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# Polymer brushes in solvents of variable quality: Molecular dynamics simulations using explicit solvent

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The structure and thermodynamic properties of a system of end-grafted flexible polymer chains grafted to a flat substrate and exposed to a solvent of variable quality are studied by molecular dynamics methods. The macromolecules are described by a coarse-grained bead-spring model, and the solvent molecules by pointlike particles, assuming Lennard-Jones-type interactions between pairs of monomers ( $\epsilon_{pp}$ ), solvent molecules ( $\epsilon_{ss}$ ), and solvent monomer ( $\epsilon_{ps}$ ), respectively. Varying the grafting density  $\sigma_g$  and some of these energy parameters, we obtain density profiles of solvent particles and monomers, study structural properties of the chain (gyration radius components, bond orientational parameters, etc.), and examine also the profile of the lateral pressure  $P_{\parallel}(z)$ , keeping in the simulation the normal pressure  $P_{\perp}$  constant. From these data, the reduction of the surface tension between solvent and wall as a function of the grafting density of the brush has been obtained. Further results include the stretching force on the monomer adjacent to the grafting site and its variation with solvent quality and grafting density, and dynamic characteristics such as mobility profiles and chain relaxation times. Possible phase transitions (vertical phase separation of the solvent versus lateral segregation of the polymers into “clusters,” etc.) are discussed, and a comparison to previous work using implicit solvent models is made. The variation of the brush height and the interfacial width of the transition zone between the pure solvent and the brush agrees qualitatively very well with corresponding experiments. © 2007 American Institute of Physics. [DOI: 10.1063/1.2768525]

## I. INTRODUCTION

Flexible macromolecules, anchored by a special end group to a substrate at sufficiently large grafting density, such that different chains overlap, form a polymeric surface layer which is called a “polymer brush.”<sup>1–7</sup> There has been an enormous interest in these systems, due to various applications, such as colloid stabilization,<sup>7,8</sup> tuning of adhesion and wetting properties<sup>7,9</sup> to lubrication, friction, and wear.<sup>5,6,10</sup> In most situations, of course, a solvent is present and the grafted polymeric layer is not at melt density; thus the interactions between solvent molecules and the monomers of the grafted chains need to be considered.

However, in most of the theoretical<sup>1,2,11</sup> and simulation<sup>3,5,11</sup> studies, solvent molecules are not explicitly considered. The good solvent case traditionally is modeled by excluded-volume-type repulsive effective interactions between the monomeric units forming the macromolecules,<sup>3,5,11</sup> and most of the theoretical and simulation works address the good solvent case exclusively. Only relatively few theoretical investigations address the case of polymer brushes in variable solvent quality, i.e.,  $\Theta$  solvents and poor solvents,<sup>12–24</sup> and even less simulation studies did address this

problem.<sup>25–27</sup> On the level of scaling and self-consistent field theories molecular detail is almost completely absent, while solvent quality enters at best via Flory-Huggins-type<sup>28–30</sup> enthalpic terms. But also the models used in the simulations<sup>25–27</sup> treat again the solvent only implicitly, compensating for the short range repulsion between monomeric units by longer range effective attractive interactions.

The understanding of polymer brushes immersed in  $\Theta$  solvents (where for large chain lengths repulsive and attractive forces between monomers effectively balance each other<sup>28–30</sup>), and in poor solvents (where the attractions dominate) is unsatisfactory in several respects: (i) as reviewed in the literature,<sup>3,4,26</sup> unresolved discrepancies exist between the results of analytical theories and simulations. (ii) Disregarding the solvent molecules renders attempts to theoretically model the response of brushes to shear deformation<sup>31–40</sup> very problematic since the hydrodynamic forces mediated by the solvent are not properly treated. Pioneering recent work including solvent molecules explicitly<sup>41–45</sup> does not suffer from this criticism but is restricted to the good solvent case. Analytic theories for polymer brushes under shear require rather drastic approximations,<sup>46–52</sup> and hence the theoretical

study of the combined effects of poor solvent quality and flow is difficult. Most of this work relies on the simple Alexander<sup>53</sup>–de Gennes<sup>54</sup> model of a polymer brush under good solvent conditions, where the free end distribution is a delta function  $\rho_e(z) \propto \delta(z-h)$  at the brush height ( $h$ ) and the monomer density distribution is a Heaviside step function,  $\rho(z) \propto \Theta(h-z)$ . However, more elaborate theories,<sup>1–4,55</sup> simulations,<sup>5,56,57</sup> and last but not least, experiments<sup>58–64</sup> have shown that the Alexander–de Gennes model of polymer brushes is only a very crude description of reality.

In the present paper, we take a further step toward the more realistic modeling of polymer brushes including an explicit solvent as done in Refs. 41–45, but now allowing for the effect of *varying solvent quality*. Thus, we can ask how the solvent density profile looks like as a function of the distance from the wall and as function of the various energy parameters of the problem. This question could simply not be asked at all in the framework of the models treating the solvent only implicitly. This step is a prerequisite to consider more complicated problems in future work, such as brushes in poor solvents under shear, phase separation effects when brushes are immersed in two-component solvents,<sup>65</sup> etc.

In the next section, we briefly describe the simulated model and comment on methodic aspects of our simulations: preparation of the initial configuration, choice of ensemble, etc. In the third section, results on density profiles of monomers, solvent molecules, chain ends are presented, as well as profiles of local pressure, bond vector orientation, etc. Also the chain linear dimensions under variable solvent conditions are discussed. The surface tension of the polymer brush against the solvent is derived, and the conditions under which the brush in the bad solvent stays laterally homogeneous are studied. In the last section, a concluding discussion is given, including comparisons to previous work where the solvent was treated only implicitly. As a reference system, we treat single free chains in solutions of variable quality in the Appendix.

## II. MODEL AND SIMULATION ASPECTS

Following previous studies of coarse-grained models for polymer brushes with molecular dynamics methods,<sup>3,5,11,66,67</sup> polymer chains are represented by the Grest-Kremer<sup>68</sup> bead-spring model, but unlike these studies we allow for a short range attractive interaction both between the effective monomeric units and between solvent particles and these beads, respectively. The interaction potential among solvent particles has been chosen purely repulsive, however.

