Brownian dynamics simulation of charged dendrimers

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INTRODUCTION

In recent years, dendrimers have been drawing much attention because of their unusual properties, which are due to their structure. Most water-soluble dendrimers contain charged groups, usually terminal ones. Therefore, the behavior of charged dendrimers in solution is especially interesting. Ionized dendrimers have numerous practical applications, mostly related to the use of host–guest systems (e.g., as nanocontainers for the transport of medicines, proteins, etc.).

Most theoretical works investigate the equilibrium properties of dendrimers. Welch and Muthukumar [5, 6] studied certain equilibrium statistical properties of charged dendrimers using Monte Carlo computer simulation. At present, studies concerning the dynamic properties of charged dendrimers are virtually absent. However, the mobility of dendrimers largely determines their practical use. Kabanov and coworkers [7, 8] experimentally investigated charged dendrimers in solution and the formation of complexes between them and oppositely charged linear chains. The dynamic properties of dendrimers are being studied using small-angle neutron scattering experiments, NMR, etc. [9–12].

There are but a few theoretical works concerning the dynamics of neutral dendrimers in solution [13–15]. Most of them use the Rouse model for spacers, i.e., linear chain segments between the branching points of the dendrimer. The Rouse model assumes that spacers are flexible and fairly long compared to the bond length. However, spacers in real dendrimers contain only a few monomers and possess a fairly high rigidity. The second frequent simplification, which was used, e.g., by Cai and Chen [13], is neglect of excluded-volume interactions. This neglect is justified for describing the dynamic properties of linear polymers in solution. But, as was shown in a number of theoretical works and computer simulations, consideration of these interactions for dendrimers fundamentally changes the equilibrium properties and structure of the dendrimer [14, 16–19]. One may expect that excluded-volume interactions also significantly affect the dendrimer dynamics. The dynamics of linear chains in solution is known to be also notably affected by hydrodynamic interactions that are due to a partial entrainment of the solvent by the moving polymer.

An analytical solution of motion equations with explicit allowance for excluded-volume, electrostatic, and hydrodynamic interactions is virtually impossible to attain. To avoid these difficulties, Chen and Cai [14] used the approximation of preaveraged hydrodynamic interactions. Various configurations of a dendrimer were constructed using the Monte Carlo technique. Excluded-volume interactions between the monomers were specified by the hard-sphere model. The diffusion coefficients were calculated, as well as various time autocorrelation functions characterizing the dynamics of dendrimers of various generations. However, those authors themselves admit that the linearized version of the Langevin equation used in their work produces erroneous results in describing the dynamics of dendrimer size fluctuations.
We know only a few direct computer simulations of dynamic properties of uncharged dendrimers. Murat and Grest [18] studied a model of neutral dendrimers of generations \( g = 5–8 \) in solutions of various qualities using the method of molecular dynamics (MD). They mostly paid attention to investigations of equilibrium dendrimer properties, such as the mean-square radius of gyration and the radial function of monomer density distribution, as well as their variations with the number of generations and the solvent quality. Among dynamic characteristics, only the autocorrelation function for the squared radius of gyration \( R_g^2 \) was considered. However, a large error in the determination of relaxation times made it impossible to obtain quantitative conclusions concerning the dependence of these times on the number of generations.

Karatasos and coauthors [19] performed an MD simulation for a series of AB2 dendrimers of generations \( g = 3–6 \) in a solvent. Excluded-volume interactions between all the particles were specified by the Lennard-Jones potential with parameters corresponding to a \( \Theta \) solvent. The studied equilibrium properties of the dendrimers show an adequate agreement with theoretical calculations based on the Zimm model for the \( \Theta \)-solvent conditions [14]. One should also mention the MD study of PAMAM-type dendrimers in water with the atom–atom interaction potentials explicitly set (Lee and coauthors [20]); the water molecules either were or were not explicitly specified. The pH value of the medium was varied. That study investigated only structural characteristics of dendrimers. On the whole, note that the need to explicitly consider the solvent in the MD simulation of polymers in solution requires a significantly longer machine time, thus limiting the time scale of the studied relaxation processes.

