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Theory of polymer relaxation times in semidilute solutions.
I : mode relaxation

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Abstract. — The rate at which the internal mode of motion of the strained polymer chains in semidilute solutions relaxes is calculated as a function of concentration. The excluded-volume and hydrodynamic interactions are taken into account. Gradual approach to the behavior of ideal chains due to the screening effect is demonstrated explicitly.

1. Introduction.

Over the years a large body of theoretical work has shaped our understanding of dynamic properties of semidilute polymer solutions. The first idea was due to des Cloizeaux [1]. He pointed out that the semidilute solutions of polymers are those solutions in which the polymer volume fraction is infinitesimally small, and yet polymer chains are sufficiently long. Even if the monomer density is infinitesimally small in the semidilute solutions, a specific chain overlaps with a significant number of other chains. Once chains overlap, it is likely that the chains start to entangle one another.

When chains overlap, the interactions within a chain and between two chains are interfered by the existence of the other chains. The static consequence is the screening of excluded-volume interactions, as was first pointed out by Edwards [2]. The concomitant dynamic feature, first imbibed by calculations of Freed and Edwards [3], is that the hydrodynamic interactions between monomers of polymer chains are also screened.

As a consequence, a theory of dynamic properties of semidilute polymer solutions should address itself to the complicated interplay of the gradual screening effect of both excluded-volume and hydrodynamic interactions and the effect of entanglements. For this reason the quantitative theory has met considerable difficulties, apart from a (more or less) successful elucidation of the asymptotic scaling behaviors [4]. In particular, the question of how the asymptotic scaling is attained as the degree of chain overlapping is varied has remained to be answered.

Theoretical analysis of such crossover behavior of dynamic properties has recently been launched, and in fact the gradual screening of both hydrodynamic and excluded-volume effects is revealed [5]. Comparison of this theoretical prediction with sedimentation (cooperative diffusion) data is made with credible agreement [6]. The entanglement constraint is also
incorporated in working out the explicit form of the crossover behavior of the self-diffusion coefficient [7] and the polymer viscosity [8].

Beside the above-mentioned dynamic quantities that have been studied so far, relaxation rates are another dynamic properties of great importance. The purpose of the present and subsequent paper is to examine the rate at which the disturbed polymer chain in semidilute solutions relaxes toward equilibrium. Our calculation of the relaxation rate explicitly shows the dependence on the degree of chain overlapping (which will be loosely referred to as concentration dependence).

Firstly in this paper we consider the relaxation time of the internal mode of motion of linear chains in semidilute solutions. In section 2 the internal mode relaxation time is defined. The theoretical problem is then reduced to calculating the equilibrium statistics of chain, namely the correlation function of conformation of a chain in solutions. In appendix, the correlation function is calculated with the aid of the renormalization-group method. With the result obtained there, the calculation of the mode relaxation time is completed to present an explicit formula for the relaxation time in terms of the overlap parameter. Section 3 checks the asymptotic scaling limit of this formula. We find that in the asymptotic semidilute limit both excluded-volume and hydrodynamic interactions are screened out completely, and that Rouse-like behavior is obtained. The overall concentration dependence to represent the crossover to this Rouse-like limit is presented in section 4.

Given the relaxation rate of the internal mode, we study the long-time scale relaxation process in the following companion paper [9], and the question of the entanglement effect is addressed.

2. Relaxation time of internal motion.

Deferring discussion of the relaxation of the global motion of chains to the subsequent paper [9], we shall here be concerned with the chain relaxation whose characteristic length scale is shorter than the size of the polymer chain. To represent such internal motions it is convenient to define the relaxation spectrum in terms of the specific viscosity, $\eta_{sp}$. To each $p$-th normal mode ($p = \text{integer}$) we may associate the mode relaxation time $\tau_p$ via the following relation [10] (in appropriate units):

$$\frac{\eta_{sp}}{\rho} = \frac{1}{N\eta_0} \sum_p \tau_p .$$

Here $N$ is the contour length of a chain and $\rho$ is the polymer monomer density, and $\eta_0$ is the bare solvent viscosity.