As a functional form for our potentials, we follow Soddemann<sup>69</sup> to truncate the Lennard-Jones potential in its minimum and shift it to some desired depth ( $\epsilon_{pp}, \epsilon_{ps}$ ), continuing from its minimum to zero with a potential having a cosine form and thus providing a potential that is both continuous and has a continuous derivative too. Thus our potential is

$$U_{\text{LJ cos}}(r) = 4\epsilon_{\text{LJ}}[(\sigma_{\alpha\beta}/r)^{12} - (\sigma_{\alpha\beta}/r)^6 + 1/4] - \epsilon_{\alpha\beta}, \quad r \leq \sigma_{\alpha\beta}2^{1/6}, \quad (1)$$

where  $\{\alpha\beta\}$  stands for the different types of pairs,  $pp$ ,  $ps$ , and

$ss$ , respectively, and we choose the range parameters identical,  $\sigma_{pp} = \sigma_{ps} = \sigma_{ss}$ . Scales for length and energy (and temperature) are chosen such that both  $\sigma_{pp} = 1$  and  $\epsilon_{\text{LJ}} = 1$  (Boltzmann's constant  $k_B = 1$ ). For  $r \geq \sigma_{\alpha\beta}2^{1/6}$  we choose the cosine potential as follows

$$U_{\text{LJ cos}}(r) = \begin{cases} \frac{1}{2}\epsilon_{\alpha\beta}\{\cos[a(r/\sigma_{\alpha\beta})^2 + b] - 1\}, & 2^{1/6} \leq r/\sigma_{\alpha\beta} \leq 1.5 \\ 0, & r \geq 1.5\sigma_{\alpha\beta}. \end{cases} \quad (2)$$

Here  $a$  and  $b$  are determined as the solutions of the two equations.

$$2^{1/3}a + b = \pi, \quad 2.25a + b = 2\pi, \quad (3)$$

which yields<sup>69</sup>  $a = 3.173\,072\,867\,8$  and  $b = -0.856\,228\,645\,44$ . As desired, both  $U_{\text{LJ cos}}(r)$  and  $dU_{\text{LJ cos}}(r)/dr$  are continuous at the potential minimum  $r/\sigma_{\alpha\beta} = 2^{1/6}$  and at the cutoff  $r/\sigma_{\alpha\beta} = 1.5$ . As mentioned above, we choose  $\epsilon_{ss} = 0$ , so only the purely repulsive part described by Eq. (1) remains for the solvent-solvent interaction, but  $\epsilon_{ps}$  and  $\epsilon_{pp}$  are varied over a wide range.

The spring potential of our bead-spring model is created by adding a finitely extensible nonlinear elastic (FENE) potential<sup>68</sup>

$$U_{\text{FENE}}(r) = \begin{cases} -\frac{1}{2}kR_0^2 \ln[1 - (r/R_0)^2], & r < R_0 \\ \infty, & r \geq R_0 \end{cases} \quad (4)$$

with the choice of the constant  $k = 30$ ,  $R_0 = 1.5$  as usually done.<sup>3,11,66,68</sup> An important characteristic for this model is the theta temperature for a single polymer chain in this solvent. Defining  $-\chi = (\epsilon_{pp} + \epsilon_{ss})/2 - \epsilon_{ps} = \epsilon_{pp}/2 - \epsilon_{ps}$ , we find (see Appendix)  $-\chi_\theta = 0.17 \pm 0.02$ . Note that this value is rather different from the corresponding result of an implicit solvent model  $\epsilon_{pp} = 0.65 \pm 0.02$  at the  $\Theta$  point.<sup>70</sup>

The grafting wall is represented by 400 static particles forming a triangular lattice with lattice spacing  $a = 1.25$ . This structure makes the wall impossible to be crossed by either monomers or solvent particles since both solvent particles and monomers interact with the wall atoms with the purely repulsive potential, Eq. (1), of strength  $\epsilon_{\text{LJ}} = 1$ . The lateral linear dimensions  $L_x$  and  $L_y$  are chosen as 25 and 21.65, respectively. The wall particles are fixed in the plane  $z = 0$ . Our simulation box contained  $N_s = 9680$  solvent particles. Three choices for the number  $N_{\text{ch}}$  of end-grafted chains, containing  $N = 60$  effective monomers each, were considered, namely,  $N_{\text{ch}} = 36, 60$ , and  $100$ . The monomers at the grafted chain end are bound with FENE potential, Eq. (4), to virtual points, located in plane  $z = 1$  and also forming a triangular lattice. At a distance of about  $z = 64$ , we choose a second (albeit structureless) wall, represented by the repulsive part of the Lennard-Jones interaction. This wall may be moved up or down in  $z$  direction, in order to maintain a constant pressure  $P = 0.67$  in the direction perpendicular to the walls in the system. The lateral linear dimensions, however, were kept fixed, and periodic boundary conditions in  $x$  and  $y$  directions were imposed. For comparison, also some runs choosing  $N = 40$  were made. Note that the values for the grafting den-

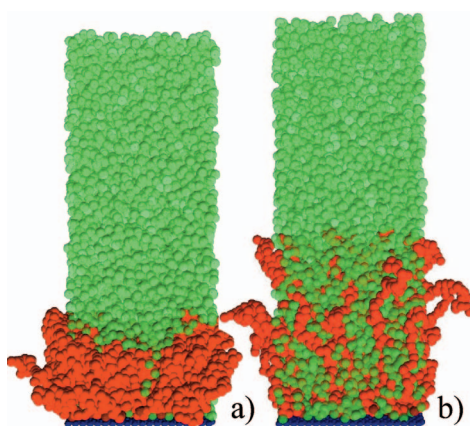


FIG. 1. (Color) Typical simulation snapshots showing the polymer brush with  $N_{\text{ch}}=100$  chains under (a) poor and (b) good solvent conditions. Interaction parameters are (a)  $\epsilon_{ps}=0.0$ ,  $\epsilon_{pp}=0.8$  and (b)  $\epsilon_{ps}=0.8$ ,  $\epsilon_{pp}=0.0$ .

sity  $\sigma_g=0.067$ ,  $0.118$ , and  $0.185$  ( $\sigma_g=N_{\text{ch}}/(L_x L_y)$ ) were chosen such that a comparison with the implicit solvent model of Refs. 11 and 66 becomes possible, where the same grafting densities were studied for a single brush at a flat substrate that was modeled in a closely related manner, while no explicit solvent molecules were included there.

