Molecular simulation of dendrimers and their mixtures under shear: Comparison of isothermal-isobaric \((NpT)\) and isothermal-isochoric \((NVT)\) ensemble systems

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Flow properties of dendrimers are studied with the aid of nonequilibrium molecular dynamics techniques. Simulations are performed in the \(NpT\) ensemble using the \(NpT\)-SLLOD algorithm [P. J. Davis and D. J. Evans, J. Chem. Phys. 100, 541 (1994)] and are compared to the results from simulations performed in the \(NVT\) ensemble reported earlier [J. T. Bosko, B. D. Todd, and R. J. Sadus, Chem. Phys. 121, 12050 (2004)]. Shear thickening observed at high strain rates vanishes in systems kept under constant pressure. Also the exponents in the power-law dependencies of the viscosity and the normal stress coefficients change. The variations are significant only at high strain rates and do not affect largely microscopic properties such as shape, alignment, or rotation of molecules. The \(NpT\)-SLLOD algorithm has been applied to study various systems including dendrimers in solution and their blends with linear chain molecules of the same molecular mass, and some results for these systems are presented. © 2005 American Institute of Physics.

I. INTRODUCTION

The standard SLLOD (Ref. 1) algorithm typically used to simulate the rheology of molecular fluids\(^2\)–\(^5\) maintains the system at constant volume (i.e., in the isochoric-isothermal ensemble). Real rheology experiments in contrast are usually performed with at least one free surface in equilibrium with the atmosphere. Consequently, systems under shear are allowed to relax to compensate for the flow-induced changes in pressure. To perform more realistic simulations of melts under shear, a constant pressure version of the SLLOD algorithm was proposed.\(^6\) In this approach, the Nosé–Hoover integral feedback mechanism has been implemented\(^6,7\) and the system is extended by adding an additional degree of freedom, which corresponds to the volume of the simulation box.

In our previous work,\(^4,5\) we presented the results of simulations of dendrimer melts under shear performed at constant volume (isochoric-isothermal ensemble). Systems of dendrimers and linear chain molecules of the corresponding molecular mass, although composed of identical interconnected model beads, behaved differently under shear. For example, the hydrostatic pressure of the systems even at equilibrium differed between systems composed of molecules of different sizes or architectures.\(^5\) The effect could be explained by taking into account the way the connection between the neighboring beads in the chain was modeled. The finitely extensible nonlinear elastic (FENE) potential\(^8\) combined with Weeks–Chandler–Anderson (WCA) interactions\(^9\) result in an average bond length shorter than the average separation between nearest nonbonded neighbors in the fluid.

Therefore the volume occupied by the molecule composed of the \(N\) beads was smaller than the volume occupied by the same number of beads but without FENE interactions between them. This feature of the model resulted in the decrease of the pressure with increasing size of the molecules composing the melt, as will be described in Sec. III.

An even more significant effect of performing simulations in the \(NVT\) ensemble could be seen in the dependence of the pressure on the strain rate in the case of fluids away from equilibrium. Different internal architectures of the molecules led to different responses of the system to the deformation, and at high strain rates an increase of the pressure can be observed. For dendrimers this seemed to be a simple monotonic growth,\(^5\) whereas for linear polymers a drop in pressure was observed before this increase at higher strain rates.\(^2,5,10\) The latter effect became more pronounced for large molecules. Similar behavior was reported for simulations of linear chains or branched polymers of various architectures.\(^2,10,11\) It was also shown that this effect becomes less significant with the increase of the degree of branching of the molecules.\(^10,12\)

It has also been demonstrated that the increase of the shear viscosity (shear thickening) at high strain rates for systems modeled using the \(NVT\)-SLLOD algorithm, not observed in real experiments, is a property of the \(NVT\) ensemble.\(^6\) The \(NVT\) ensemble also creates difficulties in estimating the shear-thinning rate in the non-Newtonian regime.\(^5\)

All the size- and structure-related influences on the thermodynamic properties derived from the simulations, although not usually large, make it difficult to compare results of the simulations with experimental data. This can also be
an obstacle in quantitative comparison of systems composed of molecules with different sizes or architectures.