Starting from the time-dependent Ginzburg-Landau equations for semidilute polymer solutions, we have recently [5] calculated the effective specific viscosity $\eta_{sp}$ which is renormalized by the presence of many other chains and the solvent velocity field in the solutions. When the excluded-volume and hydrodynamic screening effects are taken into account, the specific viscosity is given by the following coupled equations with the wave-vector dependent monomer mobility, $\xi^{-1}(q)$:

$$\eta_{sp} = -\frac{\rho/\eta_0}{2d} \int_q \Phi(q) \xi^{-1}(q),$$

$$\xi^{-1}(q) = \xi_0^{-1} + d-1 \int_k \frac{S_1(k, q)}{\eta(k)},$$

$$\eta(k) = \eta_0 k^2 + \rho \int_q \frac{S_1(k, q)}{\xi^{-1}(q)} \quad (kR_G \approx 1),$$

for $q_i \approx \rho$.
where $k$ and $q$ are conjugate momenta to the spatial position vector, $r$, and the contour variable of the monomer, $\tau$, respectively; \[ \int_k = (2\pi)^d \int dk, \int_q = 2\pi \int dq, \] and $d$ is the spatial dimensionality. Let $c_j(\tau)$ denote the position of the $j$-th chain $(j = 1, \ldots, n)$ parametrized by the contour variable $\tau (0 \leq \tau < N)$. The variable $q$ is related to the mode index $p$ through $q = 2\pi p/N$. The functions $\Phi(q)$ and $S_1(k, q)$ are Fourier transforms of the equilibrium correlation functions \[ \langle [c_j(\tau) - c_j(\tau')]^2 \rangle \] and \[ \langle \delta(r - c_j(\tau)) \delta(r' - c_j(\tau')) \rangle, \] respectively, $V$ being the volume of the system. In equations (2.3) and (2.4), $\zeta_0$ denotes the bare friction coefficient per segment of the chain, and $R_G$ stands for the gyration radius of the chain. In the above equations, the many-chain character of the semidilute regime is reflected in the concentration dependence of the correlation functions $\Phi$ and $S_1$ of a single chain in semidilute solutions, rendering $\eta_{sp}$ and $\zeta^{-1}$ concentration dependent. We might emphasize that the above set of equations (2.2)-(2.4) has been obtained without incorporating the entanglement effect, which governs the global motion of chains. With $\eta_{sp}$ thus obtained, the internal mode relaxation time $\tau_p$ is properly determined from (2.1).

In determining $\tau_p$, we first notice that the region $kR_G \gg 1$ dominates the integral in (2.3), where [5]

\[ \eta(k) = \eta_0 (k^2 + \kappa^2), \] (2.5)

$\kappa^{-1}$ being the hydrodynamic screening length. Since in the semidilute regime the mode-coupling contribution (i.e., the second term in (2.3)) dominates the bare part, we have

\[ \eta_{sp}/\rho = -(d - 1)^{-1} \int_q \frac{\Phi(q)}{J(q)}, \] (2.6)

with

\[ J(q) = \int_k \frac{S_1(k, q)}{k^2 + \kappa^2}. \] (2.7)

Thus the $p$-th-mode relaxation time is given by

\[ \tau_p = \frac{-\eta_0 \Phi(q)}{d - 1 J(q)} = \frac{\eta_0}{d - 1} \int_k \frac{\left[ \nabla_k^2 S_1(k, q) \right]_{k = 0}}{S_1(k, q)/(k^2 + \kappa^2)} \] (2.8)

Here and throughout we neglect the chain end effect (1), and have thus assumed translational invariance of the correlation functions with respect to spatial positions in arriving at equation (2.8).

Thus we need to calculate the correlation function $S_1(k, q)$. This is done with the renormalization-group method. The calculation is a straightforward but tedious one, and is

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(1) Since we are concerned with the asymptotic limit $N \rightarrow \infty$ (note, however, that the overlap parameter $X$ [see (A.8)] can still take finite values in this limit), the upper integration limit of the integral over the contour variable is extended to infinity if it converges and the integrand over the extended region is negligible. See reference [3] for the use of this limiting procedure in the related context.
presented in appendix. As given by the appendix, it then follows that, to $O(\varepsilon = 4 - d)$,

$$\tau_p = \frac{\eta_0(N/2)^{d\nu}}{(d-1) p^2} \int_0^\infty \int_0^\infty dt \int_{Q^2/(Q^2 + k^2)} \int_{J(Q, \pi)} S(Q, t; X) \cos (2 \pi pt)$$

(2.9)

