Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 45 (2004) 3901–3905

polymer

www.elsevier.com/locate/polymer

Molecular dynamics simulations of the glass transition in polymer melts

Wolfgang Paul*

Institut für Physik, Johannes Gutenberg-Universität, Staudinger Weg 7, 55099 Mainz, Germany

Received 17 May 2003; received in revised form 8 January 2004; accepted 8 January 2004

Abstract

Computer simulations of polymer models have contributed strongly to our understanding of the glass transition in polymer melts. The ability of the simulation to provide information on experimentally not directly accessible quantities like the detailed spatial arrangement of the particles allows for stringent tests of theoretical concepts about the glass transition and provides additional insight for the interpretation of experimental data. Comparing coarse-grained simulations of a bead-spring model and chemically realistic simulations of 1,4-polybutadiene the importance of dihedral barriers for the glass transition phenomenon can be elucidated.

Keywords: Glass transition; Polymer melt; MD simulation

1. Introduction

Since a long time polymers have played a central role in studies of the structural glass transition because on the one hand, metastable equilibrium of the supercooled melt is not hard to obtain (for many polymers we do not even know whether there exists a crystalline ground state at all), and on the other hand understanding the properties of glassy polymers is of high technological relevance.

In the last 15 years the focus in the studies of the glass transition has shifted somewhat. Many of the early attempts to understand the glass transition phenomenon were centered around the Kauzmann paradox of a seemingly vanishing excess entropy of the supercooled melt with respect to the crystal. For polymers this phenomenon could be reproduced within the Gibbs–DiMarzio theory [1] which predicts many experimentally observable facts (thermodynamic derivatives of the entropy), however, only produces an entropy catastrophe due to inaccurate approximations [2].

A view of the glass transition as a purely kinetic phenomenon has been advocated by mode-coupling theory (MCT) which furthermore traces the transition to a crossover in relaxation behavior in the supercooled fluid which occurs about 20% above the calorimetric glass transition (for fragile glass formers which follow a Vogel–Fulcher–Tamman law for the temperature dependence of the viscosity). This crossover happens on microscopic to mesoscopic length and time scales and is therefore well observable on the scales of, for instance, neutron scattering experiments [3] and computer simulations [4]. Molecular dynamics (MD) simulations of a bead-spring model have been analyzed in great detail within the predictions of MCT and we will present some of the results in Section 2.

Coarse-grained polymer models like the bead-spring model, however, lack a physical property that is determining much of the relaxation behavior in real polymer melts which is hindered rotation around chemical bonds described through dihedral potentials. In Section 3 we will discuss MD simulations of 1,4-polybutadiene with and without taking the dihedral potential into account to find out how these potentials influence the local dynamics in polymer melts. Section 4 will finally present some conclusions.

2. The cage effect in simulations of a bead-spring model

This model represents the polymers by Lennard–Jones spheres bonded by a finitely extendable nonlinear spring [5]. One can kinetically hinder crystallization in the course of the simulation by making the equilibrium distance between bonded monomers (in the following all quantities will be given in Lennard–Jones units), $b_{\min} = 0.96$, different from the equilibrium distance of non-bonded monomers,

---

* Tel.: +49-6131-3923644; fax: +49-6131-3925441.
E-mail address: wolfgang.paul@uni-mainz.de (W. Paul).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.01.079

$r_{\min} = 1.13$. Chains of length $N = 10$ were studied and a melt of such chains was cooled down along an isobar, where equilibration was performed in an NpT simulation and the dynamics was then studied in an NVT simulation to avoid spurious effects of the barostat. Since the characteristic ratio of these chains is close to one, $N = 10$ corresponds to about nine statistical segments, a chain length which is just long enough to display Gaussian chain statistics typical for polymers in the melt.