Maintaining and controlling hydrostatic pressure becomes even more important in simulation of dendrimers in solution at different concentrations or blends of different polymers. To achieve this, in this work the constant pressure SLLOD algorithm was implemented and applied to simulate properties of dendrimers, linear chain polymers, their blends, and their solutions under shear. The results obtained for pure melts are compared to those reported earlier by us and obtained from constant volume simulations.\(^5\) The effect of adding an additional degree of freedom associated with the volume fluctuations and maintaining constant pressure on the flow properties of the systems is discussed. The \(NpT\)-SLLOD algorithm is also applied to study the rheology of dendrimers in solution at various concentrations and blends of dendrimers with linear chain polymers.

II. SIMULATION METHOD

A. Model

Dendrimers were modeled at the coarse-grained level using uniform beads corresponding to either monomers or constituent parts of the molecule. The excluded volume of beads was incorporated using the purely repulsive WCA potential\(^6\) of the form:

\[
U_{ij}^{WCA} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} \right] + \epsilon \quad \text{for } r_{ij} < 2^{1/6},
\]

\[
U_{ij}^{WCA} = 0 \quad \text{for } r_{ij} \geq 2^{1/6},
\]

where \(r_{ij}\) is the separation between beads \(i\) and \(j\), \(\epsilon\) is the potential well depth, and \(\sigma\) is the effective diameter of the beads. Values of \(\epsilon\) and \(\sigma\) were assigned to unity and, adopting common practice, all quantities are expressed in reduced units relative to the Lennard-Jones parameters: \(r_{ij}^* = r_{ij}/\sigma\), density \(\rho^* = \rho\sigma^3\), temperature \(T^* = k_B T/\epsilon\), pressure tensor \(P^* = P\sigma^3/\epsilon\), strain rate \(\dot{\gamma}^* = (m_0\sigma^2/\epsilon)^{1/2}\dot{\gamma}\), and viscosity \(\eta^* = (\sigma^4/\epsilon m_0)^{1/2}\eta\). For simplicity of notation, hereafter the asterisk will be omitted.

In addition to the WCA potential, the distance between connected beads was maintained using the FENE potential\(^7\) of the form:

\[
\begin{align*}
U_{ij}^{FENE} &= -0.5kR_0^2 \ln \left[ 1 - \left( r_{ij}/R_0 \right)^2 \right] \quad \text{for } r_{ij} \leq R_0, \\
U_{ij}^{FENE} &= \infty \quad \text{for } r_{ij} > R_0.
\end{align*}
\]

Setting \(R_0 = 1.5\) and \(k = 30\), the average distance between the connected beads at equilibrium and at a temperature \(T = 1.25\) is approximately 0.97.

Dendrimers were modeled with trifunctional cores and branching points, and linear elements (spacers) composed of two beads. This model results in 19, 43, 91, and 187 beads per single dendrimer of generations 1, 2, 3, and 4, respectively. Henceforth, the model dendrimers (Fig. 1) will be referred to as D2G1, D2G2, D2G3, and D2G4. The length of the linear polymers studied corresponded exactly to the mass (i.e., the number of beads) of the dendrimers. Therefore, the properties of D2G1, D2G2, D2G3, and D2G4 were compared to linear chains of 19-mers, 43-mers, 91-mers, and 187-mers, respectively. For simulations involving either D2G1 or 19-mers, a system of 256 molecules was used, whereas in all other cases 125 molecules were used. In all cases, the system was first constructed at low density and then gradually compressed to a reduced density of 0.84. The compression was achieved using the SLLOD algorithm\(^1\) with nonzero diagonal elements of the velocity gradient tensor, thus ensuring that the system remained homogeneous in space and hence reducing the overall equilibration time.

