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Citation: *J. Chem. Phys.* **134**, 154108 (2011); doi: 10.1063/1.3576122

View online: <http://dx.doi.org/10.1063/1.3576122>

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Nonperiodic stochastic boundary conditions for molecular dynamics simulations of materials embedded into a continuum mechanics domain

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(Received 30 November 2010; accepted 21 March 2011; published online 19 April 2011)

A scheme is described for performing molecular dynamics simulations on polymers under nonperiodic, stochastic boundary conditions. It has been designed to allow later the embedding of a particle domain treated by molecular dynamics into a continuum environment treated by finite elements. It combines, in the boundary region, harmonically restrained particles to confine the system with dissipative particle dynamics to dissipate energy and to thermostat the simulation. The equilibrium position of the tethered particles, the so-called anchor points, are well suited for transmitting deformations, forces and force derivatives between the particle and continuum domains. In the present work the particle scheme is tested by comparing results for coarse-grained polystyrene melts under nonperiodic and regular periodic boundary conditions. Excellent agreement is found for thermodynamic, structural, and dynamic properties. © 2011 American Institute of Physics. [doi:10.1063/1.3576122]

I. INTRODUCTION

The standard way of avoiding surface artefacts in molecular dynamics (MD) simulations of bulk systems is through periodic boundary conditions (PBC): Particles leaving the periodic simulation box through one face re-enter it through the opposite face. Moreover, a particle only interacts with the closest of all periodic images of any other particle.¹ For certain problems, however, there are good reasons to employ *nonperiodic* boundary conditions.^{2–8} First, PBC can be unnecessarily costly. They require a simulation box whose shape is space-filling when periodically replicated, for example, a cube. If the simulated system consists of a globular macromolecule such as a protein in solution or a localized chemical event, less solvent has to be simulated in a spherical box instead of a cubical box. Thus, nonperiodic boundary conditions were originally designed for these cases.^{9–11} Second, PBC may introduce spurious features in structural or dynamic properties in certain systems^{12–17} (even more so when electrostatic interactions are also treated as periodic, which is not an issue in this work^{18,19}). This behavior follows from a periodicity that is artificially imposed onto intrinsically nonperiodic systems such as fluids and amorphous polymers.

Our reason for developing nonperiodic boundary conditions is different. We plan to embed a molecular dynamics domain into a larger region described by a continuum simulation technique finite element (FE) method.²⁰ The continuation of the material beyond the MD region is provided by the FE domain; therefore, there is no need and no use for a periodic continuation. For problems of fluid flow, nonperiodic MD regions have been embedded into a continuum domain

described by computational fluid dynamics schemes, in order to locally resolve flow problems at a higher resolution; for recent reviews, see Refs. 21 and 22. Two schemes are widely used. In the so-called state-variable approach, the MD and the continuum domain overlap with each other. In this coupling region, the continuum and particle descriptions are simultaneously valid and consistent.²³ Continuity of thermodynamic and transport properties (mass and momentum flux) across the interface between the particle and the continuum region is the most important issue. In other state-variable schemes, these two regions are separated from each other by a hard wall. To control the density fluctuations near the boundaries, an external boundary force is applied to the particles.^{24,25} In contrast to the state-variable approach which is based on an exchange of variables, the second technique is characterized by flux exchange.²⁶ In this method the flux boundary conditions are used to couple the MD to the continuum domain.²⁷ They guarantee that the MD domain exchanges mass, momentum, and energy with the continuum domain according to the underlying microscopic dynamics.

In the area of structural mechanics, the concept of embedding MD domains into a larger environment modeled by a continuum method has also been used, for example, to model crack propagation and materials failure.^{28–32} However, these applications have to our knowledge been limited to crystalline materials, e.g. metals. The known atom positions in these systems can be used to simplify the coupling, for example by introducing affine and synchronous deformations of atoms and finite elements. This is the case in the so-called quasi-continuum method where, roughly spoken, the resolution of a FE domain is locally increased to that of the underlying atomic lattice. Other approaches, such as the bridging domain method³³ or the Arlequin method,³⁴ define an overlap region which does not require a particle lattice any more.

