Theory of field-gradient NMR diffusometry of polymer segment displacements in the tube-reptation model

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The spin-echo attenuation in NMR field-gradient diffusometry experiments is treated for the tube model in a time scale longer than the entanglement time τ_e. The theory comprises the Doi-Edwards [M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics* (Clarendon, Oxford, 1986)] limits of the (anomalous) segment displacement as well as the (ordinary) center-of-mass diffusion. This formalism is to be distinguished from formalisms for anomalous diffusion on fractal networks: The reptation mechanism implies an intrinsically different character of the displacement probability density. It is shown that the expressions usually applied in NMR diffusometry are inadequate for the reptation problem and can cause misinterpretations. Applications of the formalism to polymer chains in bulk and confined in porous media are discussed.

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INTRODUCTION

Depending on the time limit, the mean-square displacement of segments of entangled polymers is predicted to obey certain anomalous power laws as concerns the variation of the diffusion time, that is, $\langle r^2\rangle = \alpha t^\kappa$, where $0 < \kappa \leq 1$ and α is a constant. The most prominent theory in this context is the reptation-tube model [1, 2]. Characteristic time constants, the entanglement time τ_e, the (longest) Rouse relaxation time τ_R, and the tube disengagement time τ_d, were introduced. The exponents predicted in the frame of the tube model are $\kappa = 1/2$ for $t < \tau_e$, $\kappa = 1/4$ for $\tau_e < t < \tau_R$, $\kappa = 1/2$ for $\tau_R < t < \tau_d$, and $\kappa = 1$ for $t > \tau_d$.

The limits leading to root-mean-square displacements greater than 100 Å in diffusion times $t < 1$ s, as they are typical for field-gradient NMR diffusometry [3–5], are principally accessible by this technique [6–8]. It is therefore important to know how the predicted time dependences reveal themselves in such experiments.

In pulsed-gradient experiments, spin echoes are attenuated by diffusion according to the incoherent dynamical structure factor, that is, the ensemble average

$$A_{\rm diff}(k^2,t) = \langle \exp\{i\mathbf{k}\cdot\mathbf{r}(t)\}\rangle_{\mathbf{r}}\,. \tag{1}$$

In this expression, a wave vector $\mathbf{k} = \gamma\delta\mathbf{G}$ has been defined formally. The quantity γ is the gyromagnetic ratio, δ is the width of the field-gradient pulses, $t \gg \delta$ is the effective diffusion time between the gradient pulses, and $\mathbf{G}$ is the gradient of the magnetic flux density during the gradient pulses. The segment displacement $\mathbf{r}(t)$ during t may be analyzed into $\mathbf{r}(t) = \mathbf{r_g}(t) + \bar{\mathbf{r}}(t)$, where $\mathbf{r_g}(t)$ is the displacement of the center of gravity of the polymer chain and $\bar{\mathbf{r}}(t)$ is the segment displacement relative to a reference frame fixed in the center of gravity. In the limit $t \ll \tau_d$, $\bar{\mathbf{r}}(t)$ essentially is the segment displacement in the initial tube.

Center-of-gravity diffusion follows Fick's law, whereas segment displacements in the tube do not. As the two displacement contributions are uncorrelated, we may factorize Eq. (1), resulting in

$$\begin{aligned} A_{\rm diff}(k^2,t) &= \langle \exp\{i\mathbf{k}\cdot\bar{\mathbf{r}}(t)\}\rangle_{\bar{\mathbf{r}}}\,\langle \exp\{i\mathbf{k}\cdot\mathbf{r_g}(t)\}\rangle_{\mathbf{r_g}} \\ &= \tilde{A}_{\rm diff}(k^2,t)\exp\{-k^2Dt\}, \end{aligned} \tag{2}$$

where $\tilde{A}_{\rm diff}(k^2,t) = \langle \exp\{i\mathbf{k}\cdot\bar{\mathbf{r}}(t)\}\rangle_{\bar{\mathbf{r}}}$ and D is the center-of-gravity diffusion coefficient. The problem is now to find an expression for the attenuation factor for segment diffusion in the tube.