In the Brownian dynamics simulation, the motion of a macromolecule in solution is described by the Langevin equation for a system of linked interacting Brownian particles. The solvent is regarded as a continuous viscous medium. Inertial terms in motion equations may be neglected in most cases. Hence, one can significantly reduce the number of simulated particles and increase the time scale to be considered.

In our previous paper [17], the method of Brownian dynamics was used to simulate neutral and charged dendrimers in solution with explicit allowance for excluded-volume and electrostatic interactions. The equilibrium dimensions and internal structure of a dendrimer were calculated for various numbers of generations and intensities of electrostatic interactions. In this paper, the method of Brownian dynamics is used to study the dynamic properties of neutral and charged dendrimers. The dendrimer model considered here is the same as in [17], but intramolecular hydrodynamic interactions are additionally introduced. The results of the simulation are compared with those predicted by theories based on the Rouse–Zimm models.

MODEL AND SIMULATION TECHNIQUE

Just as in [17], we use the model of a dendrimer consisting of \( N \) identical “beads” with the friction coefficient \( \zeta \) linked by rigid bonds (“rods”) of length \( l \). The spacer between the branching points consists of a single bond: \( s = 1 \). The motion of particles is simulated using a finite-difference numerical scheme based on the Ermak–McCammon equation [21]

\[
r_i = r_i^0 + \frac{\Delta t}{k_BT} \sum_j D_{ij}^0 r_j^0 + \Phi_{rj}^0(\Delta t),
\]

where \( r_i^0 \) and \( r_i \) are the radius vectors of the \( i \)th bead \((i = 0) \) corresponds to the central monomer of the dendrimer) before and after the integration step; \( k_B \) is the Boltzmann constant; \( T \) is the absolute temperature; \( D_{ij}^0 \) is the diffusion tensor; \( \Delta t \) is the integration step; \( \Phi_{rj}^0 \) is the random Brownian force exerted on the \( i \)th bead by the solvent; and \( F_{ij}^0 \) is the sum of the potential forces and bond reaction forces exerted on the \( j \)th bead by other dendrimer particles. The simulation algorithm and the construction of the initial dendrimer configuration is described in more detail in [17] (see also [22–26]).

Excluded-volume interactions are set by the Lennard-Jones repulsive potential \( U_{LJ} \) corresponding to an athermal solvent [17].

Just as in [17], we consider a dendrimer model where only terminal groups are charged. Electrostatic interactions between beads of charge \( |q| = 1 \) are set by the Debye–Hückel potential with the Debye radius \( \lambda_D \).

The main difference from the previous paper [17] is that here we allow for hydrodynamic interactions. For comparison, calculations for the free-draining model of a dendrimer are also performed. The hydrodynamic interactions are introduced using the Rotne–Prager–Yamakawa tensor [27]. The diagonal elements \( D_{ii} \) of the diffusion tensor are defined as

\[
D_{ii}^{(\alpha\beta)0} = (k_BT/\zeta)\delta_{\alpha\beta},
\]

where \( \delta_{\alpha\beta} \) is the Kronecker symbol.
The nondiagonal components of the diffusion tensor are expressed as follows:

\[
D_{ij}^{\alpha\beta} = h(\pi/3)^{1/2}(3k_BT/4\eta)(l/R_{ij})
\times \left[\frac{\delta_{\alpha\beta} + R_{ij}^{\alpha\beta}R_{ij}^{\beta\alpha}}{R_{ij}^2} + \frac{2a^2}{3R_{ij}^2}\left(\delta_{\alpha\beta} - \frac{3R_{ij}^{\alpha\beta}R_{ij}^{\beta\alpha}}{R_{ij}^2}\right)\right]
\]  
\tag{3a}

for \( R_{ij} = |R_{ij}| = |r_i - r_j| \geq 2a \)

\[
D_{ij}^{\alpha\beta} = (k_BT/\zeta)\left[\frac{1}{3} - \frac{9R_{ij}^{\alpha\beta}R_{ij}^{\beta\alpha}}{32a} + 2\frac{a}{32a}\left(\frac{R_{ij}^{\alpha\beta}R_{ij}^{\beta\alpha}}{R_{ij}^2}\right)\right]
\]  
\tag{3b}

for \( R_{ij} < 2a \).