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Our objective for embedding an MD domain into a FE surrounding is different from the above applications. Therefore, the requirements of the nonperiodic boundary conditions are different. We aim to ultimately study the behavior of polymeric materials under variable deformations. Detailed simulation studies will be necessary to estimate the maximum deformations in viscoelastic materials that can be described by a linear stress deformation relation. The materials we have in mind include—in principle—amorphous polymers, polymer blends, block-copolymers, semicrystalline polymers as well as nanocomposites. They all have an interesting elastic and plastic deformation behavior and failure mechanisms, which are not yet fully understood on a molecular scale. It is their common property that they are highly disordered and sometimes even heterogeneous and anisotropic. Affine deformation strategies of the established quasicontinuum method for crystalline materials thus cannot be employed.

In particular, we need to devise different nonperiodic boundary conditions for the MD domain for polymeric and other amorphous systems, which is the subject of this contribution. (A preliminary version of the coupling strategy has already been given,³⁵ the implementation and testing of the MD-FE hybrid scheme for amorphous materials will be fully described in a later article.) Our nonperiodic boundary conditions require a set of modifications to standard MD, which ensure the following features:

- (i) The boundary confines the molecules to the designated MD region, preventing them from evaporating into the FE domain.
- (ii) The boundary exerts pressure on the system to create a thermodynamic state (pressure, density) in its centre, which is the same as for the system under the usual PBC. It compensates the spurious surface tension.
- (iii) The boundary acts gently on the MD domain in order to produce polymer structure and dynamics as close as possible to an unperturbed periodic simulation.
- (iv) The boundary provides a heat bath for the MD region and controls its temperature.
- (v) The boundary mimics the dynamical influence of the missing material beyond the simulation box. In particular, it can be made to provide a substitute of the random collisions of MD particles with the missing external atoms and to inhibit dynamics artifacts due to the presence of the boundary.
- (vi) In view of the intended coupling to an FE environment, the boundary conditions are able to transmit displacements and forces between the two domains. In later applications the boundary conditions will be extended to allow deformations of the MD region.

Requirements (i)–(iii) and (vi) are met by defining the so-called anchor points in the boundary region, which—at the same time—confine the system and provide a handle for coupling forces between the two domains. Requirements (iv) and (v) are met by including an area of stochastic dynamics at the edge of the MD domain which may or may not coincide with the boundary region.^{9–11} In the following, we will refer to this collection of implemented features simply as stochastic boundary conditions (SBC). A sketch of the coupled SBC MD-FE system is provided in Fig. 1. The particle domain of this hybrid method is tested by comparing the results of thermodynamic, structural, and dynamic properties of a coarse-grained (CG)³⁶ model of polystyrene under normal periodic and the new stochastic boundary conditions.

II. METHODS

In our stochastic boundary condition scheme, the particle domain is divided into three regions: the MD region, the stochastic or dissipative particle dynamics (DPD) region, and the boundary region (Fig. 1). We have employed the same coarse-grained resolution in the three domains. This mapping avoids a number of problems of multiscale simulations in which particle domains of different resolution are coupled. Strategies to perform these simulations have been described in Ref. 37. Let us continue with the present MD-FE scheme. Particles in the MD region move according to standard Newtonian mechanics. This is the core region, where properties of the system are analyzed and where the interesting events are going to take place. Therefore, in this region the description of the material has to be as realistic as possible. The stochastic dynamics formalism used for the region surrounding the MD region is of the dissipative particle dynamics³⁸ type, which has the advantage over other stochastic dynamics schemes such as Brownian dynamics to be locally momentum conserving, so that shear flows can be simulated if necessary. The DPD equations of motion are used for all particles located in this region. However, the conservative forces in this region are the same as in the MD region and not the usual linear

FIG. 1. The figure illustrates the stochastic boundary conditions and the coupling to the finite element domain. All atoms in the dissipative particle dynamics and boundary region move according to the equations of the DPD thermostat.

forces often used in DPD schemes. The DPD region includes the boundary region (i.e., particles in the boundary region also follow the DPD equations of motion); however, the DPD region can be larger than the boundary region. If, on the other hand, the core part of the system (called above the MD region) could be also described by dissipative particle dynamics, there would be no reason not to use DPD in the whole particle simulation box. The third region, the boundary region, provides for the containment of the MD and DPD regions and it will be later used to communicate forces and displacements between the particle and the continuum domain. These purposes are served by space-fixed anchor points, which are distributed exclusively in the boundary region. In the following, we will discuss the model and implementation issues of the different regions.

