{\infty} dt' T^{AC}(q, \omega, t') \exp[-t' q_{x} \frac{\partial}{\partial q_{y}}]
\]

In the above equation, \( q(t) \equiv q - t \gamma q_{x} e_{x} \) and the quantity \( T^{AC}(q, \omega, t') \) is the following time ordered product:

\[
 T^{AB}(q, \omega, t') = T \exp[-\int_{t'}^{0} dt'' \Psi^{AB}(q(t''), \omega)]
\]

\[
 \Psi^{AB}(q, \omega) = G_{0}^{-1}(q, \omega)|^{AB} - i\Omega^{AB}_{\gamma}
\]

The set of equations (40), (41) and (42) can be considered as a mathematical description how the shear flow renormalizes the bare Green functions \( G_{0}^{AB}(q, \omega) \) into the Green functions \( G^{AB}(q, \omega) \) under shear. As is shown in appendix B, it is a simple matter to expand \( G^{AB}(q, \omega) \) to first order in \( \gamma \). For this purpose, it proves convenient to introduce a reduced frequency matrix \( i\Omega^{AB}_{\gamma} \) defined via \( i\Omega^{AB}_{\gamma} = 2\gamma q_{x} q_{y} i\Omega^{AB} \). For our set of three collective variables \( \{c, Q^{\parallel}, Q^{\perp}\} \), this reduced frequency matrix is given explicitly by

\[
 i\Omega_{\gamma} = \begin{pmatrix}
 0 & 0 & 0 \\
 1 & 1 & 0 \\
 -1 & 0 & -1 
\end{pmatrix}
\]

In terms of \( i\Omega_{\gamma} \) and \( \partial_{\gamma} \equiv q^{2} \partial/\partial q^{2} \) one finds:

\[
 G^{AB}_{\gamma} = G^{AB}_{0} + 2\gamma q_{x} q_{y} [i\Omega^{D} G^{DB}_{0} + \partial_{\gamma} G^{CB}_{0} + G^{CB}_{0} \partial_{\gamma}] + O(\gamma^{2})
\]

\[
 \chi^{AB}_{\gamma} = \chi^{AB}_{0} + 2\gamma q_{x} q_{y} G^{AB}_{0} [i\Omega^{D} \chi^{DB}_{0} + \partial_{\gamma} \chi^{CB}_{0} + \chi^{CB}_{0} \partial_{\gamma}] + O(\gamma^{2})
\]
The basic conclusion of the structure of these equations is that an external shear flow leads to an anisotropic first order contribution characterized by $2\gamma \hat{q}_x \hat{q}_y$. Because the Green functions have the dimension of time, the combination $2\gamma \hat{q}_x \hat{q}_y G^{AC}_\sigma$ is dimensionless. The contributions to first order in $\gamma$ are due to a combination of convection and rotation of Kuhnian segments due to the flow. Since the mathematical objects $t\Omega_\sigma$ and $\partial_\sigma$ are related to rotation and convection, respectively, it is obvious that the terms involving $t\Omega_\sigma$ are expected for a polymeric material, but would not be present in a simple liquid without orientational degrees of freedom.

Finally, it should be mentioned that equations (43) and (44), while derived for non-interacting polymers, can be easily extended to apply to polymer solutions or melts by invoking a mean-field approximation to describe the intermolecular interactions. The mean-field interactions can be used to renormalize the bare response functions via a random phase approximation (RPA). This technique was worked out for different polymeric systems by Jannink and de Gennes [28], de Gennes [29], Brochard and de Gennes [7] and Akcasu et al. [30]; in all cases retaining only the concentration fields as collective variables. The RPA technique is easily generalized to situations in which both concentration and stress fields are used as collective variables. The effect of such a random phase approximation would then be to turn $\chi^{AB}_0$ into the interacting response function $\chi^{AB}$. Moreover, the Green function $G^{AB}_\sigma$ would be renormalized to $G^{AB}$. Thus, by inserting $G^{AB}$ and $\chi^{AB}$ in the right hand sides of equations (43) and (44), one could examine how a shear flow influences the dynamical response of interacting polymers. For the sake of simplicity, however, non-interacting Rouse polymers shall only be considered here.