Here \( R_{ij} \) is the distance between beads \( i \) and \( j \) with the hydrodynamic radius \( a \). The hydrodynamic interaction force is determined by the \( h = (3/\pi)^{1/2}\zeta/(6\eta l) \) parameter, where \( \eta \) is the solvent viscosity. The free-draining \( (h = 0) \) and impenetrable \( (h = 0.25) \) models of a dendrimer are considered. The hydrodynamic radius of a bead corresponding to the latter case is equal to \( a = 0.257l \) [23].

This study uses dimensionless quantities expressed in the following units: bond length \( l \), energy \( k_BT \), time \( \zeta l^2/k_BT \), and translational friction of a bead \( \zeta = 6\eta l/\alpha \). The dimensionless integration step was \( \Delta t = 10^{-4} \). This \( \Delta t \) value was selected in order to ensure that the maximum displacement of a bead in a single step would not exceed 10% of the bond length.

**RESULTS AND DISCUSSION**

By analogy with a linear chain in solution, all dynamic processes in a dendrimer may be classified into three types: translational and orientational mobility of the dendrimer as a whole; dendrimer size and shape fluctuations; and local movements at scales of the order of the monomer length. Each of these types of motion is separately discussed below.

**Movements of the Dendrimer As a Whole**

**Translational diffusion.** To determine the translational diffusion coefficient \( D \) for a dendrimer, we calculated the mean-square displacement \( \langle \Delta R^2(t) \rangle \) of its mass center as a function of time (Fig. 1). These plots are linear at long times. The \( D \) value may be found from the Einstein equation

\[
\langle \Delta R^2(t) \rangle = 6Dt.
\]  
\tag{4}

Fairly reliable data for \( D \) may be obtained only if the mean-square displacement exceeds the mean-square dimensions of the dendrimer (squared radius of gyration \( R^2_g \)). With only a limited machine time available, we managed to obtain the values of the self-diffusion coefficient for the free-draining and impenetrable dendrimers up to generations \( g = 3 \) and 4, respectively.

For a Brownian particle with the translational friction coefficient \( \zeta_{self} \), the self-diffusion coefficient \( D \) is calculated as \( D = k_BT/\zeta_{self} \). For the free-draining model of a dendrimer, \( \zeta_{self} \) amounts to the sum of the friction coefficients \( \zeta \) of separate beads:

\[
\zeta_{self} = N\zeta.
\]  
\tag{5}

Hence, \( D = 1/N \) for the free-draining model. The results of the simulation agree with this prediction (Fig. 2a).

Just as should have been expected, the diffusion coefficient is higher for the impenetrable model of a dendrimer than for the free-draining one. Figure 1 shows this coefficient as a function of the reciprocal radius of gyration \( 1/R_g \) \( (R_g = \sqrt{R^2_g} \), where \( R^2_g \) is the mean-square radius of gyration of the dendrimer calculated in [17]). This plot is described by the power function \( D \sim R_g^{-0.8} \). In our study, hydrodynamic interactions are explicitly considered without the use of the preaveraging approximation.

Our results can be compared to the diffusion coefficients calculated by Cai and Chen [14] for the dendrimer model consisting of rigid spherical particles, with various (Fixman, Zimm, and Kirkwood) methods used for the preaveraging of hydrodynamic interactions (Fig. 3). Although the diffusion coefficients obtained in the simulation do not markedly differ from those pre-
dicted by the theory, their dependence on the number of
generations \( g \) turns out to be less significant [14].

The diffusion coefficients of dendrimers as a whole
were calculated by Karatasos and coauthors [19] using
the MD technique for the dendrimer model with a two-
bond spacer in a \( \Theta \) solvent. The diffusion coefficient as
a function of the number of particles in the dendrimer
was expressed as \( D \sim N^{-0.5} \). At the same time, the
expression derived for the radius of gyration was \( R_g \sim
N^x \) with \( x = 0.35 \pm 0.03 \). Thus, the results of [19] predict
that the dependence of the diffusion coefficients on the
radius of gyration (\( D \sim R_g^{-1.4} \)) for a \( \Theta \) solvent is more
marked than our dependence (\( D \sim R_g^{-0.8} \)) for a
dendrimer in an athermal solvent.