Molecular dynamics simulations were performed using the standard velocity-Verlet algorithm,<sup>71</sup> carrying out typically  $3 \cdot 10^6$  time steps with an integration time step  $\delta t=0.005t_0$ , where  $t_0=(\sigma^2 m/48\epsilon_{\text{LJ}})^{1/2}=1/\sqrt{48}$  (note that the masses of both monomers and solvent particles were chosen equal,  $m=1$ ). As a check, also some runs with  $\delta t=0.0005t_0$  were performed, but no significant differences could be detected. Temperature was held constant at  $T=1$  using a standard dissipative particle dynamics (DPD) thermostat<sup>72</sup> with a friction constant  $\zeta=0.5$  and a step-function-like weight function with cutoff  $r_c=1.5\sigma_{pp}$ . Figure 1 presents two representative simulation snapshots of our systems.

### III. STRUCTURE AND PHYSICAL PROPERTIES OF THE POLYMER BRUSH UNDER VARIOUS SOLVENT CONDITIONS

#### A. Density profiles

Figure 2(a) presents monomer density profiles  $\varphi_p(z)$  and solvent density profiles  $\varphi_s(z)$  for the highest available grafting density  $\sigma_g=0.185$  and various solvent conditions, realized by various choices for the energy parameters  $\epsilon_{ps}$  and  $\epsilon_{pp}$ , respectively. One sees from Fig. 2(a) that at the chosen pressure and temperature, the same constant solvent density  $\rho_s=0.32$  results at distances sufficiently far from the outer boundary of the polymer brush. The fact that in all cases we observe a region where both  $\varphi_p(z)=0$  and  $\varphi_s(z)=\rho_s=\text{const}$  shows that we have simulated a large enough system, that is not significantly perturbed by the upper wall confining the solvent. For  $\sigma_g=0.067$  and  $\sigma_g=0.118$  this confining wall was located always beyond  $z=50$ , while for  $\sigma_g=0.185$  (cf. Fig. 2) this confining wall was located at positions  $z<50$  in several cases, as is evident from the “layering” (i.e., density oscillations) of the solvent. It is interesting that there is always a pronounced first layer (and

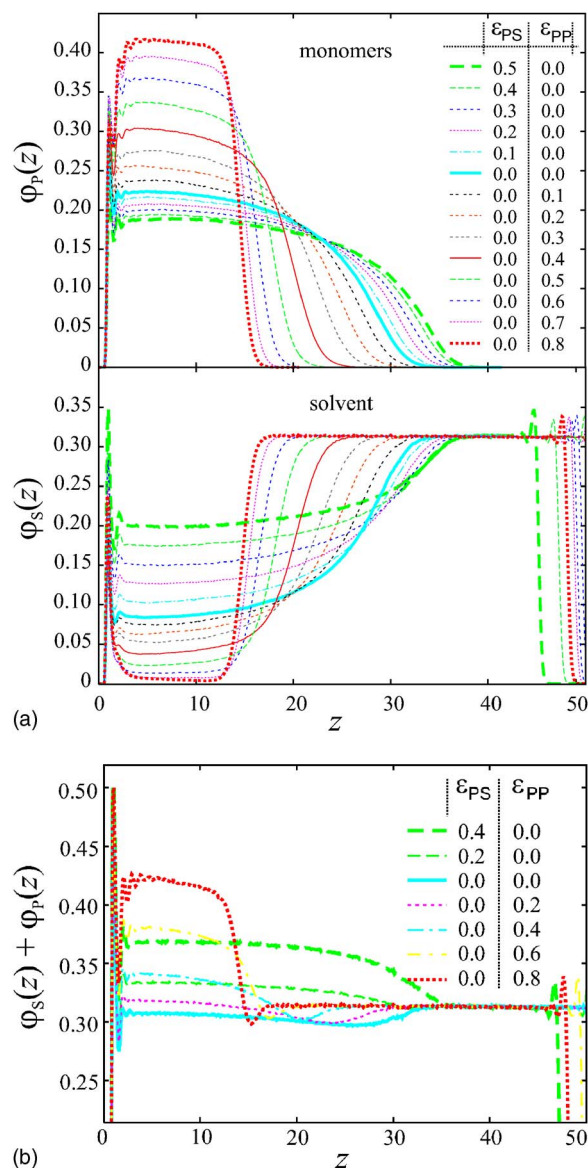


FIG. 2. (Color online) (a) Monomer density profile  $\varphi_p(z)$ , upper part, and solvent density profile  $\varphi_s(z)$ , lower part for  $\sigma_g=0.185$ . 14 combinations of  $\epsilon_{ps}$ ,  $\epsilon_{pp}$  are included. (b) Total density  $\varphi_s(z)+\varphi_p(z)$  plotted vs  $z$ , for several combinations of  $\epsilon_{ps}$  and  $\epsilon_{pp}$ .

in most cases also a second layer) of solvent adjacent to the grafting surface as well. Thus, near the grafting surface the total density in these layers attains much larger values than away from it, in order to achieve an optimal packing. Of course, all these layering effects would be much more pronounced if we worked with a higher solvent density  $\rho_s$  in the bulk. We have deliberately avoided to do so, of course, since this would slow down our simulations substantially, and furthermore pronounced layering near the grafting wall obscures somewhat the genuine brush behavior that we wish to address.