7. Phenomenological constitutive equations.

The purpose of the present section is to show how the equations of motion derived above are related to certain well-known phenomenological constitutive equations. For this purpose, equation (37) for the collective variable $Q^\parallel$ is thermally averaged. The stress relaxation rate $\Gamma^{Q^\parallel Q^\parallel}(q,\omega)$ will be, for simplicity, replaced by a phenomenological relaxation rate $1/\tau$ and the decay rate $\Gamma^{Q^\parallel Q^\perp}(q,\omega)$, which is of order $q^2$, shall be neglected. This leads immediately to

$$[\omega - \gamma q_x \frac{\partial}{\partial q_y} - t\Omega^{Q^\parallel Q^\parallel}_\gamma] < Q^\parallel > = -\frac{1}{\tau} < Q^\parallel > + t\Omega^{Q^\parallel Q^\perp}_\gamma < c > \tag{45}$$

where all external fields were assumed to be turned off. An analogous equation holds for $Q^\perp$.

These two equations can be combined into a single equation for

$$\vec{Q}(q,\omega) = (qq/q^2)Q^\parallel(q,\omega) + (\delta -qq/q^2)Q^\perp(q,\omega)$$

In real space one obtains:

$$(\partial_t + u \cdot \nabla) < k_BT \vec{Q} > - (\nabla u)^T < k_BT \vec{Q} > - < k_BT \vec{Q} > \cdot (\nabla u) = -\frac{1}{\tau} < k_BT \vec{Q} > + 2eG(0) \tag{46}$$

where $e(x,t) = (1/2)[\nabla u + (\nabla u)^T]$ denotes the rate of strain tensor for a simple shear flow characterized by $u = \gamma y e_x$ and where $G(0) = k_BT < c >$ is interpreted as the shear modulus for $t = 0$. Equation (46) is of course simply the upper convected Maxwell model [2] formulated for the deviatoric average stress variable $< k_BT \vec{Q} >$. One step beyond this phenomenological Maxwell model was taken by Marrucci [4], who included a noise term and transformed the Maxwell model into a Langevin equation. However, the stress relaxation rate was again modeled in a phenomenological manner. Thus, one can conclude that Marrucci’s model is
somewhere between the upper convected Maxwell model and the fluctuating hydrodynamic equations derived above. The integral version of the upper convected Maxwell model is known as the Lodge equation [2]. Therefore, equation (38) in combination with equations (39) and (40), which is the formal solution of the Langevin equations under shear, is a generalization of the Lodge equation to include the entire Rouse spectrum. A key ingredient of the Lodge equation is the shear modulus, which in the theory developed here is essentially replaced by the matrix of Green functions. Finally, we again note that interactions can be incorporated in a mean-field way via the random phase approximation.

Another important phenomenological constitutive equation is the so-called second order fluid model [2]. In order to understand the relationship between our results and this constitutive equation, \( \Gamma_0 Q^1 Q^1 \) must not be replaced by a frequency-independent relaxation rate \( 1/\tau \). According to equation (21), we have the relation

\[
\omega + k_BTc_0 = \frac{k_BTc_0}{\eta^*(\omega)} + O(\eta^2)
\]

where \( \eta^*(\omega) = G^*(\omega) / (i\omega) \) denotes the complex viscosity. With this expression for the decay rate, we have instead of equation (45):

\[
\left\{ 1 - \frac{\eta^*(\omega)}{k_BTc_0} \left[ \gamma_q \frac{\partial}{\partial y} + tR_q Q^1 \right] \right\} < Q^1 > = \frac{\eta^*(\omega)}{k_BTc_0} tR_q Q^1 < c >
\]

Expanding \( < Q^1 > \) and \( < c > \) in powers of the shear rate, the curly bracket on the left hand side can be replaced by 1 to leading order. It thus follows that

\[
< k_BT Q(q,\omega) > = 2\eta^*(\omega) \frac{< c >}{c_0} e(q,\omega) + O(\eta^2)
\]

This relationship can be compared with the second order fluid model

\[
< k_BT \tilde{Q} > = 2\eta[c] \tilde{e} - \Psi_1[c] \tilde{e} + 4\Psi_2[c] \tilde{e} \cdot \tilde{e}
\]

where \( \tilde{e} = (\partial_t + u \cdot \nabla) e - (\nabla u)^T \cdot e - e \cdot (\nabla u) \) denotes the upper convected derivative of the rate of strain tensor and \( \eta[c], \Psi_1[c], \) and \( \Psi_2[c] \) are viscometric coefficients: the viscosity, first, and second normal stress coefficients, respectively. In order to obtain expressions for the normal stress coefficients, it is necessary to expand the average stress to second order in the shear rate. This will not be carried out here.