An impenetrable dendrimer may be regarded as a
ball with a certain radius \( R_h \) (the hydrodynamic radius
of the dendrimer) and the friction coefficient \( \zeta_{\text{self}} \)
described by the Stokes equation (in our model, \( \zeta = 6\pi \eta a = 1 \)):

\[
\zeta_{\text{self}} = 6\pi \eta R_h = R_h/a .
\]

Accordingly, \( R_h \sim R_g^{0.8} \). The \( R_h \) value turns out to be
somewhat smaller than \( R_g \) for dendrimers of all genera-
tions. This conclusion agrees with the results obtained
by La Ferla and coauthors [28, 29] for an ideal den-
drimer (without excluded-volume interactions) and for
a dendrimer in a good solvent at various values of the
excluded-volume interaction parameter.

The diffusion coefficients of charged dendrimers
with a hydrodynamic interaction slightly decrease with
the Debye radius. However, the radii of gyration simultane-
ously increase (see [17]). As a result, the self-diffu-
sion coefficient \( D \) plotted as a function of \( 1/R_g \) for
charged dendrimers within the impenetrable model
(Fig. 2b) virtually coincides with the corresponding
plot for neutral dendrimers. Hence, the \( R_h \sim R_g^{0.8} \) relation-
ship is valid for charged dendrimers as well.

**Rotation of a dendrimer as a whole.** The rotational
mobility of a dendrimer may be characterized using the
correlation function \( C_e(t) \)

\[
C_e(t) = \langle e_g(0)e_g(t) \rangle
\]

for the unit vector \( e_g = Q_g/|Q_g| \), where

\[
Q_g = r_e - r_0 ,
\]

\( Q_g \) is the vector connecting the central junction of the
dendrimer with one of the terminal particles, \( r_e \) is the
radius vector of the \( e \)th terminal group for the den-
drimer of generation \( g \), and the \( r_0 \) vector characterizes

\[ (a) \quad \text{and} \quad (b) \]

\[ (1) \quad \text{Self-diffusion coefficient} \ D \text{ plotted vs. number of generations for the free-draining model of a neutral dendrimer, } h = 0.25. \text{ For comparison, the results obtained by Cai and Chen [14] for a dendrimer with an excluded volume and preaveraged hydrody-namic interactions are given for various approxima-tions of hydrodynamic interactions: the (2) Fixman, (3) Zimm, and (4) Kirkwood approximations.} \]
the position of the central junction (core) of the dendrimer.

The averaging in Eq. (7) is performed over the calculation time and over all terminal particles. An example of the $C_{\lambda}(t)$ function plotted vs. time is shown in Fig. 4. Two portions may be distinguished on this curve: a rapid decrease at short times and a slower one at long times. These two portions may be attributed to rotations of the $e_\gamma$ vector against the background of the quiescent dendrimer and rotation of the dendrimer as a whole, respectively. The characteristic time of the latter rotation may be determined from the slope of the $\ln C_{\lambda}(t)$ function at long times.

A scaling relationship may be assumed for the dependence of this time on the diffusion coefficient and the dendrimer dimensions:

$$\tau \sim R^2_g/D.$$  \hspace{1cm} (9)

Figure 5 shows that this dependence is indeed valid for neutral and charged dendrimers.

**Relaxation of monomer-to-core vector.** Cai and Chen [13, 14] considered the relaxation of the monomer-to-core vector $Q_\gamma$ itself. Both length fluctuations and rotations of this vector may contribute to its relaxation. To study the dynamics of this quantity for our model, the corresponding autocorrelation functions were considered:

$$C_{Q}(t) = \frac{\langle Q_\gamma(0)Q_\gamma(t) \rangle}{\langle Q_\gamma^2 \rangle}.$$  \hspace{1cm} (10)

The typical $C_{Q}(t)$ function plotted vs. time is shown in Fig. 4 by the example of a dendrimer of generation $g = 4$. The characteristic relaxation time $\tau_r$ of the $C_{Q}(t)$ function may be calculated as

$$C_{Q}(\tau_r) = 1/e.$$  \hspace{1cm} (11)