The mode-coupling scenario for the glass transition in this model has been studied in great detail [6–11] and I will here only discuss a few selected results. From the behavior of the static structure factor of the melt upon cooling one can infer that the structure stays amorphous with a first sharp diffraction peak (amorphous halo) at $q = 6.9$ [7]. This peak increases in height and sharpens and slightly shifts following the volume expansion. A first phenomenological impression of the slowing down of the relaxation processes can be obtained by looking at the temperature dependence of the center of mass diffusion coefficient of the chains. For temperatures below 1 (in units of the Lennard–Jones energy ϵ) it can be fitted with a Vogel–Fulcher law: $D(T) = D(\infty) \exp\{-E/(T - T_0)\}$ with a seemingly vanishing diffusion coefficient at the Vogel–Fulcher temperature $T_0 = 0.35$. On the other hand, one can start from a crystalline ground state at $T = 0$ where all chains are extended parallel to the z-direction and the end monomers of the chains are located on a tetragonal lattice with an additional base atom in the center [12]. Upon heating this structure slowly, one observes a melting (see Fig. 1) at a temperature $T_m = 0.75 \pm 0.05$. The temperature regime between the Vogel–Fulcher temperature $T_0 = 0.35$ and the melting temperature $T_m = 0.75$ constitutes the supercooled fluid regime of this model. Within this temperature window the mode-coupling theory (MCT) [13] of the glass transition predicts the cage effect to become dominant for the slowing down of the relaxation. This caging is predicted to lead to a two step decay of correlation functions with an intermediate plateau regime called β-regime (which should, however, not be confused with the Johari–Goldstein β-process) where the atoms are still confined in their neighbor cages and a long time structural relaxation (α process), which is predicted to obey time–temperature superposition.

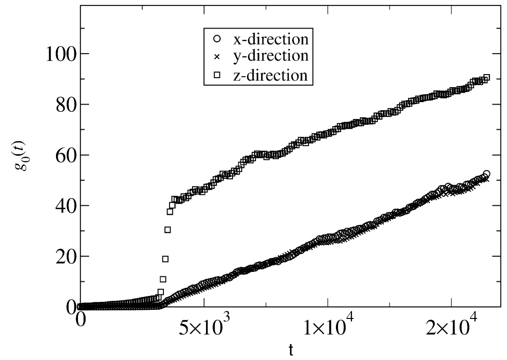

Fig. 1. Mean square displacements of the atoms in the crystalline configuration along the chain axis (z) and perpendicular to it (xy). The temperature is $T = 0.77$.

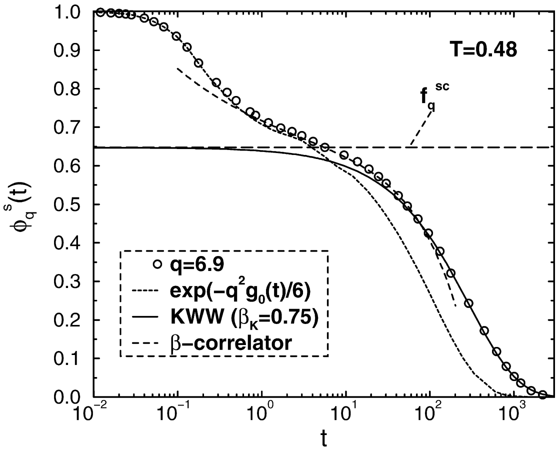

Fig. 2. Intermediate incoherent scattering function at the first sharp diffraction peak for a temperature in the supercooled melt regime. The first part of the decay is described by the mean square displacements $g_0(t)$ invoking the dynamic Gaussian approximation. Then the MCT β-correlator describes the plateau and finally the KWW stretched exponential fits the long-time decay.

In Fig. 2 we show the incoherent intermediate scattering function at the momentum transfer of the amorphous halo in the supercooled melt. The two step decay is clearly visible and the whole curve can be split into a short time ballistic and harmonic motion, where the dynamic Gaussian assumption $S(q,t) = \exp\{-q^2 g_0(t)/6\}$, g_0 being the monomer mean square displacement, still works, an MCT β-regime and the long time structural decay given by a Kohlrausch–William–Watts (KWW) stretched exponential function. On approaching the so-called MCT critical temperature T_c the idealized version of the theory predicts that the temporal extend of the plateau regime diverges and the structural relaxation arrests completely. Close to T_c the α time-scale should show a power law divergence $\tau_\alpha \propto (T - T_c)^{-\gamma}$, the time-scale of the plateau should diverge as $\tau_\epsilon \propto (T - T_c)^{-2a}$ and the amplitudes of the von Schweidler law $S(q,t) = f_q^c - h_q(T)t^b$ should vanish as $(T - T_c)^{1/2}$. Fig. 3 shows that the bead-spring polymer [5,7] model is nicely consistent with all these predictions with a $T_c = 0.45$.