Here $\kappa^{-1}$ is the scaled hydrodynamic screening length, $\kappa = \kappa (N/2)^{\nu}$, $\nu$ being the excluded-volume exponent; $\nu = (1/2)(1 + \varepsilon/8)$. The functions in the integrands are given as follows:

$$\tilde{\phi}(t; X) = 2 \nu (2 \nu - 1) e^{\varepsilon \nu/8} \tilde{\phi}(t; X),$$

(2.10)

where

$$\tilde{\phi}(t; X) = t^{2\nu - 2} \left[ 1 - \frac{2}{d\nu - 1} t X F(2 t (X + 1)) \right],$$

(2.11)

with

$$F(a) \equiv (2 \nu + 1) f_0(a) + \left( 2 + \frac{1}{\nu} \right) f_1(a) + \frac{1}{2 \nu} f_2(a),$$

(2.12)

$$f_0(a) = \frac{a(a - 2)}{(a - 1)^2} \ln a - \frac{a - 3}{2(a - 1)^2} - \frac{1}{2} e^a \text{Ei}(-a),$$

$$f_1(a) = \frac{-a(a^2 - 2 a - 2)}{(a - 1)^4} \ln a + \frac{3 a(a - 3)}{2(a - 1)^3} - \frac{1}{2} - \frac{a}{2} e^a \text{Ei}(-a),$$

$$f_2(a) = \frac{2 a^2(a^2 - 2 a - 5)}{(a - 1)^5} \ln a - \frac{2 a(a^2 - 7 a - 1)}{(a - 1)^4} + \frac{1}{2} - \frac{a}{2} e^a \text{Ei}(-a),$$

and

$$S(Q, t; X) = e^{-P_s^2} \exp \left[ -\frac{\varepsilon}{2 \pi} G(Q, t; X) \right],$$

(2.13)

where

$$G(Q, t; X) = \int_0^\infty dk \int_0^\pi d\theta k^3 \sin^2 \theta \left\{ \left[ \frac{k^2 + 2 t}{k^2 + a} \right] \left( J_1(k^2 - 2 P_s k \cos \theta) - \frac{1}{1 + k^2} \right) + \frac{e^{-k^2} (e^{2 P_s k \cos \theta} - 1)}{k^4} - \frac{4 P_s^2 k^2 \cos^2 \theta}{(1 + k^2)^3} \right\}. \tag{2.14}$$

In the above, $\zeta' = 2 - \gamma + \ln \pi$, $\gamma$ being Euler's constant ($\gamma = 0.5772..$), and $\text{Ei}(-a)$ is the exponential-integral function defined by $\text{Ei}(-a) = - \int_a^\infty dx e^{-x}/x$. The so-called overlap parameter is denoted by $X$ and is defined by (A.8); it may be roughly interpreted as the number of chains overlapping with a specific chain. Also in (2.13) we have put $P_s = \sqrt{c_s t^\nu Q}$, $c_s = 1 + \varepsilon (1/2 - \gamma + \ln \pi)/8$, and $a = 2 t (X + 1)$; the function $J_1(z)$ is defined by (A.6).

\footnote{When one takes the limit $\varepsilon \to 0$ of (2.9), it is to be understood that one puts $\nu \to 1/2$ at the last step of calculation.}
As is evident, the expression (2.9) is quite involved, and this is as far as we can go analytically in general. For Gaussian chains, however, we can carry through the integrals on the rhs of (2.9). In so doing, we first identify the Gaussian-chain case with the \( u^* \to 0 \) limit of (2.9), as is usually done in the renormalization-group theory [11]; \( u^* \) is the fixed-point value of the strength of the excluded-volume interaction. Then we find that

\[
\tau_p^G = \frac{\eta_0 (N/2)^{d/2}}{\pi \rho^2} \frac{\hat{\kappa}^3 + (2 \pi \rho)^2}{\hat{\kappa}^4 + \sqrt{2 \pi \rho (2 \pi \rho - \hat{\kappa}^2)}},
\]

(2.15)

where the superscript \( G \) indicates the case of Gaussian chains.

Before proceeding to numerically evaluating (2.9) for the general case, we study in the next section the asymptotic behavior of the result (2.9).