SEGMENT DIFFUSION IN THE TUBE-REPTATION MODEL

The segment displacement in the Euclidean space $\bar{\mathbf{r}}(t)$ is connected with a displacement $s(t)$ measured in curvilinear coordinates along the tube. That is, the end-to-end vector of the curvilinear path of length $s(t)$ is given by $\bar{\mathbf{r}}(t)$. Assuming a Gaussian probability density for the end-to-end vector of a given path length $s(t)$, we find

$$\begin{aligned} \tilde{A}_{\rm diff}(k^2,t) &= \left\langle \int \left(\frac{2\pi}{3}a|s(t)|\right)^{-3/2} \right. \\ &\quad \left. \times \exp\left\{-\frac{3\bar{r}^2}{2a|s(t)|}\right\}\exp\{i\mathbf{k}\cdot\bar{\mathbf{r}}\}\,d^3\bar{\mathbf{r}} \right\rangle_s \\ &= \left\langle \exp\left\{-\frac{1}{6}k^2a|s(t)|\right\}\right\rangle_s , \end{aligned} \tag{3}$$

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where a is the step length of the primitive path [2]. For $t \ll \tau_d$ the curvilinear segment displacements may be considered as the result of a one-dimensional ordinary diffusion process, i.e., they are distributed according to a Gaussian probability density. Hence

$$\begin{aligned}\tilde{A}_{\rm diff}(k^2,t) &= \int_{-\infty}^{\infty} [2\pi\langle s^2(t)\rangle]^{-1/2} \exp\left\{-\frac{s^2}{2\langle s^2(t)\rangle}\right\} \\ &\quad\times \exp\left\{-\frac{1}{6}k^2 a|s(t)|\right\} ds \\ &= \exp\left\{\frac{k^4a^2\langle s^2(t)\rangle}{72}\right\} \\ &\quad\times \mathrm{erfc}\left\{\frac{k^2 a\sqrt{\langle s^2(t)\rangle}}{6\sqrt{2}}\right\}. \end{aligned} \tag{4}$$

MEAN-SQUARE CURVILINEAR DISPLACEMENT

The mean-square curvilinear segment displacement is given by [2]

$$\begin{aligned}\langle s^2(t)\rangle &= 2\frac{D_0}{N}t + \frac{2Nb^2}{3\pi^2}\sum_{p=1}^{\infty}\frac{1}{p^2}\left(1-\exp\left\{-\frac{tp^2}{\tau_R}\right\}\right) \\ &\approx 2\frac{D_0}{N}t + \frac{2b\sqrt{D_0 t}}{\sqrt{3\pi}+18\frac{\sqrt{D_0 t}}{Nb}}, \end{aligned}\tag{5}$$

where $D_0 = k_B T/\zeta$ is the monomeric diffusion coefficient. ζ is the friction constant of a Kuhn segment of length b. The polymer chain is assumed to be composed of N Kuhn segments. The approximation implies the correct limits for $t \ll \tau_R$ and $t \gg \tau_R$ (see [2]).

Equation (5) is valid in the limit $t \ll \tau_d$. In the opposite limit, that is, $t \gtrapprox \tau_d \gg \tau_R$, the treatment of the mean-square curvilinear segment displacement can be considered as a one-dimensional restricted-diffusion problem with reflecting boundaries at curvilinear tube coordinates $x_s = 0$ and $x_s = L \approx L_t$, where L_t is the tube length. The free-diffusion length L depends on the position of the considered segment in the tagged chain. Let $P(x_s, x_{s0}, t)$ be the probability density that the segment is at a position x_s at time t if it was at the position x_{s0} at time 0. The diffusion equation

$$\frac{\partial}{\partial t}P(x_s,x_{s0},t) = \frac{D_0}{N}\frac{\partial^2}{\partial x_s^2}P(x_s,x_{s0},t) \tag{6}$$

must be solved for the boundary conditions

$$\frac{\partial}{\partial x_s}P(x_s,x_{s0},t)|_{x_s=0,L} = 0. \tag{7}$$

The solution is

$$\begin{aligned}P(x_s,x_{s0},t) &= \frac{1}{L} + \sum_{p=1}^{\infty}\frac{2}{L}\cos\left(\frac{\pi}{L}px_s\right)\cos\left(\frac{\pi}{L}px_{s0}\right) \\ &\quad\times\exp\left\{-\left(\frac{\pi}{L}p\right)^2\frac{D_0}{N}t\right\}. \end{aligned}\tag{8}$$