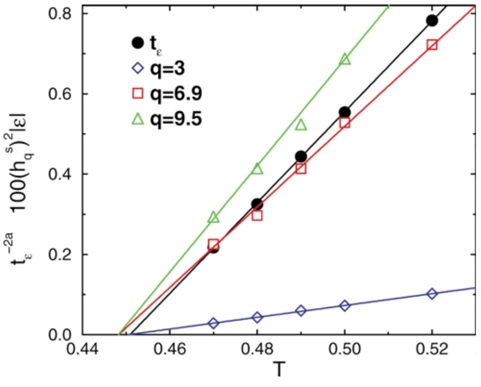

Fig. 3. Test of the MCT predictions for the β-scaling giving $T_c = 0.45$.

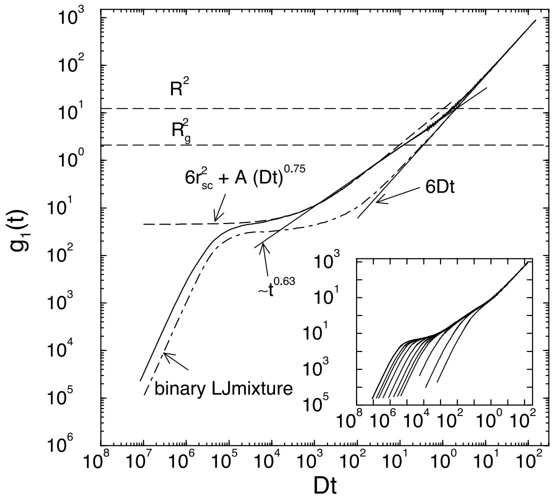

Fig. 4. Master curve of the mean squared monomer displacement of center monomers of the bead-spring chains compared to that of a binary Lennard–Jones mixture [14]. The inset shows the construction procedure before removing the parts not on the master curve.

This also holds for single-chain coherent or melt coherent scattering [10].

$$\lambda = \frac{\Gamma(1-a)^2}{\Gamma(1-2a)} = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)} \qquad \gamma = \frac{1}{2a} + \frac{1}{2b} \tag{1}$$

The measured exponent parameter $\lambda = 0.635$ which determines all other exponents according to Eq. (1), does not depend on the thermodynamic path used to approach the transition [8]. The polymer typical melt dynamics as described by the Rouse model is enslaved to the caging process and follows the α-scaling [9]. This is understandable through Fig. 4 which shows a mean square displacement master curve obtained from plotting the mean squared displacement of center monomers at different temperatures versus time times the center of mass diffusion coefficient of the chains.

The caging occurs on a length scale which is much smaller than the bond length of this model. On these length scales the monomers do not really feel the connectivity constraint of being part of a polymer. Therefore, the behavior is also very similar to what was observed in the MD simulation of a binary LJ mixture by Kob et al. [14], even to the point that the mode-coupling critical temperatures are almost identical ($T_c = 0.45$ versus 0.435 for the Lennard–Jones mixture) between the two very different models. The late part of the decay out of the plateau, however, is influenced by connectivity and instead of crossing over to a free diffusion behavior like in the LJ mixture, for the polymers the Rouse mode dominated regime sets in with an exponent 0.63 which is smaller than the von Schweidler exponent $b = 0.75$ of the plateau decay. This behavior has recently also been incorporated into a mode-coupling theory by extendeding it to not only include the melt structure factor but partial structure factors $S_{\mathrm{nm}}(q)$ for the correlations between monomers at different positions n and m along one chain [15], taking connectivity into account in this way.

But can it really be true that connectivity is just another way to prevent crystallization and all molecular details do not matter for the actual caging process in a polymer melt? Considering the fact that we are not treating large-scale universal phenomena with the cage effect this seems rather unlikely.

3. Dihedral barriers and caging dynamics

One of the experimentally best studied glass forming polymers is 1,4-poly-butadiene (also including a varying degree of vinyl content). There have been some early MD studies of chemically realistic models of polybutadiene melts [16–18]. To improve on these simulations to be able to perform a parameter free quantitative comparison with experiment we needed a highly optimized, quantum chemistry based force-field. This was developed in Ref. [20] and later tested at high temperatures against neutron scattering results [21,22], nuclear magnetic resonance results on spin lattice relaxation times [21,23] and dielectric data [24].