3. Asymptotic scaling.

For the purpose of scaling argument in semidilute solutions, it is convenient to introduce two overlap parameters, static and dynamical [5]:

\[
X = 4 \, c\, u^* (N/2)^{d/2}, \quad Y = 4 \, c\, \zeta^* (N/2)^{d/2},
\]

(3.1)

where \( c \equiv \rho/N \) is the polymer number density; \( \zeta^* \) is the fixed-point value associated with the coupling constant of the hydrodynamic interaction. We shall first consider the asymptotic limit of the Gaussian-chain case:

i) Gaussian-chain solutions \( (X = 0) \).

In the limit of dilute solution, i.e., \( Y \to 0 \) for the Gaussian-chain case, \( \hat{\kappa} \) tends to zero. We find from (2.15) that for \( d = 3 \)

\[
\tau_p^G \sim N^{3/2}
\]

(3.2)

The familiar Rouse-Zimm behavior is recovered as required. In the opposite limit (the semidilute limit), \( Y \to \infty \), we know [5] that \( \hat{\kappa} \sim Y \) at \( d = 3 \), so that

\[
\tau_p^G \sim \rho \, N^2
\]

(3.3)

We obtain the Rouse-like behavior in the semidilute limit due to the complete screening of the hydrodynamic interaction.

ii) Self-avoiding chains.

Similarly, for good-solvent solutions the asymptotic limits can be extracted from (2.9). For the dilute limit of \( X, \, Y \to 0 \),

\[
\tau_p \sim N^{d/2},
\]

(3.4)

thus reproducing the nondraining result. On the other hand, in the semidilute limit \( (X, \, Y \to \infty) \), the numerator and the denominator of the rhs of (2.9) behave as \( X^{-c/8} \) and \( \hat{\kappa}^{(p-1)/p} \), respectively. Since \( \hat{\kappa} \sim Y^{c/(d-1)} \) in this limit [5], we find

\[
\tau_p \sim \rho^{-(d/2 - 2)(d-1)} \, N^2
\]

(3.5)

It is easy to prove that the result (3.4) is in accord with the scaling hypothesis for \( \tau_p \). Again Rouse-like behavior emerges in the semidilute limit since in this case both excluded-volume interactions and hydrodynamic interactions become totally screened out.
Having thus confirmed that the result (2.9) captures the correct scaling behavior of the relaxation time asymptotically, we now demonstrate the actual crossover.

4. Numerical result and discussion.

As we are interested in the universal structure of the relaxation times which is independent of microscopic details of the system, we first construct a universal ratio from (2.9). Namely, we take up the ratio of (2.9) to its dilute limit. Moreover, in the same spirit, we set \( p = 1 \) to consider only the primary relaxation time, \( \tau_1 \). Then the universal ratio associated with \( \tau_1 \) is deduced from (2.9) as

\[
\frac{\tau_1}{\tau_1^D} = \frac{\int_0^\infty dt \cos (2 \pi t) \int_0^\infty dQ \int_0^\infty d\tau S_D(Q, t) \cos (2 \pi t)}{\Gamma(2 \nu - 1) \sin (\nu \pi) (2 \pi)^{1 - 2 \nu} \int_0^\infty dQ \int_0^\infty d\tau [Q^2/(Q^2 + \hat{\kappa}^2)] S(Q, t; X) \cos (2 \pi t)},
\]

(4.1)

where \( S_D(Q, t) = S(Q, t; 0) \), and \( \tau_1^D \) is the dilute limit counterpart of \( \tau_1 \), \( \Gamma(z) \) being the Gamma function. For the Gaussian-chain solution, the universal ratio is immediately reduced from (2.15) to be

\[
\frac{\tau_1^G}{\tau_1^{GD}} = \frac{\hat{\kappa}^4 + 4 \pi^2}{2 \sqrt{\pi} [\hat{\kappa}^3 + \sqrt{\pi} (2 \pi - \hat{\kappa}^2)]}
\]

(4.2)

With the screening length \( \hat{\kappa}^{-1} \) already obtained in reference [5] as a function of the overlap parameter \( X \), we have evaluated (4.1) numerically by setting \( \nu = 4 - d = 1 \). The result is illustrated in figure 1. The upper curve in the figure represents the Gaussian case (4.2), where the abscissa should be interpreted as \( Y/4 \). The figure clearly demonstrates that as the hydrodynamic screening effect (along with the static screening effect) prevails, the gradual crossover from the nondraining to ideal behavior occurs with the increase of concentration.