We also note that for  $\epsilon_{ps}>0$  (and  $\epsilon_{pp}=0$ ), the brush is more stretched than in the “neutral” case  $\epsilon_{ps}=\epsilon_{pp}=0$ , while for the case of  $\epsilon_{pp}>0$  (and  $\epsilon_{ps}=0$ ) the brush is compressed. For the larger values of  $\sigma_g$ , one can clearly see the crossover from a brush density profile resembling a parabola (apart from the characteristic tail near the brush end) to an almost



rectangular density profile under poor solvent conditions. Note that the choice  $\epsilon_{pp}=0.4$  is close to theta conditions in a bulk dilute solution. Then the monomer density inside the brush is distinctly higher than the solvent density outside of the brush, and a rather sharp interface between brush and solvent can clearly be identified, unlike the good solvent case.

Particularly interesting is the variation of the total density profile as a function of the various energy parameters [Fig. 2(b)]. For the fully repulsive case ( $\epsilon_{ps}=\epsilon_{pp}=0$ ) the total density in the brush is slightly smaller than in the pure solvent. However, the total density is enhanced both for the case of polymer-solvent and polymer-polymer attraction, although the brush structures are so different.

When we compare our density profiles to corresponding calculations for models where the solvent was only implicitly taken into account,<sup>11,25–27</sup> we note qualitative similarity of the monomer density profiles  $\varphi_p(z)$ , although there are also some differences. For example, now the layering of the monomers near the grafting wall in the present explicit solvent model is somewhat less pronounced, since also the solvent particles take part in the layering, while in the implicit solvent model, all the effects due to packing of particles at a hard wall are due to the monomers only. However, we did not attempt to perform a more quantitative comparison of the different models: this would require us to map the scales of the energy parameters of the different models onto each other. Such a transfer of parameters from one model to another one is a nontrivial problem, that we are not addressing here.

From Fig. 2(a) it is evident that (when we vary the solvent quality) the monomer density  $\varphi_p(z)$  in the center of the brush increases by a factor of 2–3, and at the same time the brush height decreases by a corresponding factor. This densification of the brush when the solvent quality deteriorates is not a sharp phase transition; however, it is only a gradual change. This is clearly seen when we plot the gyration radius component  $R_{g\perp}$  in the direction perpendicular to the grafting surface as a function of  $\chi = \epsilon_{ps} - (\epsilon_{pp} + \epsilon_{ss})/2$ , a quantity proportional to the well-known Flory Huggins parameter<sup>28–40</sup> (Fig. 3). For the smallest grafting density ( $\sigma_g=0.067$ ),  $R_{g\perp}$  exceeds the corresponding value of a free chain in implicit solvent only slightly, even for good solvent conditions ( $\chi \geq 0.2$ ): this is a clear indication that we are in a mushroom regime. Only for  $\sigma_g=0.185$  do we see for  $\chi \geq 0.2$  a pronounced stretching ( $R_{g\perp}$  exceeds the free chain value by about a factor of 2), typical for real brush behavior. These findings are compatible with an examination of the corresponding monomer profiles  $\varphi_p(z)$ , of course [Fig. 2(a)]. While the dependence of  $R_{g\perp}$  is rather weak for  $\chi > 0$ , a clear contraction of the chains starts to set in as soon as  $\chi$  is negative. The maximum slope  $(dR_{g\perp}/d\chi)_{\max}$  occurs near  $\chi = -0.15$ , i.e., near the theta point ( $\chi_\Theta = -0.17 \pm 0.02$ , see Appendix), while for  $\chi \approx -0.4$  the contraction stops and  $R_{g\perp}$  does not seem to decrease much further.

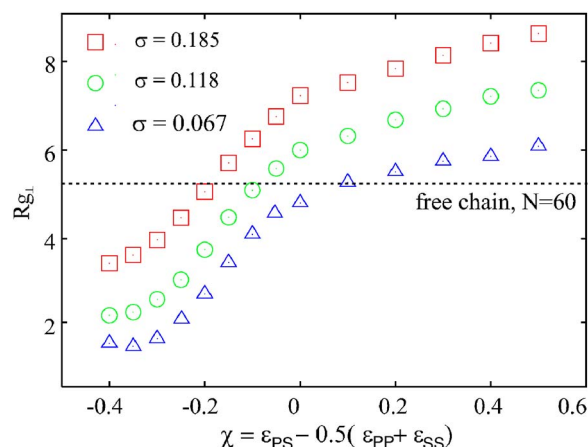


FIG. 3. (Color online) Plot of the gyration radius component  $R_{g\perp}$  in the direction perpendicular to the grafting surface vs  $\chi = \epsilon_{ps} - (\epsilon_{pp} + \epsilon_{ss})/2$ . Results for three values of the grafting density are included, as indicated. The horizontal broken straight line indicates the value of a gyration radius component of a free (nongrafted) chain under good solvent conditions ( $\epsilon_{ps} = \epsilon_{pp} = 0$ ).

## B. Pressure profiles and surface tension

From the difference  $\Delta P(z) = P_{\perp} - P_{\parallel}$  of the pressure tensor components, one can obtain the surface tensions between the solvent and the grafting wall, using the formula<sup>73</sup>

$$\gamma = \int_0^{\infty} \Delta P(z) dz. \quad (5)$$

The pressure tensor components are readily sampled applying a local version of the virial theorem;<sup>74</sup> note that the forces due to the particles forming the grafting wall are included in the virial in exactly the same way as all the interparticle forces in the system. Figure 4 shows our results for  $\Delta P(z)$  for the same combinations of parameters  $\sigma_g$ ,  $\epsilon_{ps}$ , and  $\epsilon_{pp}$ , for which already the profiles  $\varphi_p(z)$ ,  $\varphi_s(z)$  were shown. Figure 4(c) shows that for most of the parameters  $\gamma$  is negative, i.e., the polymer-coated wall and the solvent fluid attract each other. Only for sufficiently negative  $\chi$  do we have a positive surface tension. Note that this fluid-wall surface tension, appropriate for our model, must not be confused with the surface tension between unmixed fluid phases in the bulk: the latter “interface tension” must be non-negative, it vanishes only at the critical point of the considered liquid-liquid phase separation. In contrast, fluid-wall surface tensions can have any sign, depending on the nature of the fluid-wall interactions, and hence also a state where  $\gamma$  changes sign is possible: this point does not correspond to any phase transition in the system. If a phase transition would occur, we would expect a jump of  $\gamma$  (in the case of a first order phase transition) or a singularity of the slope  $d\gamma/d\epsilon$  (in the case of a second order phase transition). Thus our data for  $\gamma$  lead to the same conclusion as those for  $R_{g\perp}$ , namely, the changes in the state of the polymer brush with variable solvent quality are completely gradual, they do not involve any phase transition. It is also instructive to examine the behavior of the pressure tensor profile  $\Delta P(z)$  in more detail (Fig. 4). Deep in the solvent region, for values of  $z$  far beyond the outer boundary of the brush,  $\Delta P(z)=0$  indepen-