The calculation of the dielectric response of a 1,4-polybutadiene melt may serve to illustrate one of the strong points of the computer simulation approach. Dielectric measurements are a $q = 0$ technique, i.e., they measure the response of the whole sample volume. To assign molecular motions underlying the observed relaxation is an involved process relying heavily on models for the actual motion of the polymer. The simulations for 1,4-polybutadiene [24] were performed without including interactions due to the small partial charges on the molecule. It is therefore expected that a calculation of the dipole moment by reinserting charges into the stored trajectories will not display correlations between the dipole moments of different chains, so that the average squared dipole moment of the box is just the sum of the squared dipole moments of the individual chains. Further comparison with the time scales of different Rouse modes, which measure the typical reorientation time for segments of varying length (depending on mode number) of the chain, showed, that the dielectric measurement in this case is observing the reorientational motion of a chain segment of about six backbone bonds, which is about a Kuhn segment length of the chain. The relaxation map shown in Fig. 5 shows that the simulation data are in good quantitative agreement with experimental information suggesting that also in the experiment the observed relaxing quantity is the dipole moment of a Kuhn segment.

The excellent agreement between simulation and experiment for the local reorientational motion as observed in dielectrics or NMR experiments relies strongly on the quality of the dihedral force field used in the simulation. These relaxation processes are exponentially sensitive to the

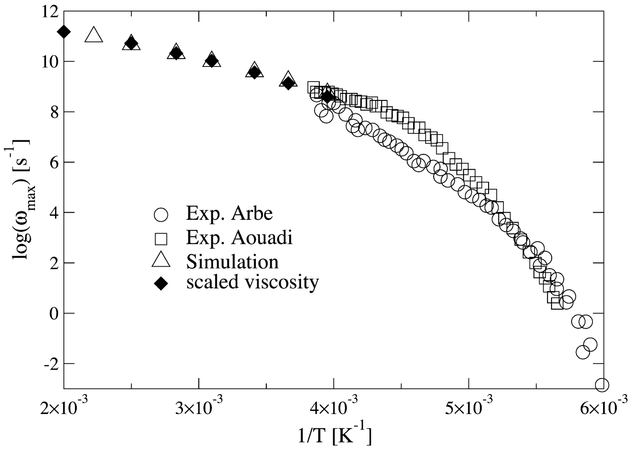

Fig. 5. Relaxation map of the structural relaxation in 1,4-polybutadiene as observed in dielectric spectroscopy. The experiments observe the dielectric α-relaxation whereas the simulations are in the temperature window of the combined α–β process.

values of the barriers in the dihedral potentials. It is natural to ask what the influence of these barriers on the mean square displacement behavior of the monomers is, similar to the study in Ref. [19] where the effect of the barrier heights in a polyethylene model on the glass transition temperature in the simulation was studied. To investigate this, we compare the chemically realistic simulation of 1,4-polybutadiene (CRC) with another one, where we turned off all dihedral potentials (FRC, freely rotating chain model). Polybutadiene is a special case, in that this has no influence on the melt structure (as shown in Fig. 6) or on the single chain structure factor [25]. This can be traced to the symmetry (all isomers are iso-energetic) of the dihedral potentials in this polymer.

In MCT the structural relaxation is completely determined through the structure factors. All coupling constants between different modes are functionals of these static pair correlation functions. Consequently, these two polymer models should show the same dynamics, if MCT were applicable to them. In Fig. 7 we compare mean square displacements of the CH_2 groups along the chain between the two models for several temperatures well above the mode-coupling T_c of PBD which is 220 K. Clearly, the CRC model develops a well-defined plateau regime which is reminiscent of the caging effect discussed for the bead-spring model in the previous section. At the same temperature, however, the FRC model shows no indication of this plateau so that this ‘caging’ can not be traced to the intermolecular packing. It is due to the dihedral barriers. The short time vibrational motion is damped out on the time scale of 1 ps for typical carbon-based polymers. At high temperatures thermal activation is fast enough, so that the typical time scale between jumps over dihedral barriers is of the same size. With decreasing temperature this time-scale increases in an Arrhenius fashion [23] and the relaxation is halted until a thermal activation happens. The dihedral potentials, which depend on the position of four adjacent atoms induce four-body correlations, which do not factorize into two-body correlations as assumed in the closure of the MCT equations. Consequently, one of the central results of MCT, the factorization theorem for the β-relaxation (i.e. the von Schweidler law discussed above) does not hold for this plateau regime [25].