The boundary area is the outermost region. It contains particles, which are mobile and follow the DPD equations of motion. This is in contrast to some other SBC schemes where the boundary region is formed by rigidly fixed particles⁵ or by a static external potential of the hollow-sphere type.^{4,6} In order to be able to exert an external force on the particle domain, we introduce the so-called anchor points. To each anchor point, one of the mobile particles is connected by a harmonic potential $V(\mathbf{r}, \mathbf{r}_0) = (k/2)(\mathbf{r} - \mathbf{r}_0)^2$. The force constant k can be considered as a penalty factor in the suggested coupling scheme, which does not represent a material property. The actual position of the particle is defined by the vector $\mathbf{r}$. The anchor point is presently space-fixed at the position $\mathbf{r}_0$. (Later, when the coupling to the FE surroundings is introduced, the anchor point will be fixed to a relative position in the finite element, which overlaps the particle domain in the boundary region.) As the anchor point is not mobile, no equations of motion are solved for it. The force exerted on the anchor point by the molecular system is then given by $\mathbf{F}(\mathbf{r}, \mathbf{r}_0) = -(\partial V(\mathbf{r})/\partial \mathbf{r}_0) = k(\mathbf{r} - \mathbf{r}_0)$ and the tensor of the force derivatives as

$$\partial \mathbf{F} / \partial \mathbf{r}_0 = \begin{pmatrix} -k & 0 & 0 \\ 0 & -k & 0 \\ 0 & 0 & -k \end{pmatrix} = \text{constant}.$$

The forces and force derivatives will be needed in the MD-FE coupling scheme. The force gradients are a key parameter in the Newton-type energy minimization of the coupled scheme.^{34,35} The advantage of using anchor points instead of space-fixing all or a subset of the atoms is that the force on the anchor point comes only from a simple harmonic potential. There are no many-body or curvilinear terms (bond angle and dihedral forces)¹ and no complex analytical³⁹ or tabulated numerical potentials^{40,41} involved here. All these complicated interactions are allowed exclusively between particles, but not between particles and anchor points. We notice that a spherical container made up of harmonically restrained particles has been used previously to implement nonperiodic boundary conditions.³

The particles tethered to anchor points are allowed a local mobility which is defined by the force constant k of the harmonic potential, but they cannot leave the box. Thus, the particles feel the anchor points as a static external potential, and the sum of the harmonic forces from the anchor points

determines the pressure inside the box. In other words, the anchor points assume the role of a wall around the particle domain. Particles exert forces on the wall and in turn the wall exerts a force on the particles.

If the system consists of polymers, it is not necessary to connect all particles in the boundary region to anchor points. For a polymer chain, it is sufficient to connect one or two of its monomers to anchor points to keep the whole molecule at its place (Fig. 1). This may be advantageous, as we intend to perturb the system as little as possible by the boundary conditions. Hence, both the number of anchored particles and the force constant k should be chosen as small as possible, the criterion being that their choice must still sufficiently confine the particles in the particle domain. We try to further minimize distortions under the influence of the anchor points by their spatial distribution. We use an exponential distribution for the anchor point density in the boundary region. It decreases from one at the outer surface of the box to zero at the inner end of the boundary region where it borders the DPD region. This exponential anchor point distribution places more confinement near the surface, where particles have a higher chance of escape, and less rigidity on the inner side, where anchor points could potentially disturb the properties in the analysis region.

An additional role of the anchor points will be in the future to couple the particle domain to the continuum domain. This will be described in detail elsewhere; only a short outline is given here. In the boundary region, particle domain and continuum domain overlap (Fig. 1). A deformation of the surrounding continuum region, which is modeled by finite elements, will entail a deformation of the elements of the boundary region, too. The anchor points will no longer be space-fixed but will be connected to the finite elements in the boundary region. Thus, a deformation of the finite elements will translate into a displacement of the anchor points. If the prescribed deformation of the FE domain is not too large, this displacement is small, but it creates a change of the external field felt by the particles via the spring constant k . In the intervening molecular dynamics steps (there will be many MD steps per one FE step) the particles move in this field and they exert forces on the anchor points (see above). These forces and their gradients, time-averaged over the MD steps after equilibration, are then used in the next FE step, representing the response of the particle region to a deformation by the FE domain. Vice versa, the influence of the FE region on the MD part is expressed in the positions of anchor points, which are updated in each FE step.