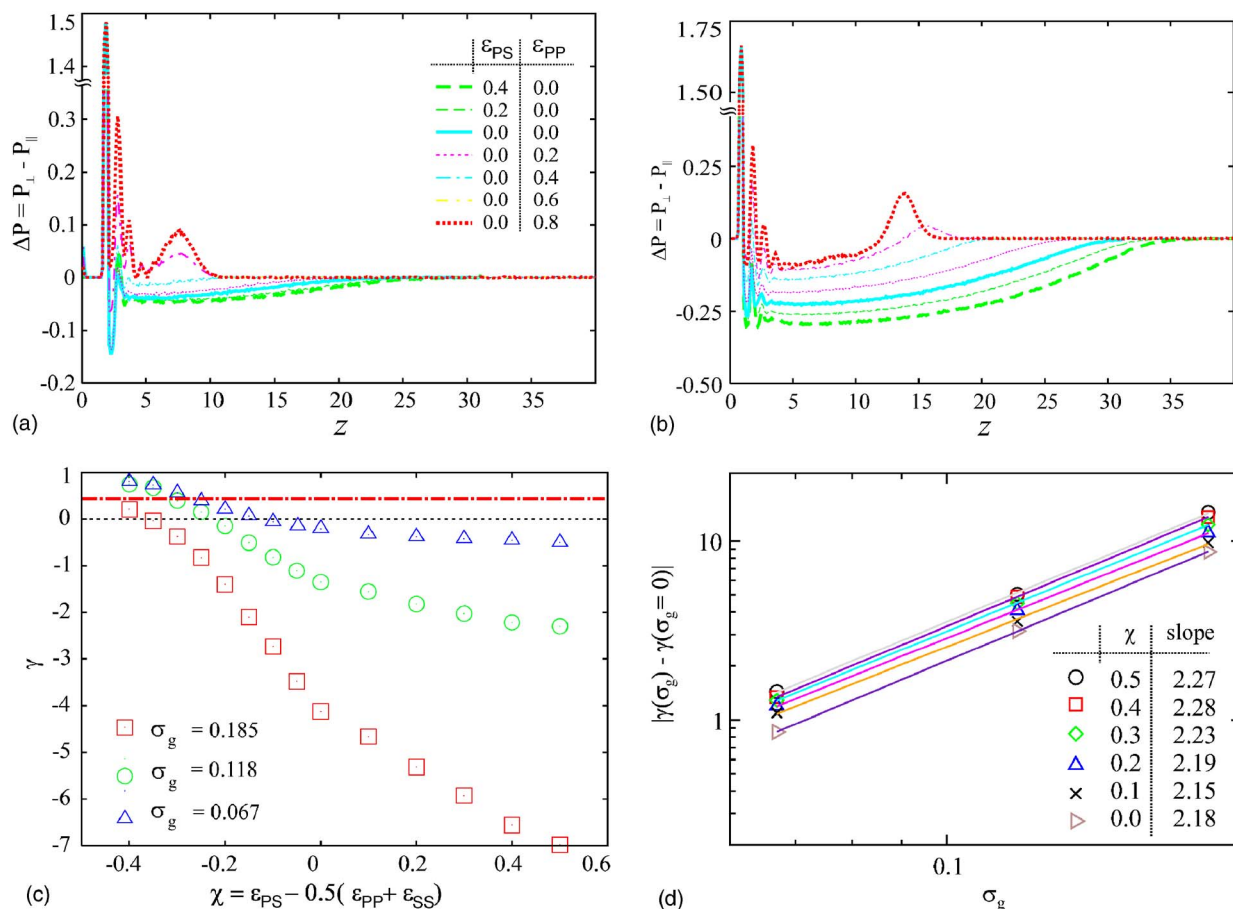


FIG. 4. (Color online) Difference between the pressure tensor components  $\Delta P(z) = P_{\perp} - P_{\parallel}$  plotted vs  $z$  for  $\sigma_g = 0.067$  (a) and  $\sigma_g = 0.185$  (b). Several combinations of energy parameters  $\epsilon_{ps}$ ,  $\epsilon_{pp}$  are included in each figure. (c) Surface tension  $\gamma$  plotted vs  $\chi$ , for the values of the grafting density, as indicated. The dash-dotted straight line indicates the value  $\gamma = 0.44 \pm 0.02$  of the wall-solvent surface tension in the absence of grafted polymers. (d) Log-log plot of  $|\gamma(\sigma_g) - \gamma(\sigma_g=0)|$  vs  $\sigma_g$ . Six values of  $\chi$  are included, as indicated.

dent of  $z$ : this is a nice consistency check that we have a well equilibrated solvent, with typical bulk behavior not affected by the upper wall, so the pressure must be homogeneous and isotropic. In the good solvent case,  $\Delta P(z)$  then gradually turns negative where the brush begins, until one comes close to the wall, where the pronounced oscillations in  $\Delta P(z)$  reflect the layering of the density profiles (Fig. 2). More interesting, however, is the behavior in the bad solvent case: there we recognize a well-developed peak of  $\Delta P(z)$  at the solvent-brush interface. Thus, in this case the total solvent-wall surface tension has two contributions,

$$\gamma = \gamma_{\text{brush}} + \gamma_{\text{int}}, \quad \gamma_{\text{brush}} = \int_0^{z_0} \Delta P(z) dz, \quad (6)$$