Before closing the paper, several comments are in order. In this paper, the relaxation time of the internal mode for semidilute solutions is calculated without taking account of the entanglement effect. This effect should be negligible for the internal motion whose characteristic length scale is much shorter than the size of the polymer chain. For larger length scales, however, the entanglements present are expected to be relevant. Therefore, one should regard the foregoing arguments in this paper, and the results (4.1) and (4.2) in particular, as being the ones for a more or less fictitious case without entanglements that enables one to assess the entanglement effect. The entanglement effect is incorporated into the theory in paper II.

In this connection, it is important to note that we have obtained the ideal chain behavior in the limit \( X (\infty Y) \rightarrow \infty \) (which we have termed the semidilute limit) while keeping the strength of excluded-volume interactions fixed nonzero at \( u^* \). This is because the screening renders the net swelling to vanish in the semidilute limit even if \( u^* \neq 0 \). Put in other words, the semidilute limit does not imply \( u^* \rightarrow 0 \) but the correlation length \( \rightarrow 0 \). The fact \( u^* \neq 0 \) ensures that polymer chains cannot pass through each other, thus fulfilling the correct condition of topological constraint, i.e., entanglement. Therefore, although as far as static properties are concerned the semidilute limit may be studied with a Gaussian chain model (for which \( u^* = 0 \)), the dynamics is different from that of Gaussian chains. This distinction becomes important when we consider the solution viscosity or the longest relaxation time by incorporating the entanglement effect.
We stress that in semidilute solutions the monomer density $\rho$ is infinitesimally small, so that $\rho$ is not a natural variable. (We have used it in Sect. 3 only for convenience sake of comparison with other related work.) For static quantities, we now know that the good parameter is the overlap parameter $X$, which is proportional to $\rho N^{d_x-1}$. There is a dynamical counterpart of $X$, also proportional to $\rho N^{d_x-1}$. Namely, it is the so-called dynamical overlap parameter $Y$ defined by (3.1). The latter parameter becomes particularly important when one considers the dynamics of Gaussian-chain solutions, for which $X = 0$ by definition. The presence of this fundamental parameter in the description of the semidilute solution dynamics has not received due attention in the literature except for reference [12].

The fourth remark to be observed is that the viscosity formula (2.2) is extracted from the dressed equation for the solvent viscosity [5]. Hence it does not contain the pure solute contribution to the solution viscosity. For this reason the relaxation time defined via our $\eta_{sp}$ does not yield at infinite dilution a scaling of the form $\tau_p \sim N^{\nu (2 + \nu^{-1})}$ as found in reference [13].

Finally, we note that Muthukumar [14] calculated the internal mode relaxation time from (2.2)-(2.4) by a different method. Without repeating the comment on his formulation, which has been given elsewhere [5], we just point out the internal inconsistency of this theory. The results were obtained by assuming that the hydrodynamic interaction is screened for the characteristic length scales of the internal motion. Therefore, for his theory to be consistent, it is required that $\kappa^{-1} \ll R_G^0$, where $R_G^0$ is the radius of gyration at infinite dilution. On the other hand, we find the screening length in his theory to scale as $\kappa^2 \sim X (R_G^0)^{-2}$, because, using his notations, $cA p^{-\kappa} \sim X$. Apparently the above two relations are incompatible because his theory is valid only in the region where $X \ll 1$. 

**Fig. 1.** — Ratio of the primary mode relaxation time $\tau_1$ to its dilute limit against the overlap parameter $X$. The upper curve represents the polymer solution when no excluded-volume interaction is present.
Acknowledgements.

I am indebted to Phil Baldwin for the clarifying comments on this work through a great deal of correspondence.

Appendix.

In this appendix we calculate the correlation function \( \langle \delta (r - c_j(\tau)) \delta (r' - c_j(\sigma)) \rangle \) with the renormalization-group method [11] to derive equations (2.9)-(2.14).

The Hamiltonian with which we take the canonical average \( \langle \cdots \rangle \) is the so-called Edwards' Hamiltonian [15]:

\[
H(\{c\}) = \frac{1}{2} \sum_{j=1}^{n} \int_{0}^{\infty} d\tau \left[ \frac{dc_j(\tau)}{d\tau} \right]^2 + \frac{v}{2} \sum_{j, \ell} \int d\tau \int d\sigma \delta (c_j(\tau) - c_{\ell}(\sigma)).
\]  

(A.1)

The parameter \( v \) represents the strength of the repulsive excluded-volume interaction. The important static behavior in the semidilute solutions arises from the gradual screening of the excluded-volume effect with the increase of concentration. We must therefore have a systematic formal procedure for capturing this static screening effect. For that purpose there exists the now-familiar formalism [16], to which the reader is referred for details.