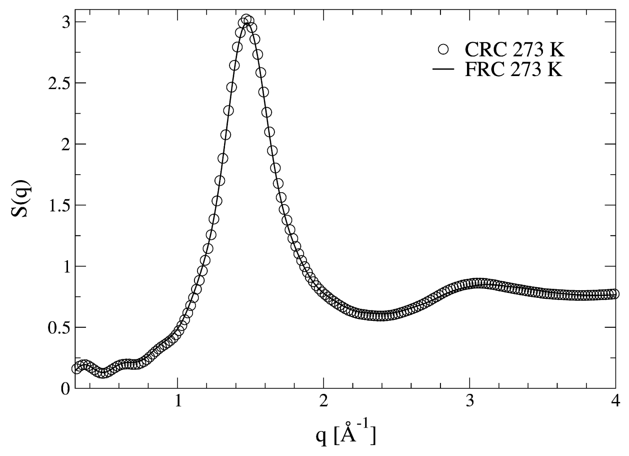

Fig. 6. Melt structure factor for the chemically realistic model of 1,4-polybutadiene (CRC) and the freely rotating chain model (FRC).

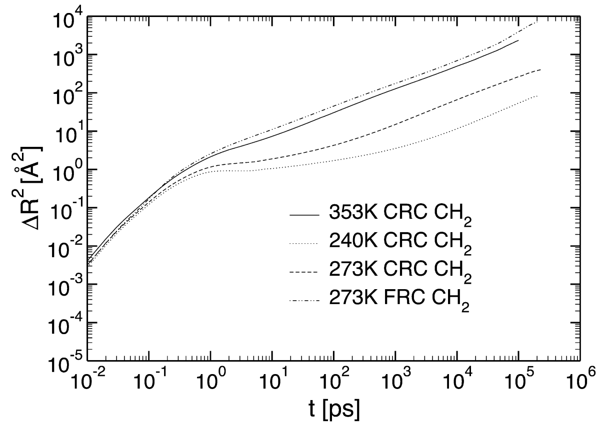

Fig. 7. Mean square displacements of CH_2 groups compared between the CRC and the FRC model at high temperatures.

4. Conclusions

We have discussed in this contribution several results from the computer simulation efforts of the last decade to help understand the glass transition in polymer melts. As most polymers do not crystallize easily they could be studied in (meta-)stable equilibrium since a long time and much is known about the phenomenology of the polymer glass transition.

The view of the glass transition as a purely kinetic phenomenon nowadays is mainly connected with the mode-coupling theory of the glass transition. Although this theory was developed for simple liquids, experimentally it was mostly tested on molecular or polymeric liquids, with the exception of sterically stabilized colloids. We know in polymer physics that all the universal phenomena of this class of materials rely on the presence of excluded volume and chain connectivity. Therefore, a MD simulation of a simple bead spring model was performed to study the applicability of MCT to the polymer glass transition. Within the supercooled fluid regime of this model a temperature interval could be identified, where a two step decay of correlation functions developed. The features of this two step decay in the plateau regime (β-regime) and the long-time decay (α-relaxation) were nicely consistent with the predictions of MCT. Since the caging happened on length scales much shorter than the bond length in this coarse-grained model, the connectivity played no important role for the cage effect and the polymer dynamics as described by the Rouse model simply followed the scaling of the α-process. The influence of connectivity on the late stages of the β-regime and the α-process could recently also be included into a mode-coupling approach.