$$\gamma_{\text{int}} = \int_{z_0}^{\infty} \Delta P(z) dz, \quad (6a)$$

$z_0$  being the position, where  $\Delta P(z=z_0)=0$  at the left side of this interfacial peak of  $\Delta P(z)$ . While  $\gamma_{\text{brush}}$  is always negative,  $\gamma_{\text{int}}$  per definition is a positive quantity, it reflects the solvent-brush phase separation. The state where  $\gamma=0$  then simply reflects the condition that the above two terms cancel each other, while the condition where  $\gamma_{\text{int}}=0$  should reduce to the  $\Theta$  point of the polymer solution in the bulk, when

we consider the appropriate limit where the chain length  $N \rightarrow \infty$  and the grafting density is sufficiently small. For our cases where  $N=60$ , we find that  $\gamma$  vanishes for  $\chi = -0.12$  ( $\sigma_g = 0.067$ ),  $\chi = -0.23$  ( $\sigma_g = 0.118$ ), and  $\chi = -0.34$  ( $\sigma_g = 0.185$ ), respectively. Note that the wall-fluid surface tension for a wall interacting with a pure solvent (no grafted polymers) is  $\gamma = 0.44 \pm 0.02$  for our model. One can see that  $\gamma$  gets reduced due to the grafted chains, except for states deeply inside the bad solvent regime.

Figure 4(e) demonstrates that over the range of grafting densities studied here, this reduction can be represented by a power law,  $|\gamma(\sigma_g) - \gamma(\sigma_g=0)| \propto \sigma_g^{\zeta}$  with an exponent  $\zeta \approx 2.2 \pm 0.1$ , for a broad range of  $\chi$  values. We do not have a theoretical explanation for this power law, however.

### C. Structural properties of the chains

From the monomer density profile  $\varphi_p(z)$ , one also can obtain the brush height as measured by the first moment  $\langle z \rangle = \int_0^{\infty} \varphi_p(z) z dz / \int_0^{\infty} \varphi_p(z) dz$ , as well as the width  $W_s$  defined from the slope  $d\varphi_p(z)/dz$  in the inflection point of the profile by  $W = \varphi_p^{\text{max}} / |\varphi_p(z)/dz|$ , where  $\varphi_p^{\text{max}}$  is the maximum value of  $\varphi_p$  reached in the flat region of the profile. Note the striking similarity of our variation of  $W$  with  $z$  with corresponding experimental data of Karim *et al.*<sup>62</sup>

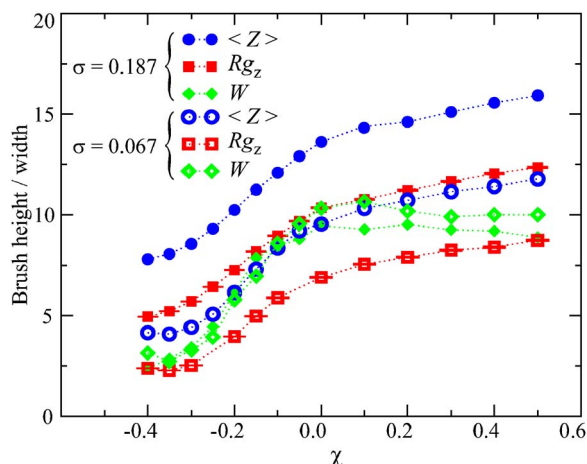


FIG. 5. (Color online) Plot of the brush height  $\langle z \rangle$ , gyration radius component  $R_{gz}$ , and width  $W$  vs  $\chi$ , for two choices of grafting density  $\sigma_g$ , as indicated.

In Fig. 5 these quantities are plotted versus  $\chi$  for two grafting densities and compared to  $R_{gz}$ . While for  $\chi > 0$  both  $\langle z \rangle$  and  $R_{gz}$  increase with  $\chi$  almost linearly,  $W$  stays approximately constant. For  $\chi < 0$ , all three quantities decrease with  $\chi$  and saturate at about  $\chi = -0.4$ . This behavior is consistent with our conclusions drawn from an examination of the density and pressure difference profiles, as described above.

It is also of interest to discuss the stretching of the chains in the brush. We use the average bond orientations measured via the second Legendre polynomial  $P_2(\theta) = (3\langle \cos^2 \theta \rangle - 1)/2$ ,  $\theta$  being the angle between the considered bond and the  $z$  axis, for this purpose. Note that positive values imply a preference of the bonds to orient parallel to the grafting surface, while  $P_2(\theta) = 0$  means the orientations are random. Figure 6 plots  $P_2(\theta)$  versus the sequential number  $n$  of the bonds along the chain, starting out at the grafting site up to the free end of the chain. These orientations always are very weak in the mushroom case, but get more pronounced as the chains get more stretched. As expected,  $P_2(\theta) \rightarrow 0$  when one approaches the free chain end: the end bonds are randomly oriented. However, there is also a very pronounced effect of solvent quality:  $P_2(\theta)$  is uniformly weakly negative in the mushroom regime, reflecting the tendency of the chain to avoid stretching away from the grafting surface toward the solvent, and rather extending in the directions parallel to the grafting surface. For a dense brush in bad solvents (e.g.,  $\sigma_g = 0.185$ ,  $\epsilon_{pp} = 0.8$ ), the outer half of the bonds ( $n \geq 30$ ) are almost randomly oriented.

An issue that deserves concern is the question of lateral homogeneity of the polymer brush under poor solvent conditions. In fact, while in the first theoretical studies applying the self-consistent field approach this issue was disregarded,<sup>16,17</sup> simulations of implicit solvent models<sup>25–27</sup> discovered that for short enough chains and/or not too high grafting densities strong lateral inhomogeneities occurred due to “dimple” formation. Allowing for this possibility also in the theoretical formulation, these findings were confirmed<sup>19–23</sup> and also corresponding experimental observations were reported.<sup>75</sup> Here we show that these phenomena