The $\tau_r$ times for neutral dendrimers with and without hydrodynamic interactions are plotted in Fig. 6a. For the free-draining model of a dendrimer with an excluded volume, the dependence of these times on the number of beads in the chain is expressed as $\tau_r \sim N^{1.6}$. The resultant times were compared to those predicted by Cai and Chen [13] (the Rouse model) for an ideal dendrimer:

$$\tau_r = 2^{g/2} \zeta/K,$$  \hspace{1cm} (12)

where $K$ is the effective force constant of the spring connecting two adjacent branching points ($K = 3k_BT/l^2$, where $l^2$ is the mean-square distance between two adjacent branching points) and $\zeta$ is the friction coefficient of the monomer. The number $N$ of monomers in a dendrimer of generation $g$ is proportional to $2^g$. Thus, Eq. (12) predicts that $\tau_r$ is a linear function of $N$. Note that the relaxation time of the vector connecting the ends of an $N$-monomer chain is proportional to $N^2$ for the Rouse model. The dependence of the relaxation time $\tau_r$ on the molecular mass obtained by Cai and Chen is less pronounced than in our studies; this is probably due to the absence of excluded-volume interactions in the phantom model of a dendrimer considered by those authors [13].

For dendrimers with hydrodynamic interactions, we established a weaker dependence $\tau_r \sim N^{1.3}$ than within the free-draining model. The resultant values of the
relaxation times $\tau_r$ may be compared with the corresponding times obtained by Cai and Chen [14] for the dendrimer model with preaveraged hydrodynamic interactions (Fig. 6a). For the impenetrable model, the theory also predicts shorter times $\tau_r$ with a weaker dependence on the molecular mass $N (\tau_r \sim N^{1.1})$ in comparison with the results of the simulation (Fig. 6a).

For charged dendrimers, the relaxation times $\tau_r$ slightly increase with increasing Debye radius $r_D$, reaching a saturation at large $r_D$ values (Fig. 7). However, the exponent of the power function $\nu \sim 1.3$ coincides with the value obtained for neutral dendrimers (Fig. 6b).

The relaxation times remain virtually constant at Debye radii $r_D \geq 2$.

To analyze why our results for the $\tau_r$ times differ from those theoretically predicted by Cai and Chen, we compared the correlation function $C_Q(t)$ with the correlation function $C_e(t)$ of the corresponding unit vector. These functions are virtually identical for neutral and charged dendrimers (Fig. 5). This implies that the relaxation of a monomer-to-core vector in our model is mostly determined by its rotation, whereas the contribution of its length fluctuations is small because of the rigidity of spacers in our model. Cai and Chen [13, 14] considered dendrimers with flexible spacers described by the subchain model. For such soft models, the contribution of internal motions to the relaxation of a monomer-to-core vector is significant. Therefore, dendrimers with flexible spacers display a weaker $\tau_r(N)$ dependence compared to our results for dendrimers with rigid spacers between the branching points (Fig. 6a).

**Dendrimer Size Fluctuations**

**Autocorrelation function of squared radius of gyration.** The dynamics of dendrimer size fluctuations
may be characterized by the autocorrelation function $C_{R^2}(t)$ for the squared radius of gyration:

$$C_{R^2}(t) = \frac{\langle R^2(0)R^2(t) \rangle - \langle R^2 \rangle^2}{\langle R^4 \rangle - \langle R^2 \rangle^2}. \quad (13)$$

The relaxation of the $C_{R^2}(t)$ function takes place only owing to internal motions in the dendrimer. The rotation of the dendrimer as a whole does not affect the relaxation of this function. Figure 8 presents the typical $C_{R^2}(t)$ functions plotted vs. time for neutral dendrimers of generations $g = 1–3$.

The characteristic times $\tau_{R^2}$, defined as $C_{R^2}(\tau_{R^2}) = e^{-1}$, are plotted in Fig. 9. The relaxation times $\tau_{R^2}$ are much shorter than the $\tau_r$ times calculated earlier (Fig. 6). Murat and Grest [18] also obtained $\tau_{R^2} < \tau_r$ in their MD simulation. At the same time, $\tau_{R^2}$ values coincide with $\tau_r$ for the model considered by Cai and Chen [13, 14]. For the free-draining model of a dendrimer [13], the equality $\tau_{R^2} = \tau_r$ may be due to the use of the phantom viscoelastic model without excluded-volume interactions. For the model with preaveraged hydrodynamic interactions and with the presence of excluded-volume interactions, Cai and Chen note that the equality $\tau_{R^2} = \tau_r$ is an artifact of the theory, which appeared due to the use of the linearized form of the Langevin equation [14]; in reality, $\tau_{R^2}$ must be smaller than $\tau_r$. Our results confirm these conclusions. It is interesting that, in contrast to the predictions made by Cai and Chen [13, 14], our resultant times $\tau_{R^2}$ change only to a minor extent when hydrodynamic interactions are introduced. This implies that the relaxation times $\tau_{R^2}$ are associated with local processes in a dendrimer, which are not highly sensitive to the presence of hydrodynamic interactions.