8. Summary and discussion.

Most of the familiar constitutive equations used for polymer melts and solutions contain some phenomenological coefficients such as relaxation rates [2]. As was shown in the preceding sections, the projection operator technique allows one to deduce generalized constitutive equations in which the transport coefficients can be related to an underlying semi-microscopic model, the Rouse model. A crucial point is that in the equation of motion for the stress variable, a coupling exists to the concentration fluctuations. Thus, unlike conventional constitutive equations which treat the fluid as a homogeneous medium, composition fluctuations and non-uniformities can be explicitly accounted for. In situations where no external fields are present, equations (36) and (37) yield the expressions:

\[
\left( \omega - \gamma_q \frac{\partial}{\partial y} \right) c(q,\omega) = -\Gamma_c^c(q,\omega) c(q,\omega) - \Gamma_0^Q(q,\omega) Q^1(q,\omega) + \theta^c(q,\omega)
\]

\[
Q^1(q,\omega) = G^c_q(q,\omega) \theta^c(q,\omega) + G^Q q^1(q,\omega) \theta^Q(q,\omega)
\]
This set of Langevin equations, when averaged, can be considered a type of generalized constitutive equation. Similar equations of this type were derived and solved by Helfand and Fredrickson [1], Onuki [3], and by Milner [6] in the context of the steady state structure factor of sheared polymer solutions. The goal here was less ambitious: to show explicitly how the transport coefficients involved in such fluctuating hydrodynamic descriptions can be related to an underlying microscopic model.

Similar sets of coupled Langevin equations can be derived for more complicated polymer mixtures and for copolymers. Because our approach is based on linear response theory, the random phase approximation can be conveniently invoked to incorporate isotropic or anisotropic (e.g. Maier-Saupe) interactions among chains. Such calculations could be used to derive interesting new constitutive equations for polymer blends and copolymers. Another important point is that the formalism developed here for non-interacting (or with the RPA, weakly interacting) chains is not restricted entirely to the Rouse model. For example, related calculations could be performed on the basis of single-chain dynamics in the reptation model. To follow our scheme, one simply requires that the matrices of linear response and correlation functions can be computed for the collective variables chosen and the single-chain dynamical model of interest.

Finally, we point out that dynamical response functions under shear were developed as a byproduct of our approach. It should be emphasized that the shear flow was not treated (initially) as a perturbation, but linear responses were computed to weak external fields. However, subsequent expansions in the shear rate were used to show how the response functions under shear are related to the bare response functions. A characteristic property of sheared polymeric systems was found to be the simultaneous rotation and alignment of Kuhn segments. Simple fluids composed of isotropic molecules, in contrast, experience only convection and remain isotropic at laboratory shear rates. The present formalism provides a clear separation of these two effects.

Appendix A.

Correlation and response functions.

The purpose of this section is to outline the calculation of the static and dynamic correlation functions among the collective variables \( c(q,t) \) and \( \bar{Q}(q,t) \). Both quantities are examples of a collective field \( K(q,t) \) with the following structure:

\[
K(q,t) = \frac{c_0}{N} \int_0^N ds \ e^{-i q \cdot r(s,t)} K_r(s,t)
\]  

(50)

The quantity \( K_r(s,t) \) refers to the contribution at monomer position \( r(s,t) \) to the collective field. For the concentration \( c(q,t) \) one has simply \( c_r(s,t) = 1 \), while the collective field \( \bar{Q}(q,t) \) is characterized by

\[
\bar{Q}_r(s,t) = \frac{3}{b^2} \frac{dr(s,t)}{ds} \frac{dr(s,t)}{ds} - \delta
\]

The general structure of the collective variables allows one to write the dynamical correlation function \( C^{KL}_0(q,t) \) among two collective variables \( K \) and \( L \) as

\[
C^{KL}_0(q,t) = \frac{c_0}{N} \int_0^N ds \int_0^N ds' < K_r(s,t) L_r(s',0) e^{-i q \cdot [r(s,t)-r(s',0)]} >_0
\]  