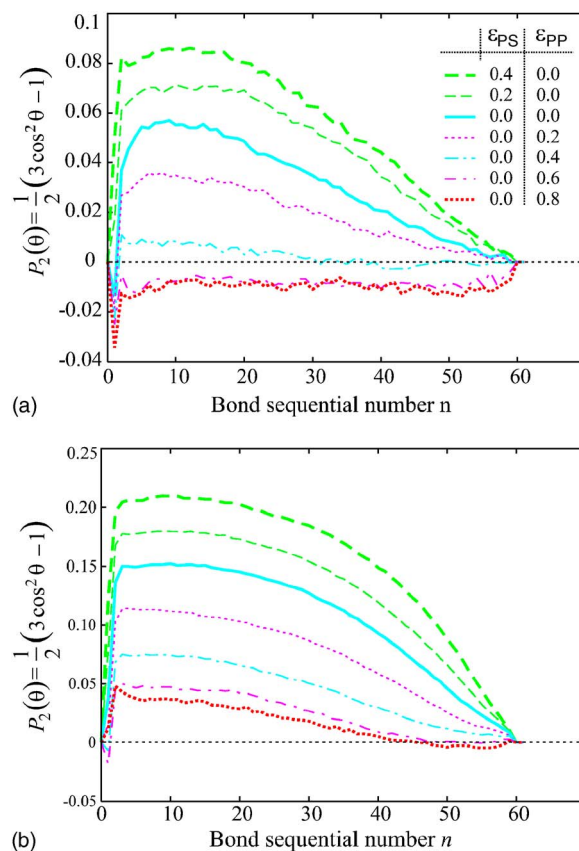


FIG. 6. (Color online) Average bond orientations  $P_2(\theta)$  plotted vs the bond sequential number  $n$  (for definitions, cf. main text). Three grafting densities [ $\sigma_g = 0.067$  (a) and  $0.185$  (b)], and various choices of  $\epsilon_{ps}$ ,  $\epsilon_{pp}$  (as indicated in the figure) are shown.

also occur in our model containing explicit solvent (Fig. 7). Looking on monomer density profile, we see that this dimple formation causes only very weak anomalies in the average profile  $\varphi_p(z)$ . As expected, this lateral inhomogeneity in the poor solvent case is a fairly universal phenomenon that occurs for a broad variety of theoretical models as well as of experimental systems.

Another interesting issue that is straightforwardly accessible is the framework of our molecular dynamics simulation is the stretching force  $f_{pull}$  pulling at the anchor points of the grafted chains (Fig. 8). This force has a clear minimum for

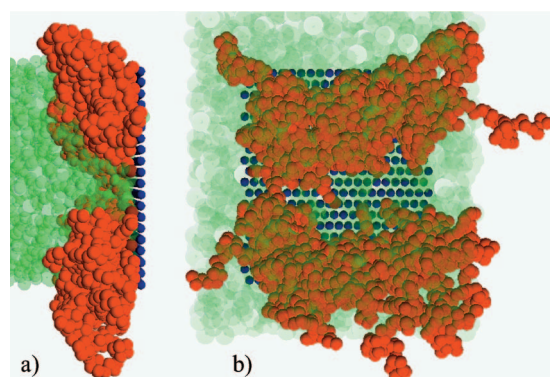


FIG. 7. (Color) Typical simulation snapshots showing the polymer brush with  $N_{ch} = 36$  chains under bad solvent conditions ( $\epsilon_{pp} = 0.8$ ,  $\epsilon_{ps} = 0$ ). Case (a) shows a side view and case (b) a top view of the same brush.



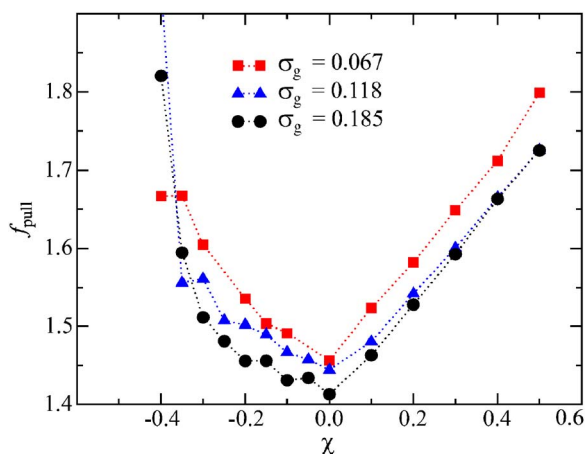


FIG. 8. (Color online) Stretching force  $f_{\text{pull}}$  at the anchor points of the grafted chains plotted vs  $\chi$ , for three choices of the grafting density, as indicated.

$\chi=0$ . The almost linear increase with  $\chi$  for  $\chi>0$  is attributable to the elastic energy stored in the chains that are increasingly stretched out when  $\chi$  increases. While for  $\chi>0$  this stretching force hence is of entropic origin, for  $\chi<0$ , the enthalpy that can be won when like monomer cluster together is responsible for the pronounced increase  $f_{\text{pull}}$  for  $\chi<0$ . It is also important to note that the scaled force  $\sigma f_{\text{pull}}(\chi)$  in the whole regime of interest does not exceed  $2k_B T$ : from experiments, it is known that often the grafted chains are bound to the substrate with an energy of only  $6-8 k_B T$ .<sup>10</sup> If the scaled stretching force would exceed this binding energy, chains would unbind from the substrate. Such unbound chains subsequently are pulled out from the polymer brush.<sup>56</sup>

## D. Dynamic properties

As a final point of our study, we take first (modest!) steps toward studying the dynamics of our system: indeed it is the great merit of the molecular dynamics simulation technique that full information on dynamic response as well as dynamic correlation of fluctuations is accessible. Including explicit solvent in our model and using the DPD thermostat that does not disturb the hydrodynamic forces,<sup>72</sup> we ensure that our model should describe the brush dynamics qualitatively in a correct way (note that the implicit solvent models<sup>25-27</sup> cannot model the effect of hydrodynamic interactions on the dynamic behavior, of course). A first test concerns the mobility of the solvent particles: Fig. 9 shows that even under poor solvent conditions, where most of the solvent particles are expelled from the brush, there is only a moderate reduction of the mobility of the few remaining solvent particles in the brush, in both lateral and perpendicular directions.