B. Equations of motion

To simulate shear flow of the melts we applied the molecular version of the constant pressure homogeneous isothermal shear algorithm (\(NpT\)-SLLOD) (Ref. 6) in conjunction with standard Lees–Edwards periodic boundary conditions.\(^13\) The equations of motion for bead \(\alpha\) in molecule \(i\) were given by

\[
\begin{align*}
\dot{r}_{ia} &= \frac{p_{ia}}{m_{ia}} + i\gamma y_i + \dot{\epsilon} r_i, \\
\dot{p}_{ia} &= F_{ia} - i m_{ia} \gamma p_{yi} - \dot{\gamma} \frac{m_{ia}}{M_i} p_i - \dot{\epsilon} m_{ia} p_i, \\
\dot{V} &= 3\dot{\epsilon} V,
\end{align*}
\]

where \(r_{ia}\) and \(p_{ia}\) represent the position and thermal momentum of bead \(\alpha\) on molecule \(i\), \(r_i\) is the center of mass of molecule \(i\), \(p_i\) is the momentum of the molecular center of mass of molecule \(i\), and \(M_i\) is the mass of molecule \(i\). The strain rate is defined by \(\dot{\gamma} = \partial u_x/\partial y\), where \(u = iu_x\) is the fluid streaming velocity in the \(x\) direction. The streaming velocity of the molecule is determined by the position of its center of mass and has the form \(i\dot{y} \gamma y_i\), where \(\gamma y_i\) is the \(y\)-component position of the molecular center of mass; no further assumptions are made on the rotational degrees of freedom of the molecules. The multiplier \(\dot{\epsilon}\) depends on the difference between the instantaneous and required pressure, and it is found by solving the differential equation:
\[ \dot{\varepsilon} = \frac{(p - p_0)V}{QNk_BT}, \]  

where \( Q \) is a damping factor chosen by trial and error to give good damping of the pressure fluctuations, \( p_0 \) is the required pressure, whereas \( p \) is the instantaneous pressure. The simulations were performed at constant temperature using a molecular version of the Gaussian thermostat with a constraint multiplier \( \xi^M \) given by

\[ \xi^M = \frac{\sum_{i=1}^{N} (F_i \cdot \dot{p}_i - \gamma p_i \dot{p}_i)/M_i}{\sum_{i=1}^{N} \dot{p}_i^2/M_i} - \dot{\varepsilon}, \]

where \( N \) is the number of molecules in the system. The thermostat constrains the molecular kinetic temperature of the systems defined as

\[ \sum_{i=1}^{N} \frac{p_i \cdot \dot{p}_i}{2M_i} = \frac{3N - 3}{2} k_B T_M. \]

All simulations were performed at a molecular temperature \( T_M = 1.25 \). The algorithm has been discussed in detail previously by Edberg et al.\textsuperscript{14} The justification for using the molecular version of the SLLOD algorithm with a thermostatted molecular kinetic temperature has been discussed in detail by Travis et al.\textsuperscript{15}

The equations of motion of all beads were integrated using a fifth-order Gear predictor corrector differential equation solver\textsuperscript{16,17} with reduced time step \( \Delta_t = 0.001 \). After achieving steady state (typically several million time steps), the bead trajectories were accumulated and ensemble averages were calculated.

Coupling of the simulated systems to the barostat introduced unphysical oscillations of volume, pressure, or atomic temperature with a period depending on the damping factor \( Q \). Although its value is chosen \textit{ad hoc}, two conditions have to be satisfied. Firstly, the simulations must be long enough to include sufficiently many oscillations. This ensures that the thermodynamical properties derived from the trajectories are averaged over many periods of the barostat-induced oscillations. It can be achieved by either choosing small values of \( Q \), or performing long enough simulation runs. Secondly, \( Q \) has to be chosen so that the oscillation period is large compared to the characteristic decay time of dynamical correlation functions, e.g., the velocity autocorrelation function. It ensures that the unphysical oscillations are decoupled from the real molecular dynamics. For example, the velocity autocorrelation function for a linear chain melt for systems similar in size to those studied here typically decays to zero in approximately 1 Lennard-Jones (LJ)\textsuperscript{18} time unit. Therefore, the period of volume oscillations should be at least several LJ time units. This condition prefers large values of the damping factor \( Q \). The optimal value must be estimated for the studied systems by trial and error.

A series of simulations of dendrimers in the melt with different values of \( Q \) has been performed. Figure 2 shows the fluctuations and convergence of the pressure and the bead density for the system of dendrimers of generation 1 (D2G1) maintained at temperature \( T = 1.25 \) and pressure \( p = 4.5 \) with the damping factor \( Q = 500 \). The latter value affects not only the time required to reach the required pressure, but also the frequency and amplitude of the fluctuations from the mean value. We found that with the increase of \( Q \) the period of the oscillations, as well as the time required for the amplitude of these oscillations to converge to the steady value increase.