The second component of our boundary conditions is a region near the boundary where dissipative particle dynamics is operating, the DPD region for short. The particles in this region follow the equations of motion of DPD, i.e., in addition to the systematic forces, there are pairwise random forces and pairwise friction forces acting on them.⁴² However, we are not using the conservative interparticle forces customarily associated with DPD, which are generic and soft core. Instead, we use the interparticle forces of our coarse-grained polymer model. This combination of DPD equations of motion with a coarse-grained polymer model has been very successful in reproducing the correct polymer dynamics.⁴³ The

DPD region's main *raison d'être* is to pretend that there is a large mass of polymer beyond the confines of the particle region. In addition, it serves as a canonical thermostat, since the combination of a random noise amplitude σ and a friction coefficient γ defines a temperature T by way of a fluctuation dissipation theorem: $\sigma^2 = 2\gamma k_B T$.⁴² The performance of the thermostat defined by its ability to maintain the temperature in the central MD region at the target value depends on the length of the time step and the friction. We observe deviations of up to 12.5 K below the target temperature when using too large time steps (10 fs) and too large friction constants (1200 pN ps nm⁻¹). This behavior has been traced back to artifacts of the integrator.⁴⁴ Therefore, only in a certain range of the DPD friction, the DPD thermostat can control the temperature well.⁴³ To adopt large time steps in the simulation, a DPD friction as small as possible has to be chosen. We have found that the combination of a time step of 5 fs and a friction of 12 pN ps nm⁻¹ is a useful combination, as it maintains the target temperature of 300 K with a fluctuation of ± 1.5 K.

Particles inside the central MD region move according to Newton's equations of motion, all particles outside according to the DPD equations of motion (note that particles interact with the same potentials in both regions). Particles switch their dynamics when crossing between the regions: A particle which is near the border, but inside the MD region has only conservative interactions, even with those particles in the DPD region, which are within its cutoff. In contrast, a particle in the DPD region has conservative interactions with all particles in its cutoff, but friction and random interactions only with particles, which are also located in the DPD region. The passage of particles between the DPD and MD region implies that the number of particles in the MD region is not constant, but should fluctuate around an equilibrium value. The exchange of particles between the two domains is important to preserve the equilibrium structure and the structural fluctuations in the MD region.

III. SIMULATION DETAILS AND RESULTS

To derive the coarse-grained potential for test calculations under stochastic boundary conditions we followed a strategy described previously for amorphous polystyrene (PS).⁴⁵ The tabulated potential has been obtained by Iterative Boltzmann inversion,⁴⁶ which optimizes the coarse-grained potential to reproduce structural distribution functions of a reference atomistic model. It uses one superatom per chemical repeat unit placed at its center of mass.⁴⁵ In atactic PS, the repeat units have different absolute conformations (R and S), which are treated in the model as two different bead types. All simulations were carried out by our software package IBIsCO, which is able to handle tabulated potentials.⁴⁷ The new stochastic boundary conditions were also implemented into this code. The polymer was simulated both with SBC and, for comparison, with orthorhombic periodic boundary conditions.

Simulations under PBC were carried out to generate reference results for comparison as well as to generate initial configurations for the subsequent SBC simulations. The PBC

simulations contained 4104 atactic PS chains of 20 monomers at 300 K. The Berendsen thermostat (coupling time 500 fs) and barostat (coupling time 5000 fs, isothermal compressibility 1.0×10^{-6} kPa⁻¹) were used.⁴⁸ Time steps of 5 fs have been chosen. A nonbonded cutoff of 1.7 nm has been combined with a neighbor list cutoff of 1.8 nm. The PBC system was simulated for 10 ns.