(51)
where the bracket \(< \cdot, \cdot >_0\) denotes a thermal average for a single Rouse polymer. From a technical point of view, the Gaussian nature of the Rouse model is of great advantage, because it allows one to make use of a generalized Wick theorem established in reference [31]. This theorem states the following: If \(Y\) is any linear combination of a set of Gaussianly distributed variables \(x_n\) with mean zero and covariance \(< x_n x_m >\) then

\[
< x_{n_1} x_{n_2} \cdots x_{n_r} e^Y > = < x_{n_1} x_{n_2} \cdots x_{n_r} ||Y|| e^Y >
\]

where

\[
< x_{n_1} x_{n_2} x_{n_r} ||Y|| > = \sum_{j=0}^{r} < x_{n_1} x_{n_2} \cdots x_{n_r} [Y^j] >'
\]

While \(r\) may be odd or even, the prime on the average in the last equation indicates that the sum over all pairings is to be carried out with the restriction that the \(Y\)'s must be paired with the \(x\) set in brackets and not with each other. The Rouse model has the required character, where the role of the Gaussianly distributed random variables is played by the set of Rouse modes \(x_{p\alpha}(t) = (1/N) \int_0^\infty ds \cos(p\pi s/N)r_\alpha(s, t)\). Consequently, it is always possible to rewrite equation (51) as

\[
C_{KL}^0(q, t) = \frac{C_0}{N} \int_0^N ds \int_0^N ds' W_{KL}^0(q, s, s', t)S_0(q, s, s', t)
\]

(52)

The quantity \(S_0(q, s, s', t)\) is the dynamical structure factor of an individual monomer

\[
S_0(q, s, s', t) = < e^{-i\mathbf{q} \cdot [r(s, t) - r(s', 0)]} >_0
\]

and the weight \(W_{KL}^0(q, s, s', t)\) characterizes the nature of the collective variables

\[
W_{KL}^0(q, s, s', t) = < K_{r(s, t)} L_{r(s', 0)} || - i\mathbf{q} \cdot [r(s, t) - r(s', 0)] >_0
\]

(53)

Of particular interest are the correlation functions among the collective variables of concentration and stress. The calculation of \(W_{KL}^0\) requires knowledge of how to calculate correlation functions in the Rouse model among different orientations \(dr(s, t)/ds\) or among an orientation and a position. Thus, one is interested in the quantity

\[
< \frac{dr_\alpha(s_1, t_1)}{ds_1} \frac{dr_\beta(s_2, t_2)}{ds_2} >_0 = \delta_{\alpha\beta} I_m(s_1, s_2, |t_1 - t_2|)
\]

where \(m \in \{0, 1\}\). By using Rouse modes, one can explicitly calculate these averages. In terms of \(S_{ps} = \sin(p\pi s/N)\) and \(C_{ps} = \cos(p\pi s/N)\) one finds:

\[
I_0(s_1, s_2, t) = -2D \sum_{p \geq 1} (p\pi/N) S_{ps_1} C_{ps_2} \tau_p e^{-t/\tau_p}
\]

\[
I_1(s_1, s_2, t) = +2D \sum_{p \geq 1} (p\pi/N)^2 S_{ps_1} S_{ps_2} \tau_p e^{-t/\tau_p}
\]

where \(D = k_B T/\zeta N\) and \(\{\tau_p\}\) are the diffusion constant and the Rouse relaxation times [24] respectively. All the quantities \(W_{KL}^0\) of interest in the present paper can now be expressed by \(I(s, s', t) \equiv I_1(s, s', t)\) and the two linear combinations

\[
L(s, s', t) = I_0(s, s, 0) - I_0(s, s', t)
\]
\[ L'(s, s', t) = I_0(s', s', 0) - I_0(s', s, t) \]

Also, in computing \( W_0^{Q_0} \), where the stress tensor is involved twice, one is faced with a fourth rank tensor that can be decomposed into the following basic tensors:

\[
\begin{align*}
\Delta_{\alpha\beta\gamma\delta}^{(0)} &= \delta_{\alpha\gamma} \delta_{\beta\delta} + \delta_{\alpha\delta} \delta_{\beta\gamma} \\
\Delta_{\alpha\beta\gamma\delta}^{(2)} &= \eta_{\alpha\gamma} \eta_{\beta\delta} + \eta_{\alpha\delta} \eta_{\beta\gamma} + \eta_{\beta\delta} \eta_{\alpha\gamma} + \eta_{\beta\gamma} \eta_{\alpha\delta} \\
\Delta_{\alpha\beta\gamma\delta}^{(4)} &= \eta_{\alpha\delta} \eta_{\beta\gamma}
\end{align*}
\]