The mean-square curvilinear displacement is then

$$\langle s^2(t)\rangle = \int_0^L dx_s \int_0^L \frac{dx_{s0}}{L}(x_s - x_{s0})^2 P(x_s,x_{s0},t). \tag{9}$$

Combining Eqs. (8) and (9) leads to

$$\begin{aligned}\langle s^2(t)\rangle &= \left(\frac{4L}{\pi^2}\right)^2 \sum_{p\,\mathrm{odd}}\frac{1}{p^4}\left[1-\exp\left\{-\left(\frac{\pi p}{L}\right)^2\frac{D_0}{N}t\right\}\right] \\ &\approx \frac{2\frac{D_0}{N}t}{1+\frac{12D_0 t}{NL^2}} \qquad (10)\\ &= \begin{cases} 2\frac{D_0}{N}t & \text{if } t \ll \frac{L^2N}{\pi^2 D_0} \propto \tau_d \\ \frac{L^2}{6} & \text{if } t \gg \frac{L^2 N}{\pi^2 D_0} \propto \tau_d. \end{cases} \qquad (11)\end{aligned}$$

The latter formulas are valid in the limit $t \gg \tau_R$. An expression of the mean-square curvilinear segment displacement in the whole time range of interest is obtained by combining the second term of Eq. (5) and Eq. (10), that is,

$$\langle s^2(t)\rangle = \frac{2\frac{D_0}{N}t}{1+\frac{12D_0t}{NL^2}} + \frac{2b\sqrt{D_0 t}}{\sqrt{3\pi}+18\frac{\sqrt{D_0 t}}{Nb}}. \tag{12}$$

SPIN-ECHO ATTENUATION

According to Eqs. (2) and (4), the total spin-echo attenuation factor is

$$\begin{aligned}A_{\rm diff}(k^2,t) &= \exp\left\{\frac{k^4a^2\langle s^2(t)\rangle}{72}\right\} \\ &\quad\times\mathrm{erfc}\left\{\frac{k^2a\sqrt{\langle s^2(t)\rangle}}{6\sqrt{2}}\right\}\exp\{-k^2Dt\}, \end{aligned}\tag{13}$$

where $\langle s^2(t)\rangle$ is given by Eq. (12). Let us now determine the quantity L. In the limit $t \gg \tau_d$, $k \to 0$, Eq. (1) may be approximated by

$$A_{\rm diff}(k^2,t) = \exp\left\{-\frac{1}{6}k^2\left(2R_g^2 + 6Dt\right)\right\}, \tag{14}$$

where $R_g = Nb^2/6$ is the radius of gyration. Equation (13) may be approximated in the same limit by

$$A_{\rm diff}(k^2,t) = \exp\left\{-\frac{1}{6}k^2\left(\sqrt{\frac{2}{\pi}}a\sqrt{\langle s^2(t)\rangle}+6Dt\right)\right\}, \tag{15}$$

where we have used the approximation $\mathrm{erfc}(x) \approx 1 - 2x/\sqrt{\pi} \approx \exp\{-2x/\sqrt{\pi}\}$, which is valid for $x \ll 1$.

Equations (14) and (15) must become identical in the limit $t \gg \tau_d$. That is,

$$\sqrt{\frac{2}{\pi}}k^2a\sqrt{\langle s^2(t)\rangle} = k^2 2R_g^2 = \frac{1}{3}Nb^2k^2. \tag{16}$$

Using Eq. (11), we find

$$\sqrt{\frac{2}{\pi}}a\sqrt{\frac{L^2}{6}} = \frac{1}{3}Nb^2 \tag{17}$$

so that

$$L = \sqrt{\frac{\pi}{3}}\frac{Nb^2}{a} = \sqrt{\frac{\pi}{3}}L_t \approx L_t, \tag{18}$$

where $L_t = Nb^2/a$ [2]. The final result of the spin-echo attenuation by segment diffusion in the reptation-tube model is

$$A_{\text{diff}}(k^2,t) = \exp\left\{\frac{k^4a^2\langle s^2(t)\rangle}{72}\right\} \times \text{erfc}\left\{\frac{k^2a\sqrt{\langle s^2(t)\rangle}}{6\sqrt{2}}\right\}\exp\{-k^2Dt\}, \tag{19}$$

$$\langle s^2(t)\rangle = \frac{2\frac{D_0}{N}t}{1+\frac{12D_0t}{NL_t^2}} + \frac{2b\sqrt{D_0t}}{\sqrt{3\pi}+18\frac{\sqrt{D_0t}}{Nb}}, \tag{20}$$

where $D_0 = k_BT/\zeta$, $L_t = Nb^2/a$, $D = D_0N_e/(3N^2)$, $a = b\sqrt{N_e}$, and N_e is the number of Kuhn segments corresponding to the step length a of the primitive path.