From the final configuration of the PBC simulation the starting configuration for the SBC simulations was generated by shifting all monomers into the original periodic cell. Polymer chains, which were not located completely in the box, were divided into smaller fragments. Therefore, there is a small number of polymers with different chain lengths near the surface of the box. The periodic cell after equilibration under NPT conditions had a length of about 24 nm, which is therefore also the length of the nonperiodic simulation box. Within this box, the central region of 19 nm length was designated as MD region, cf. Fig. 1. Thus, on all sides the MD region is 2.5 nm away from the edge of the particle domain and, hence, from the vacuum. This distance is larger than the cutoff radius (1.7 nm) and avoids a direct influence of the vacuum boundary on the MD region. The thickness of the boundary region (containing anchor points, DPD equations of motion) was 1.7 nm, equal to the cutoff. The DPD region (no anchor points but DPD equations of motion) is therefore 0.8 nm wide. With these choices, we ended up with initially 41298 MD and 40782 DPD particles.

The next step was to define the anchor point positions. Every anchor point is attached to one particle. Hence, we took the anchor-point position to be the same as that of the particle it was attached to. The selection algorithm ensured that there was at least 1 anchor point per polymer chain in the boundary region. In addition, an exponential density of anchor points falling from the outer to the inner end of the boundary region was imposed. We calculated the probability for every particle in the boundary region to be connected to an anchor point based on its position. The tethered particles were then selected with this probability using a random number. As it was discussed in the method section we would not like to perturb the MD region by using too much anchor points. But when using a small number of anchor points may cause a deviation in density and pressure in the MD region from the target value. To solve this problem we have used a method to optimize the force constant. Furthermore we compressed the box for pressure correction without using too many anchor points.

The control parameters in the SBC simulations were essentially the same as described above for the MD calculations under PBC, save for a few changes and additions due to the boundary implementation. For the DPD equations of motion a random force amplitude $\sigma = 10$ pN ps^{1/2} and a friction coefficient $\gamma = 12$ pN ps nm⁻¹ were used. This combination was previously shown to control the temperature well in a similar system.⁴³ The temperature is controlled only in the DPD region, not in the MD region. However, the temperature of the MD region quickly equilibrates to that in the DPD region after an initial transient behavior (Table I). We also found that the number of anchor points has no influence on the temperature and a minor influence on the density of the MD region. Even for the smallest number of anchor points,

TABLE I. Properties of melts of polystyrene chains of 20 monomers at 300 K. Comparison of properties evaluated in the molecular dynamics region calculated under nonperiodic stochastic boundary conditions with different numbers of anchor points and under periodic boundary conditions. For all SBC simulations, the DPD parameters are $\sigma = 10$ pN ps^{1/2} and $\gamma = 12$ pN ps nm⁻¹ and the anchor point force constant is $k = 1400$ kJ mol⁻¹ nm⁻².

Condition	Number of anchor points	Density (kg/m ³)	Temperature (K)	Squared radius of gyration (nm ²)	Squared end-to-end distance (nm ²)
PBC		1020 ± 0.43	300 ± 0.36	1.004 ± 0.02	6.17 ± 0.22
SBC	7262	1015 ± 2.5	300.7 ± 0.91	1.006 ± 0.0032	6.192 ± 0.040
SBC	10954	1017 ± 0.8	300.7 ± 1.08	1.008 ± 0.0015	6.181 ± 0.019
SBC	13780	1019 ± 2.5	301.3 ± 1.12	1.006 ± 0.0018	6.189 ± 0.022

the density of the reference PBC simulation is reproduced to about 0.5%.

Also the force constant k of the anchor point potential is an important parameter of the method, as it has an influence on the number of particles that can leave the box, leading to polymer chains protruding into the continuum region. If the spring is too slack, the anchored particles can move out of the way, when unanchored particles are squeezed out of the particle domain. This is clearly visible in Fig. 2, which shows the final number of monomers, which have escaped from the particle domain within 5 ns of simulation, as a function of the anchor point force constant, for an SBC simulation at 300 K with 7262 anchor points. The curve saturates at $k = 1400$ kJ mol⁻¹ nm⁻². Thus, this is the minimum force constant to be used. For the other number of anchor points collected in Table I we found the same value for the force constant. An additional requirement on the choice of k is that the tethering should not lead to an increase of the highest vibrational frequencies, so that no shorter time step is necessary. This condition is fulfilled, since the stiffest effective force constants in the systems are those of the nearest-neighbor bonded interactions. From the curvature of this potential they are also estimated to be approximately 1400 kJ mol⁻¹ nm⁻². As is shown in Table I, the choice of $k = 1400$ kJ mol⁻¹ nm⁻² (used in this work if not indicated otherwise) not only mini-