The dependence of the relaxation times $\tau_{R^2}$ on the number of generations $g$ turns out to be less pronounced than the theoretically predicted one [13, 14] (Fig. 9). The relaxation times obtained by Stark and coauthors for carbosilane dendrimers in neutron scattering experiments [9], as well as the relaxation times obtained from the $T_1$ and $T_2$ times for PAMAM dendrimers in NMR experiments [11, 12], also demonstrate a weaker dependence on $g$ in comparison with the predictions by Cai and Chen [13, 14].

For charged dendrimers, an increase in the Debye radius causes a shortening of the relaxation time $\tau_{R^2}$ (Fig. 10). The introduction of electrostatic interactions leads to a higher internal stress in the dendrimer and, accordingly, to its higher effective rigidity. As a result, the relaxation times decrease (Fig. 10).
Relaxation of center-of-mass-to-core vector fluctuations. Cai and Chen [13] considered the relaxation of fluctuations of the center-of-mass-to-core vector $S$ for a dendrimer:

$$S = \frac{1}{N+1} \sum_{i=0}^{N} (r_i - r_0).$$ (14)

The corresponding correlation function $C_S$ is defined as

$$C_S(t) = \frac{\langle S(0)S(t) \rangle}{\langle S^2 \rangle}$$ (15)

and characterized by the relaxation time $\tau_{com}$. For the free-draining dendrimer model without excluded-volume interactions and with flexible spacers, Cai and Chen derived an expression for these times in the form $\tau_{com} \sim \zeta/(K(3 - 2\sqrt{2}\cos(\pi/(g + 1))))$ [13].

We calculated the $C_S$ function for our model. The corresponding $\tau_{com}$ values were plotted vs. number of generations $g$ for neutral (Fig. 11a) and charged (Fig. 11b) dendrimers. To compare our results with the corresponding theoretical predictions, we assumed that the mean-square spacer length $l^2$ in the expression for the elastic modulus $K = \frac{3k_BT}{l^2}$ is equal to the squared bond length in our model. One can observe a significant discrepancy between the theoretical predictions and the results of the Brownian dynamics simulation. The Rouse model [13] predicts that the times $\tau_{com}$ must be virtually linear functions of the number of generations $g$. The relaxation times $\tau_{com}$ found using the Brownian dynamics technique nonmonotonically depend on $g$. At small $g$ values, the times $\tau_{com}$ exceed the theoretical values; then they reach a maximum and subsequently decrease for large numbers of generations $g$. It is interesting that the times $\tau_{com}$ obtained in the simulation depend on the number of generations $g$ for the free-draining model in the same way as for the impenetrable model. For charged dendrimers, the pattern of the $\tau_{com}(g)$ plot remains the same but the times themselves increase with increasing Debye radius (Fig. 11b).

We believe that the difference between the $\tau_{com}(g)$ dependence describing the results of the Brownian dynamics simulation and the one predicted by Cai and Chen [13] is due to the flexibility of spacers and to the absence of excluded-volume interactions in the theoretical model. For flexible spacers [13], a larger number of generations $g$ leads to longer relaxation times $\tau_{com}$ because of a higher effective friction coefficient of the dendrimer as a whole. At the same time, the flexibility of its spacers does not change. Our dendrimer has rigid spacers. Therefore, as the number of generations
increases, internal stresses in the dendrimer increase because of excluded-volume interactions. As a result, the total rigidity of the dendrimer increases. At small \( g \), the main contribution to the changes in \( \tau_{\text{com}} \) is due to the increase in the total friction; therefore, the relaxation times increase. At large \( g \), the increase in the dendrimer rigidity starts to have its effect and the relaxation times decrease. It is the combination of these factors that produces the observed nonmonotonic pattern of \( \tau_{\text{com}} \) plotted vs. number of generations \( g \) (Fig. 11).