DISCUSSION

In the limit $t \gg \tau_d$, the factor $\exp\{-k^2Dt\}$ dominates. The spin-echo attenuation curve then corresponds to ordinary diffusion of the center of gravity. The opposite limit $t \ll \tau_d$ is connected with anomalous (segment) diffusion, i.e., the above factor virtually does not vary in this time scale. The spin-echo attenuation is then governed by

$$A_{\text{diff}}(k^2,t) = \exp\left\{\frac{k^4a^2\langle s^2(t)\rangle}{72}\right\}\text{erfc}\left\{\frac{k^2a\sqrt{\langle s^2(t)\rangle}}{6\sqrt{2}}\right\} \approx \begin{cases} 1-\sqrt{\frac{2}{\pi}}\frac{k^2a\sqrt{\langle s^2(t)\rangle}}{6} & \text{if } \frac{k^2a\sqrt{\langle s^2(t)\rangle}}{6\sqrt{2}} \ll 1 \\ 6\sqrt{\frac{2}{\pi}}\frac{1}{k^2a\sqrt{\langle s^2(t)\rangle}} & \text{if } \frac{k^2a\sqrt{\langle s^2(t)\rangle}}{6\sqrt{2}} \gg 1, \end{cases} \tag{21}$$

where we have used the approximations $\text{erfc}(x) \approx 1 - 2x/\sqrt{\pi}$ for $x \ll 1$ and $\text{erfc}(x) \approx \exp\{-x^2\}/(x\sqrt{\pi})$ for $x \gg 1$. Equation (21) implies the situations expected for region II, that is, $\tau_e \ll t \ll \tau_R$, and region III, that is, $\tau_R \ll t \ll \tau_d$, of the tube-reptation model [2]. For region II, we must set $\langle s^2(t)\rangle \approx 2b\sqrt{D_0t}/\sqrt{3\pi}$, whereas $\langle s^2(t)\rangle \approx 2D_0t/N$ in region III. The latter corresponds to a result following from the argument in [9] after correction of some errors in that reference.

Spin-echo attenuation by anomalous diffusion has also been discussed in [10]. In this work a Gaussian propagator for Euclidean-space displacements has been assumed. However, this assumption is not adequate for the situation in the tube-reptation model: Here the curvilinear displacements inside the tube have a Gaussian character [1, 2], whereas the Euclidean-space displacements strongly deviate from this behavior. Therefore, attempts to apply the formalism of Ref. [10] to cases where the tube-reptation model is assumed to be adequate necessarily must lead to misinterpretations.

The spin-echo attenuation in entangled polymer melts and solutions indicates anomalous behavior in the short time-displacement regime [6–8, 11]. In [12] it was concluded from field-gradient NMR data that the strict reptation picture does not apply. However, in that study a Gaussian propagator was used for the evaluation. If the correct formalism presented above had been employed, the discrepancy of the experimental finding from the predictions of the reptation-tube model would even be worse.

An evaluation attempt on this basis was published in [7]: Although experimental data measured with polydimethylsiloxane melts with different molecular weights and in different time scales can be well described on this basis, the fitted parameters a and b turned out to be too large by more than one order of magnitude to be in reasonable agreement with the reptation-tube model.

Furthermore, the results of field-cycling NMR relaxometry [13, 14] strongly favors the validity of the renormalized Rouse theory [15]. These studies refer to the limit of short times, but also show that some basic assumptions of the Doi-Edwards tube model are not compatible with experimental results. Beyond the short time limit where the renormalized Rouse theory applies very well, the correct representation of the dynamics of entangled polymer chains is still an open question.

On the other hand, polymers confined in a network of narrow pores such as porous glass appear to behave as predicted by the original reptation model so far one can judge from field-cycling NMR relaxometry [16]. Spin-echo attenuation experiments to which the above formalism is expected to be applicable are in progress.

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