FIG. 2. The number of monomers, which leave the designated particle domain in a simulation of 5 ns duration at 300 K depends on the harmonic force constant of the atoms tethered to the anchor points.

mizes the particle escape and allows to maintain the time step, but also keeps the correct density in the central MD region.

Also the global structure of the polymer chains in the MD region (end-to-end distance and radius of gyration, Table I) is identical in PBC and SBC simulations and is independent of the number of anchor points. The same holds for the short-range structure as captured by the radial distribution functions (RDF). This is shown in Fig. 3, where the three RDFs (RR, SS, and RS corresponding to superatoms describing monomers of different chirality) are shown. The SBC curves displayed were obtained from the simulation with 7262 anchor points; the agreement is equally perfect for the other SBC simulations.

The dynamical behavior of the polymer chains is characterized by the autocorrelation function of the end-to-end vector $\langle R(0)R(t) \rangle / \langle R^2 \rangle$. In Fig. 4 we compare the SBC (MD region only, simulation with 7262 anchor points) and PBC results. In both cases the autocorrelation function decays to zero in 800 ps. To determine the relaxation time (τ), the autocorrelation functions were fitted to exponential curves $\exp(-t/\tau)$. The relaxation times amount to 162.5 ps for PBC and 161.8 ps for SBC. A similar agreement is found for other numbers of anchor points.

FIG. 3. Nonbonded radial distribution functions (excluding first and second neighbours on the same chain) for polystyrene chains of 20 monomers at 300 K; solid line: periodic boundary conditions; circles: stochastic boundary conditions, molecular dynamics region only. (a) between R monomers; (b) between S monomers; (c) between R and S monomers.

FIG. 4. Autocorrelation function of the end-to-end vector for polystyrene chains of 20 monomers at 300 K. Solid line: periodic boundary conditions; circles: stochastic boundary conditions, molecular dynamics region only.

In order to further check the correctness of the SBC approach, we conducted a second set of simulations with a different chain length (6000 chains of 10 monomers) and temperature (500 K). In the preparation of the PBC and SBC systems, we proceeded analogously to the previous case (20 mers, 300 K). The final box length in equilibrium was ~ 22.3 nm. The cutoff radius was kept and, thus, the setup of the SBC box was the same. The thicknesses of the boundary and DPD regions were again 1.7 nm and 0.8 nm, respectively. With these dimensions the length of the MD region was roughly 17.3 nm and there were 31 874 DPD and 28 126 MD particles. We simulated this system with different numbers of anchor points. In Table II it can be seen that the outer DPD thermostat provides an efficient temperature control in the inner region. After the optimization of the force constant there is a small deviation in the density, which is about 0.8% too low, irrespective of the number of anchor points used (Table II, values in parentheses). This small deviation has, however, a large influence on the pressure in the MD region (which is calculated to be between -1100 and -2500 kPa) and also on the forces on the anchor points. To overcome these prob-

TABLE II. Properties of melts of polystyrene chains of 10 monomers at 500 K. Comparison of properties evaluated in the molecular dynamics region calculated under nonperiodic stochastic boundary conditions with different numbers of anchor points and under periodic boundary conditions. For all SBC simulations, the DPD parameters are $\sigma = 10$ pN ps $^{1/2}$ and $\gamma = 7.2$ pN ps nm $^{-1}$ and the anchor point force constant is $k = 1400$ kJ mol $^{-1}$ nm $^{-2}$. Values in parentheses refer to the systems before compression (see text).