While by definition \( W_0^{Q_0}(q, s, s', t) = 1 \), the remaining quantities are given by:

\[
\begin{align*}
W_0^{Q_0}(q, s, s', t) &= -(3/b^2) L'(s, s', t) L'(s, s', t) \eta_{\eta_{\eta_{\eta}}}
\end{align*}
\]

where in the last line the arguments of \( I, L, \) and \( L' \) were suppressed. It is now possible to calculate the static and dynamic correlation functions by referring to equation (52). Using the notation \( C^{KL}_{QQ}(q, 0, 0) \), one obtains for the non-vanishing static correlation functions the following result:

\[
\begin{align*}
C^{cc}_{qq} &= c_0 N f(Nx) \\
C^{Q_0}_{qq} &= C^{Q_0}_{Q_0} = - (1/2) c_0 N x f(Nx) \\
C^{Q_0Q_0}_{qq} &= 2c_0(1 - x) + (1/4) c_0 N x^2 f(Nx) \\
C^{Q_0Q_0}_{Q_0} &= 2c_0
\end{align*}
\]

where \( x = b^2 q^2 / 6 \) and where \( f(y) = (2/y^2)(e^{-y} - 1 + y) \) denotes the Debye function. While the static correlation functions can be calculated for the entire range of the \( q \)-vector, the calculation of the dynamical correlation function is much more complex. Actually it is more convenient to write down the dynamical response functions, which in combination with the static correlation functions give access to the dynamical correlation functions. In terms of

\[
\begin{align*}
G(t) &= \frac{k_B T c_0}{N} \sum_{p \geq 1} \exp[-\tau_p^{-1} t] \\
H(t) &= \frac{k_B T c_0}{N} \sum_{p,q} \exp[-(\tau_p^{-1} + \tau_q^{-1}) t] \cosh[2t/\sqrt{\tau_p \tau_q}]
\end{align*}
\]

the response functions are given to leading order in \( q^2 \) by the following expressions:

\[
\begin{align*}
k_B T \chi^{cc}_{0}(q, t) &= + \Theta(t) c_0 N e^{-Dq^2 t} Dq^2 [1 - 2Dq^2 \frac{N}{k_B T c_0} \int_0^t dt' G(t')] \\
k_B T \chi^{Q_0}_{0}(q, t) &= - \Theta(t) 2c_0 N e^{-Dq^2 t} Dq^2 [G(t)/k_B T c_0] \\
k_B T \chi^{Q_0}_{Q_0}(q, t) &= - \Theta(t) 2c_0 N e^{-Dq^2 t} Dq^2 [G(t)/k_B T c_0]
\end{align*}
\]
\[ k_B T \chi_0 Q^+ Q^\dagger (q, t) = +\Theta(t) \frac{2}{k_B T} e^{-D q^2 t} \left[ -\frac{dG(t)}{dt} \left( 1 - \frac{R^2 q^2}{3} \right) + [2G(t) - H(t)]D q^2 \right] \]  
\[ k_B T \chi_0 Q^- Q^\dagger (q, t) = +\Theta(t) \frac{2}{k_B T} e^{-D q^2 t} \left[ -\frac{dG(t)}{dt} \left( 1 - \frac{R^2 q^2}{3} \right) + [G(t) - 3H(t)]D q^2 \right] \]

where \( \Theta(t) \) is the Heaviside step function.

**Appendix B.**

**Perturbation theory for small shear rates.**

In this appendix we show how the matrix \( G_{AB}(q, \omega) \) of Green functions under shear can be calculated to first order in the shear rate \( \dot{\gamma} \). If the external fields in equation (37) are set to zero, this equation can be rewritten with the aid of equation (42) as:

\[ -\dot{\psi}_A(q, \omega) = -\psi_{AB}(q, \omega)B(q, \omega) + \theta_A(q, \omega) \]  

(63)

By introducing the time dependent wavevector \( q(t') = q - t' \dot{\gamma} q_y e_y \), one can solve this equation by means of the method of characteristics. One then encounters the following quantity:

\[
\psi_{AB}(q(t'), \omega) = \exp[-t' \dot{\gamma} q_y \frac{\partial}{\partial q_y}] \psi_{AB}(q, \omega)
\]

\[
= [1 - t' \dot{\gamma} q_y \frac{\partial}{\partial q_y} + O(\dot{\gamma}^2)][-i\Omega_{AB} + G_0^{-1}(q, \omega)]^{AB}
\]

\[
= G_0^{-1}(q, \omega)|^{AB} + 2i\dot{\gamma} q_y \Omega_{AB} - t' \partial_\omega G_0^{-1}(q, \omega)|^{AB} + O(\dot{\gamma}^2)
\]