To study the influence of solvent molecules on the flow properties and conformation of macromolecules under shear, a generic model of the dendrimers in solution is used. Solvent molecules were included explicitly in the model as spherical WCA beads, the same as those used to construct dendrimer molecules. Interactions between solvent molecules and dendrimers are also maintained unchanged, i.e., no interaction preferences between different components of the system were incorporated. Therefore, in accordance with the rest of this study, the main interest is in the conformational changes of the system caused by the solvent rather than in the particular type of solvent and its chemical properties. The concentration used in this study is defined as the mass fraction of dendrimers to the mass of the whole system. Therefore, assuming that the mass of the solvent molecules equals the mass of the beads constituting dendrimers, a concentration of 0.5 (50\%) indicates that half of all beads in the simulation box are not chemically bonded and represent the solvent.

In the study of blends of dendrimers with linear chain polymers, only mixtures of molecules of the same molecular mass (number of beads) were taken into account. Interactions
between the beads composing the molecules were kept unchanged, and only the ratio of dendrimers to linear chains was varied.

C. Viscoelastic properties

The rheological properties of molecular melts are typically analyzed using standard material functions. To characterize the rheological properties of the dendrimer melt under steady shear flow we compute the shear viscosity \( \eta(\dot{\gamma}) \), and the first \( \Psi_1(\dot{\gamma}) \) and second \( \Psi_2(\dot{\gamma}) \) normal stress coefficients. All the viscometric functions are expressed in terms of the components of the molecular pressure tensor \( P^M \) calculated as

\[
P^M V = \sum_{i=1}^{N} \frac{p_i}{M_i} - \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{p=1}^{n} r_{ij} F_{ijp},
\]

where \( V \) is the instantaneous volume, \( r_{ij} \) is the center-of-mass separation of molecules \( i \) and \( j \), \( F_{ijp} \) is the force on site \( \alpha \) in molecule \( i \) due to site \( \beta \) in molecule \( j \), and \( n \) is the total number of interaction sites in a molecule.

The shear viscosity is defined as

\[
\eta = \left( \frac{-P_{xy} + P_{yx}}{2\dot{\gamma}} \right),
\]

whereas the first and second normal stress coefficients are

\[
\Psi_1 = \left( \frac{P_{yy} - P_{xx}}{\dot{\gamma}^2} \right),
\]

\[
\Psi_2 = \left( \frac{P_{zz} - P_{yy}}{\dot{\gamma}^2} \right).
\]

III. RESULTS AND DISCUSSION

A. Simulations of pure melts

The flexible bonds between connected beads of the molecules maintained by FENE+WCA interactions results in the shorter bond length in comparison to the average separation between the nonbonded beads. This feature of the model leads to differences between pressures of various systems kept at the same bead density. In Fig. 3 the changes in the equilibrium pressure with the molecular mass and the topology for dendrimers and linear chain polymers are presented. The way the melts respond to shearing also depends on the molecular architecture. The variation of the pressure with strain rate in constant volume simulations was presented in our earlier work.\(^5\) In Fig. 4 the variation of the pressure observed in the \( NVT \) simulations is compared with the changes in the bead density observed in the \( NpT \) simulations. The latter condition is required to maintain constant pressure in the systems.