**Local orientational mobility.** The local orientational mobility of separate bonds within a dendrimer may be characterized by autocorrelation functions \( P_1 \) and \( P_2 \):

\[
P_1(t) = \langle b_i(0)b_i(t) \rangle, \tag{16}
\]

\[
P_2(t) = \frac{3}{2} \left( \langle b_i(0)b_i(t) \rangle^2 - \frac{1}{3} \right), \tag{17}
\]

where \( b_i(t) \) is the unit vector for the \( i \)th bond.

For a rigid dumbbell molecule, there exists a simple relationship between \( P_1 \) and \( P_2 \) [30]:

\[
P_2(t) = P_1^3(t). \tag{18}
\]

This relationship turned out to be true for all the studied dendrimers both for the free-draining model and for the impenetrable one. An example of such an equality is shown in Fig. 12 for the impenetrable model.

In our further analysis, we consider only the autocorrelation function \( P_1(t) \). The results of the simulation show that hydrodynamic interactions and changes in the Debye radius significantly affect the dynamics of bonds pertaining to generation \( g = 0 \) (bonds 1–3) (Figs. 13, 14). An increase in the Debye radius leads to a slower relaxation of \( P_1 \). The effect of electrostatic interactions decreases for bonds of next generations (Fig. 13). The introduction of hydrodynamic interactions leads to a somewhat faster orientational mobility in comparison with the free-draining model (Fig. 14). This effect is intensified for large generations \( (g > 3) \). Two portions, a faster and a slower ones, may be distinguished on the \( P_1 \) plots. The slope at long times, which

**Fig. 12.** Autocorrelation functions (solid curves) \( P_2 \) and (dashed curves) \( P_3 \) plotted vs. time for a neutral dendrimer of generation \( g = 5 \), impenetrable model, \( h = 0.25 \). Bonds 1–3 are attached to the core, whereas bonds 94–189 are terminal for the dendrimer of generation \( g = 5 \).

**Fig. 13.** Autocorrelation function \( P_1 \) for the first three bonds attached to the core for a dendrimer of generation \( g = 5 \) at various values of the Debye radius, impenetrable model. (1) Neutral and (2, 3) charged dendrimers with \( r_D = (2) 0.8 \) and (3) 8.96.

**Fig. 14.** Effect of hydrodynamic interactions on the autocorrelation function \( P_1 \) for the first three bonds attached to the core for neutral dendrimers of generations \( g = (1) 0, (2) 1, (3) 2, (4) 3, (5) 4, and (6) 5; h = (solid curves) 0 and (dashed curves) 0.25.
corresponds to the slower process, virtually coincides with the slope of the correlation function \( C_e(t) \) for the unit vector. Presumably, two types of processes contribute to the relaxation of \( P_1 \). The initial stage of the relaxation (up to times \( t \sim 0.1\)–0.2) can take place owing to faster “pulsating” motions in the dendrimer. The relaxation at long times is due to rotational motions of the dendrimer as a whole.

Except for the dendrimer of generation \( g = 0 \), which consists of four beads, dendrimers of different generations display the same behavior of \( P_1 \) for terminal groups (Fig. 15a). Hydrodynamic interactions do not significantly affect \( P_1 \) of terminal groups either. Such a similarity in the behavior, both for the free-draining and for the impenetrable models, is apparently due to the fact that terminal groups can move independently enough. The MD simulation performed by Karatasos and coauthors [19] also showed (for their model of a dendrimer with the spacer length \( s = 2 \)) that the orientational relaxation times of terminal groups are independent of the dendrimer size up to generations \( g = 6 \). The low sensitivity of the rotational mobility of terminal groups to the number of generations in a dendrimer was experimentally demonstrated by Stark and coauthors [9] for dendrimers with fluorinated terminal groups.

Ionization of terminal groups significantly affects their mobility. For charged dendrimers, the decline of \( P_1 \) for terminal groups slows down as the Debye radius increases (Fig. 15b).

This is probably due to the fact that the overall dendrimer rigidity increases with increasing intensity of electrostatic interactions, which leads to a stronger correlation between the rotation of terminal groups and the rotation of the dendrimer as a whole.

**REFERENCES**