Condition	Number of anchor points	Density (kg/m 3)	Temperature (K)
PBC	...	932.0 ± 1.2	500 ± 0.87
SBC	6219	(924.6 ± 1.9)	(500.4 ± 2.5)
		930.8 ± 1.9	501.8 ± 2.2
		(925.9 ± 1.3)	(500.6 ± 1.4)
SBC	9158	931.8 ± 1.3	500.6 ± 2.1
		(925.7 ± 0.3)	(499.9 ± 2.2)
		931.7 ± 1.5	500.9 ± 2.1

FIG. 5. Number of atoms in the MD region from stochastic-boundary simulations for polystyrene chains of (a) 20 monomers at 300 K (b) 10 monomers at 500 K.

lems, we equilibrated the box until the desired pressure of 101.3 kPa was reached. During the correction of the pressure we fixed the number of anchor points and the value of the force constant. This approach is similar in spirit to NpT simulations with a Berendsen barostat.⁴⁸ Instead of changing the box size in a periodic simulation, however, we scaled the positions of the anchor points and all atoms in a weak-coupling scheme with a coupling time of 5000 fs and an isothermal compressibility of 1.0×10^{-6} kPa $^{-1}$. In contrast to the periodic NpT approach, we calculated the local pressure⁴⁹ only in the MD region. After 5 ns of NpT equilibration we fixed the anchor points to their positions averaged over another 5 ns. Then we simulated for another 10 ns. The average densities (Table II; values without parentheses) agree with the PBC reference value within the error bars. Note that the manual adjustment of the anchor points to reproduce the pressure in the interior of the MD region was only necessary because of the still missing external pressure. In the final hybrid FE-MD scheme, the FE environment will take the role of moving the anchor points in response to deformation forces, which include the pressure components in the MD region.

Due to the exchange between the MD and DPD region, the particle number in the MD domain was not constant (Fig. 5). It fluctuated between 27 600 and 27 900 (about 1%) around its equilibrium average. Thus, the migration between the MD and DPD region did not lead to a flow into one direction.

IV. SUMMARY

A scheme has been developed for performing molecular dynamics simulations on polymeric materials under nonperiodic stochastic boundary conditions. It has been designed to allow the embedding of a particle domain treated by molecular dynamics into a continuum environment treated by finite elements. The scheme combines the use of anchor points, to which a small number of particles in the boundary region is harmonically tethered, as a means of confining the particle region, with the use of dissipative particle dynamics as stochastic equations of motion to ensure the dissipation of

energy and to thermostat the simulation. While none of the individual ingredients is new, the combination described here is particularly suited for hybrid simulations. The use of flexibly tethered particles as confinement is less perturbative to the core of the particle region than the sometimes used position-constrained particles. The employment of anchor points allows an efficient and flexible transmission of forces into the finite-element domain, much more than containers based on hard walls or static potentials of mean force. It also provides a mechanism to allow—within certain limits—shapes and deformations of the particle domain, in contrast to some nonperiodic schemes, which enforce, for example, a spherical shape. Dissipative-particle dynamics near the boundary ensures that the particle dynamics is sufficiently randomized and that the heat bath of the degrees of freedom, which are missing beyond the boundary, is better emulated than with straight molecular dynamics. Moreover, its ability to remedy the artificially enhanced mobility of coarse-grained polymer models is well documented.

The nonperiodic boundary conditions have been tested for two systems of atactic short-chain polystyrene described with a standard coarse-grained model. In both cases, the nonperiodic boundary conditions reproduce excellently thermodynamic quantities such as the density and temperature, the global structure (radius of gyration, end-to-end distance), local structure (radial distribution functions) and the dynamics (relaxation time of the end-to-end vector) of molecular dynamics simulations of these systems under regular periodic boundary conditions. Note that in both cases, the nonperiodic simulation cells were rectangular. It may be concluded that the polystyrene in the inner region of the particle domain (called MD region above) behaves as though it were surrounded by an infinite mass of particulate polystyrene. We thus feel well equipped to combine the present treatment of the particle domain with a finite element surrounding to develop a new hybrid method. Its implementation and testing is underway and will be described in a later paper.

ACKNOWLEDGMENTS

This work is supported by the European Union under the FP7-NMP-2007 program, Nanomodel Grant Agreement SL-208-211778. Fruitful discussions with Professor Hossein Eslami are gratefully acknowledged.

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