To study the effect of performing simulations at constant pressure, the simulations of dendrimers of generations 1–4 were performed using the \( NpT\)-SLLOD algorithm and compared to the results obtained from the \( NVT \) simulations.\(^5\) All simulations were performed at constant pressure \( p=5.42 \), i.e., the pressure of the D2G2 system at equilibrium. As shown earlier, the coupling of the systems with a barostat introduces additional oscillations of the volume of the simulation box. However, in each case the value of the damping factor \( Q \) was chosen in such a way as to ensure that the effect on the molecular dynamics is minimized. The melts in these simulations were therefore allowed to relax (expand or contract) to compensate the flow-induced changes in the pressure.
Figure 5 shows the dependence of the viscosity on the strain rate for dendrimers of generations 1–4. In Fig. 6 the same curves for dendrimers of generations 2 and 3 are compared to those obtained from the simulations in the $NVT$ ensemble. In each case the flow curves do not change much for small values of the strain rate; the zero shear viscosity is the same, and so is the strain rate at which the onset of the shear thinning occurs. However, the results are different in the non-Newtonian regime. As expected, shear thickening at high strain rates is not observed in $NpT$ simulations. Instead, a monotonic decrease of the viscosity is observed. Consequently the rate of shear thinning changes and it is found to be larger than estimated from the flow curves obtained in the $NVT$ simulations. For dendrimers under $NVT$ simulation conditions, the rate of shear thinning in the non-Newtonian regime varied from 0.28 for D2G1 to 0.36 for D2G4. At constant pressure their values vary in a much narrower range from 0.37 to 0.39.

The fact that shear thickening observed earlier in the $NVT$ simulations is absent when the isobaric ensemble is considered indicates that this effect is related to the thermodynamical ensemble rather than being an artifact of the molecular SLLOD algorithm. Similar absence of shear thickening due to changing thermodynamic ensemble from $NVT$ to $NpT$ was reported in simulations of decane under shear and other linear polymer melts.

In Figs. 7 and 8, the first and second normal stress coefficients for selected dendrimer systems are compared to the relationships observed in $NVT$ simulations. In every case the slope of the function in the non-Newtonian regime (high strain rates) is larger than reported earlier for systems kept at constant density. The values of these exponents obtained from the linear fits to the log-log plots are presented in Table I. The slope of the first normal stress coefficients typically decreases with the exponent $\sim 1.27$ ($\sim 1$ for $NVT$ simulations), whereas the slope of the second normal stress coefficients is approximately 1.23 (in contrast to $\sim 1$ for $NVT$ simulations).

Except for the highest shear rates, the microscopic properties of the simulated systems, such as radius of gyration, molecular alignment and rotation, distribution of mass, etc., are not affected by the change from isochoric to isobaric ensemble.
B. Dendrimers in solution

Dendrimers of generation 2 (D2G2) were generated in solution at concentrations of 33%, 50%, 67%, and 100% (melt). The systems were equilibrated and subjected to planar shear flow under the same pressure \( p = 5.42 \). The obtained flow curves (viscosity versus shear rate) are presented in Fig. 9. The viscosity of solutions at any shear rate increases with increasing content of dendrimers. All systems exhibit transition from Newtonian to non-Newtonian regimes. However, the rate of shear thinning decreases with the decrease of concentration from 0.39 for melt (100%), through 0.26, 0.20, and down to 0.13 for 67%, 50%, and 33%, respectively. A similar behavior was observed experimentally for solutions of highly branched poly(etherimide)s.\(^{21}\) At low concentrations the systems exhibited shear-independent properties, whereas at higher concentrations (>30%), when the entanglement and contribution from interactions between molecules became more significant, the non-Newtonian viscosity was reported.

<table>
<thead>
<tr>
<th></th>
<th>NpT</th>
<th>NVT</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>( \beta )</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>D2G1</td>
<td>1.207(6)</td>
<td>1.08(2)</td>
</tr>
<tr>
<td>D2G2</td>
<td>1.270(5)</td>
<td>1.23(2)</td>
</tr>
<tr>
<td>D2G3</td>
<td>1.301(3)</td>
<td>1.23(1)</td>
</tr>
<tr>
<td>D2G4</td>
<td>1.278(6)</td>
<td>1.26(2)</td>
</tr>
</tbody>
</table>

Similar to the viscosity, the normal stress coefficients of the solutions also decrease with the decrease of the concentration of dendrimers. In Fig. 10 the dependence of normal stress coefficients on shear rate is shown.