In real polymers, however, there exists a strong influence of dihedral barriers on the qualitative and quantitative behavior of relaxation processes. A chemically realistic model of 1,4-polybutadiene with a carefully optimized, quantum chemistry based force field is able to quantitatively reproduce the relaxation behavior of this polymer in the melt. In a computer simulation one can selectively change aspects of the model to look at their importance for a given phenomenon. In this spirit a freely rotating chain model of PBD (where all dihedral potentials were switched off) and a chemically realistic model of PBD were studied. Even far above the glass transition temperature the chemically realistic model of PBD shows a plateau regime in the mean squared monomer displacements, whereas the FRC model at the same temperature shows no such effect. Since the structural properties of the two models as quantified by the melt and chain structure factors are identical, this can not be rationalized within a mode-coupling approach, where the dynamics is uniquely determined through these static two-body correlation functions. Dihedral potentials describe four-body correlations, which do not factorize into two-body correlations. The barriers in the potential lead to a slowing down, because further relaxation can only occur through thermal activation. This is similar to the cage process, although of different physical origin. It has also been shown that in the studied temperature range the temperature dependence of the mean rate of torsional transitions is given by the rotational barrier height alone [23], so that there are no discernible packing effects on the barrier crossing yet at this temperture. This may change at lower temperatures and it is an interesing whether there will be a crossover from mainly intramolecular caging at high temperatures to packing dominated slowing down at low temperatures. Existing claims in the literature not withstanding [26], it remains to be seen to what degree MCT will be applicable to the relaxation behavior at lower temperatures.

Acknowledgements

It is a pleasure to thank M. Aichele, J. Baschnagel, D. Bedrov, C. Bennemann, K. Binder, O. Borodin, J. Buchholz, B. Dünweg, S. Krushev, and G.D. Smith for a fruitful collaboration. Financial support from the DFG through SFB 262 and grant PA 473/3 and from the BMBF through grants 03N8000C and 03N6015 is greatfully acknowledged.

References

[1] Gibbs JH, Di Marzio EA. J Chem Phys 1958;28:373–83.
[2] Wolfgardt M, Baschnagel J, Paul W, Binder K. Phys Rev E 1996;54: 1535–43.
[3] Richter D, Monkenbusch M, Arbe A, Colmenero J. J Non-Cryst Solids 2001;287:286–96.
[4] Binder K, Baschnagel J, Paul W. Prog Polym Sci 2003;28:115–72.
[5] Bennemann C, Paul W, Binder K, Dünweg B. Phys Rev E 1998;57: 843–51.
[6] Bennemann C, Donati C, Baschnagel J, Glotzer SC. Nature 1999;399: 246–9.
[7] Bennemann C, Baschnagel J, Paul W. Eur Phys J B 1999;10:323–34.
[8] Bennemann C, Paul W, Baschnagel J, Binder K. J Phys: Condens Matter 1999;11:2179–92.
[9] Bennemann C, Baschnagel J, Paul W, Binder K. Comput Theor Polym Sci 1999;9:217–26.
[10] Aichele M, Baschnagel J. Eur Phys J E 2001;5:229–43. Aichele M, Baschnagel J. Eur Phys J E 2001;5:245–56.
[11] Varnik F, Baschnagel J, Binder K. J Phys 2000;10:239–42.
[12] Buchholz J, Paul W, Varnik F, Binder K. J Chem Phys 2002;117: 7364–72.
[13] Götze W, Sjögren L. Rep Prog Phys 1992;55:241–376. Götze W. J Phys: Condens Matter 1999;11:A1–A45.
[14] Kob W, Andersen HC. Phys Rev E 1995;51:4626–41.
[15] Chong SH, Fuchs M. Phys Rev Lett 2002;88:185702.
[16] Kim E, Misra S, Mattice WL. Macromolecules 1993;26:3424–31.
[17] Gee RH, Boyd RH. J Chem Phys 1994;101:8028–38.
[18] Gee RH, Boyd RH. Polymer 1995;36:1435–40.
[19] Gee RH, Boyd RH. Comput Theor Polym Sci 1998;8:93–8.
[20] Smith GD, Paul W. J Phys Chem A 1998;102:1200–8.
[21] Smith GD, Paul W, Monkenbusch M, Willner L, Richter D, Qiu XH, Ediger MD. Macromolecules 1999;32:8857–65.
[22] Smith GD, Paul W, Monkenbusch M, Richter D. Chem Phys 2000; 261:61–74.
[23] Smith GD, Borodin O, Bedrov D, Paul W, Qiu XH, Ediger MD. Macromolecules 2001;34:5192–9.
[24] Smith GD, Borodin O, Paul W. J Chem Phys 2002;117:10350–9.
[25] Krushev S, Paul W. Phys Rev E 2003;67:021806.
[26] van Zon A, de Leeuw SW. Phys Rev E 1998;58:R4100–3.