It is convenient to consider the Fourier transform (in space) defined by (neglecting end effects)

\[
\tilde{h}(k, \sigma) = \int d(r - r') e^{ik \cdot (r - r')} \delta (r - c_j(\tau + \sigma)) \delta (r' - c_j(\tau)) \langle \cdots \rangle.
\]

(A.2)

We may also define the function \( \tilde{G}_0(k, \sigma) \) by

\[
\tilde{G}_0(k, \sigma) = \int d(r - r') e^{ik \cdot (r - r')} \delta (r - c_j(\tau + \sigma)) \delta (r' - c_j(\tau)) \langle \cdots \rangle_0,
\]

(A.3)

where the average \( \langle \cdots \rangle_0 \) is taken with the Gaussian Hamiltonian, i.e., with respect to the first term of the rhs of (A.1). We can then develop a diagrammatic formalism for calculating \( \hat{h}(k, \sigma) \) to lowest order in \( v \) is shown in figure 2. Diagrams are constructed with \( \tilde{G}_0 \) as a bare propagator and \( v \) as an interaction line. Intermediate lines are integrated; particularly, for contour positions the integration range may be extended to infinities when appropriate, since we are always interested in the translationally symmetric case.

After performing simple integrals, we then find

\[
\tilde{h}(k, \sigma) = e^{-K^2} - (2\sigma)^d \sigma^2 \int_L v_s(\sqrt{2/\sigma L}) \left\{ \left( 1 + 2L^{-2} \right) e^{-K^2} \times \right. \\
\quad \left. \times \left[ J_1([K - L]^2 - K^2) - J_1(L^2) \right] + L^{-4}[e^{-|K - L|^2} - e^{-(K^2 + L^2)}] \right\},
\]

(A.4)

with \( \int_L = (2\pi)^{-d} \int dL \), and

\[
v_s(p) = \frac{v}{1 + X_0 J_2(Np^2/2)}
\]

(A.5)
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understood to be renormalized variables. Accordingly, we denote the renormalized
\( \tilde{h}(k, \sigma) \) as \( S(Q, t; X) \) with \( t = \sigma/N \).

Then we find, to \( O(\epsilon = 4 - d) \),
\[
S(Q, t; X) = e^{-p^2} \left[ 1 - \frac{u^*}{4 \pi^2} \left( \frac{1}{2} - \gamma + \ln \pi \right) \right. \\
- 4 u^* \int L \left[ \frac{2 + t^{-1} L^2}{2 + 2 X + t^{-1} L^2} Y(\hat{P}, L) - \frac{4(\hat{P} \cdot L)^2}{(1 + L^2)^3} \right] \right], \quad (A.9)
\]

where
\[
Y(\hat{P}, L) = \left( 1 + \frac{2}{L^2} \right) \left[ J_1(L^2 - 2(\hat{P} \cdot L)) - \frac{1}{1 + L^2} \right] + e^{-L^2}(e^2 \hat{P} \cdot L - 1) \gamma L^4, \quad (A.10)
\]

with \( \hat{P} = t^\nu Q, \nu = (1/2)(1 + \epsilon/8) \) and \( u^* = (\pi^2/2) \epsilon \). In (A.9) the integral is now over four
dimensional space, and \( \gamma \) is the Euler's constant, \( \gamma = 0.5772.. \) Finally, the correction of order \( \epsilon \) may be exponentiated to yield (2.13) in the main text.

Substituting the expression (note that the upper limit of the contour integration is extended to
infinity due to our approximation of neglecting chain end effects)
\[
S_1(k, q) = 2 N \int_0^\infty dt \cos(2\pi pt) S(Q, t; X) \quad (A.11)
\]
in (2.8), and performing an integration by parts in the numerator yields (2.9) with
\( \delta(t; X) = -(1/2) \partial^2\left[ V_0 S(Q, t; X) \right]_Q = \partial \vec{r}^2; \) with (2.13) inserted, \( \delta \) is easily evaluated, and finally follows (2.10).

References

[10] SAITO N., Introduction to Polymer Physics (Syokabo, Tokyo, 1971);