(64)

where \( i\Omega_{AB} = 2\dot{\gamma} q_y \Omega_{AB} \). Note that \(-\dot{\gamma} q_y \partial_\omega G_0^{-1}(q, \omega)|^{AB} = -2i\dot{\gamma} q_y \partial_\omega G_0^{-1}(q, \omega)|^{AB} \), where \( \partial_\omega = q_y \partial / \partial q_y \), because \( G_0^{-1}(q, \omega)|^{AB} \) depends only on \( q_y \^2 \). Therefore, in writing

\[
\psi_{AB}(q(t'), \omega) = G_0^{-1}(q, \omega)|^{AB} + V^{AB}(q, \omega, t')
\]

(65)

one defines an interaction matrix \( V^{AB} \) that is first order in \( \dot{\gamma} \). In the following analysis, it is convenient to combine the method of characteristics with a (quantum mechanical) interaction picture. Defining

\[
A_I(t') = \exp[t' G_0^{-1}(q, \omega)]^{AB} B(q(t'), \omega)
\]

\[
V_{AB}(t') = \exp[t' G_0^{-1}(q, \omega)]^{AC} V^{CD}(q, \omega, t') \exp[-t' G_0^{-1}(q, \omega)]^{DB}
\]

\[
\theta_I(t') = \exp[t' G_0^{-1}(q, \omega)]^{AB} \theta^B(q(t'), \omega)
\]

equation (63) can be rewritten as:

\[
\partial_\omega A_I(t') = -V_{AB}(t') B_I(t') + \theta_{AB}(t')
\]

Since \( A(q, \omega) = A_I(0) \) and \( A_I(-\infty) = 0 \), one finds via integration with respect to \( t' \)

\[
A(q, \omega) = \int_{-\infty}^0 dt' \{ T \exp[- \int_{t'}^0 dt'' V_{AB}(t'')] \theta_I(t') \}
\]

(66)
where $T$ denotes time ordering. Next, one can identify:

$$G^A_B(q,\omega) = \int_{-\infty}^{0} dt' \{ T \exp[- \int_{t'}^{0} dt'' V^A_{t''} (t'')] \exp[t' G^{-1}_0(q,\omega)]^C_B \exp[-t' \frac{\partial}{\partial q_y}] \}$$

which is identical to equation (40). The interaction picture adopted here, however, has the advantage that the time ordering is not relevant if one only retains terms to linear order in $V^A_{t''}(t'')$, i.e. first order in the shear rate:

$$T \exp[- \int_{t'}^{0} dt'' V^A_{t''} (t'')] = \delta^{AC} - \int_{t'}^{0} dt'' V^A_{t''} (t'') + O(\dot{\gamma}^2)$$

Next, we note that the translation operator $\exp[-\dot{\gamma} q_x \frac{\partial}{\partial q_y}]$ acting on the noise $\theta^B(q,\omega)$ can also be written as $1 - 2\dot{\gamma} q_x \frac{\partial}{\partial q_y} + O(\dot{\gamma}^2)$, and the Green function $G^A_B(q,\omega)$ can be determined to first order in $\dot{\gamma}$ by carrying out the integrations with respect to $t'$ and $t''$. Note also that

$$\int_{-\infty}^{0} dt' \exp[t' G^{-1}_0(q,\omega)]^A_B \equiv G^A_B(q,\omega)$$

giving the correct zeroth-order contribution. To first order in $\dot{\gamma}$, one has to calculate integrals like

$$\int_{-\infty}^{0} dt' \int_{t'}^{0} dt'' G^{-1}_0(t'' \dot{\gamma} + t' \dot{\gamma}) G^{-1}_0 = G_0 \dot{\gamma}$$

From the considerations given above, it now follows that the Green functions have the following structure:

$$G^A_B(q,\omega) = G^A_0(q,\omega) + 2\dot{\gamma} q_x G^A_1(q,\omega) + O(\dot{\gamma}^2)$$

where $G^A_1(q,\omega)$ is given by the expression in equation (43). The dynamical response functions can be calculated in a similar fashion. The required modification is simply to replace in equation (63) the quantity $\theta^A(q,\omega)$ by $-\Lambda^A_0(q,\omega) \delta \dot{h}^B(q,\omega)$. This leads directly to $\chi^A_1(q,\omega)$ as given in equation (44).

References