Although the melts and mixtures were kept at the same pressure (therefore similar densities), the structure of dendrimers is strongly affected by the presence of solvent molecules. In the melt, entanglement and interpenetration between dendrimers are suppressed due to the high density and level of branching of their arms. As a consequence dendrimers are found in compact globular conformations.\(^{5}\) In contrast, small solvent molecules can easily penetrate the interior of dendrimers. This phenomenon is sometimes referred to as swelling of the molecule in solution. In polar solvents the configurational effects can be strongly enhanced in the...
case of hydrophilic systems or suppressed in hydrophobic ones. In this study the latter effects are not taken into account. The extension of a molecule in space can be characterized by its radius of gyration. The average tensor of gyration is given by the expression:

\[
\mathbf{R}_{g} = \left\langle \sum_{\alpha=0}^{n} m_{\alpha} \left( \mathbf{r}_{\alpha} - \mathbf{g} \right) \left( \mathbf{r}_{\alpha} - \mathbf{g} \right) \right\rangle,
\]

where \( \mathbf{g} \) is the position of the molecular center of mass, and \( \langle \cdots \rangle \) denotes an ensemble average. The value of the squared radius of gyration is defined as the trace of the tensor

\[
R_{g}^{2} = \text{Tr}(\mathbf{R}_{g}^{2}),
\]

which can be compared with experimentally measured radial sizes of the dendrimers.

Figure 11 shows the variation of the radius of gyration of dendrimers with concentration, where a monotonic decrease of the size with decreasing separation between molecules is observed. At highest strain rates the molecules are fully stretched, thus their size does not depend on the concentration anymore and is the same as for the melts. A full discussion on the scaling properties and the behavior of the radius of gyration of dendrimers in the melt was presented in our earlier work.

\[ \text{C. Blends of dendrimers with linear chain polymers} \]

Dendrimers are considered to be potential candidates to use as rheology modifiers. Due to their unusual flow properties, they could be used as additives to modify and tune properties of polymeric blends. In this section some results of the explicit modeling of blends are presented. At this stage only blends of molecules of the same molecular weight are taken into account. Three different ratios were considered: 1:3, 1:1, and 3:1 resulting in blends containing 25%, 50%, and 75% of dendrimers, respectively (weight fraction).

In Fig. 12 the viscosity of the blends is plotted against the shear rate. The properties of the systems change gradually with the composition and are between those of pure systems. In the Newtonian regime the viscosity decreases with the amount of dendrimers in the system, whereas in the non-Newtonian regime the trend is opposite, and the addition of dendrimers increases the viscosity of the blends. Also the onset of shear thinning shifts towards larger strain rates with the increase of the dendrimer fraction. A similar decrease of the Newtonian viscosity was observed experimentally in blends of linear polymer with hyperbranched polyesters or with highly branched polyphenylenes.

Figure 13 shows the effect of composition on the normal stress coefficients. Due to the statistical uncertainty at lower strain rates, only the high shear rates are taken into consideration. In the case of the first normal stress coefficient, the pressure difference (between the \( x \) and \( y \) diagonal elements of the pressure tensor) is stronger for linear chain polymers than for dendrimer systems, and it monotonically decreases with the amount of dendrimers in the blends. For the second normal stress coefficient the effect of compositions is less profound. However, the trend can be observed in which addition of dendrimers to the linear chain system increases the normal pressure difference (between \( y \) and \( z \) components of the pressure tensor).

\[ \text{IV. CONCLUSIONS} \]

A constant pressure version of the SLLOD algorithm has been implemented and applied to study the flow properties of dendrimers, linear chains, and their mixtures. It was demonstrated that the shear thickening observed earlier in \textit{NVT} simulations is related to the shear-induced changes of pressure, and it disappears when the value of the pressure is maintained constant. Elimination of these effects results in
different values of the exponents in the power-law regions of viscosity and normal stress coefficients in comparison to those previously reported from the NVT simulations. Due to the fact that the hydrostatic pressure of systems under shear varies only at high strain rates, we did not observe significant changes in the microscopic properties characterizing the structure and dynamics of the molecules constituting melts and solutions. The application of the $NpT$ algorithm to blends of dendrimers and linear chains indicates that the onset of shear thinning shifts towards larger strain rates with the increase of the dendrimer fraction which is consistent with the experimentally observed behavior for blends containing hyperbranched polymers.

ACKNOWLEDGMENTS

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FIG. 13. First and second normal stress coefficients of blends of dendrimers of generation 2 (D2G2) with linear-chain molecules of the same molecular weight (43-mers) at various ratios.