From the autocorrelation function of the parallel ( $\parallel$ ) and the perpendicular ( $\perp$ ) components of the chain gyration radius characteristic relaxation times  $\tau_{\parallel}, \tau_{\perp}$  are extracted (Fig. 10). In the good solvent regime, the component perpendicular to the surface clearly relaxes more slowly than the parallel component and moreover  $\tau_{\perp}$  increases with  $\chi$ . This behavior is expected, of course, since  $R_{g\perp}$  itself increases with

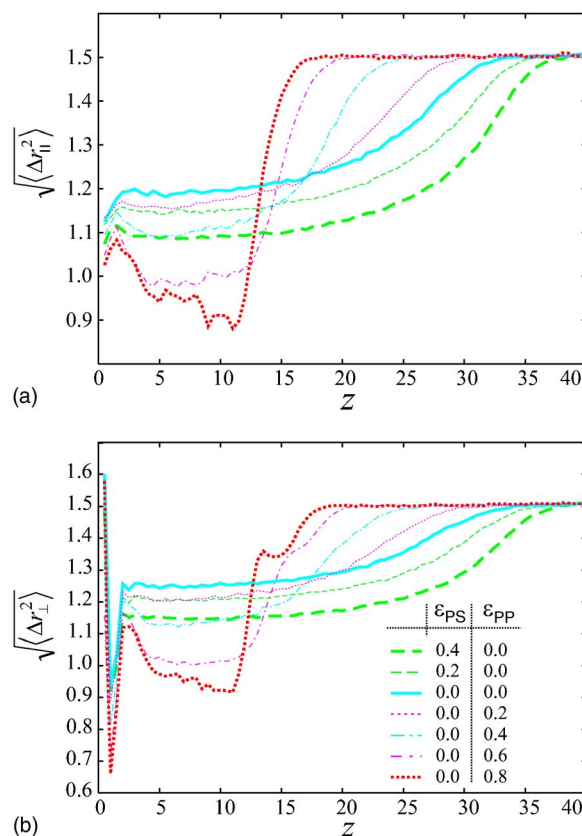


FIG. 9. (Color online) Mobilities, i.e. typical distances  $\sqrt{\langle \Delta r_{\parallel}^2 \rangle}$  (upper part) and  $\sqrt{\langle \Delta r_{\perp}^2 \rangle}$  (lower part) of solvent particles traveled during  $\tau=1$  (MD time) unit in a brush at grafting density  $\sigma_g=0.185$ . Various choices of the energy parameters  $\epsilon_{ps}$  and  $\epsilon_{pp}$  are shown, as indicated in the figure.

$\chi$  as well, and one may estimate the relaxation time crudely as<sup>76</sup>  $\tau_{\perp} \propto R_{g\perp}^2/D$ , where  $D$  is an effective diffusion constant of the chain center of mass [for a free chain in the solvent, we would have  $D \propto (\eta_s R_g)^{-1}$ , where  $\eta_s$  is the solvent viscosity, while  $D \propto 1/N$  when the hydrodynamic interactions are screened out, as is the case in a dense brush]. Since increasing  $\chi$  in the good solvent regime implies an increase of  $R_{g\perp}$ , cf. Fig. 5, an increase of  $\tau_{\perp}$  should result.

Interestingly,  $\tau_{\perp}$  reaches a minimum in the region  $-0.3 < \chi < -0.2$  and increases again for solvents of even

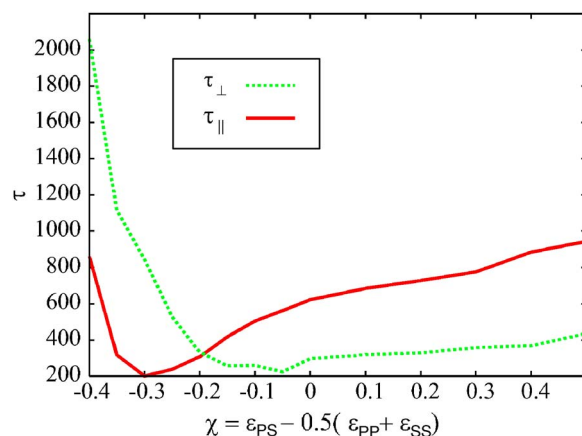


FIG. 10. (Color online) Relaxation times  $\tau_{\parallel}, \tau_{\perp}$ , of the parallel and perpendicular gyration radius components plotted vs  $\chi$  for  $\sigma_g=0.067$ .



poorer quality, although there  $R_{g\perp}$  no longer changes. We attribute this behavior to a decrease in the effective monomeric mobility, for very dense configurations of the polymer chains in the collapsed polymer brush, in particular, if dimple formation occurs, which is expected to slow down the chain dynamics significantly. In fact, in this region also  $\tau_{\parallel}$  is found to increase rather strongly. Clearly, a more detailed study of chain dynamics in this regime would be very interesting, but due to the large values of the relaxation times in the poor solvent regime this is very difficult. In fact, already for  $\sigma_g=0.185$  no reliable estimates for  $\tau_{\perp}$ ,  $\tau_{\parallel}$  could be extracted from our data any longer.

#### IV. CONCLUSIONS

In the present work we have performed a study of static and dynamic properties of polymer brushes under variable solvent conditions, using an explicit solvent of pointlike particles which repel each other. We keep the chain length of our flexible chains, that are described by a coarse-grained bead-spring model where beads interact with each other and with the solvent particles with a modified Lennard-Jones potential [Eqs. (1) and (2)], fixed at  $N=60$ , but choose three grafting densities that correspond to the regime from weak ( $\sigma_g=0.067$ ) to moderately strong stretching ( $\sigma_g=0.185$ ). The resulting monomer density profile (Fig. 2) resembles very closely the results of Grest and Murat<sup>26</sup> for a similar off-lattice model but with implicit solvent. In the latter study, it was also found that even under bad solvent conditions, there is a region somewhat depleted of monomers immediately adjacent to the grafting wall, before the monomer density reaches a flat plateau characteristic for a dense brush where the monomer density corresponds to that of a concentrated polymer solution or melt, respectively. Our results now show that there is a thin layer of solvent attached to the wall, in spite of the fact that there is no enthalpic attractive force between the solvent particles and the wall at all; the solvent attraction to the wall hence is purely entropy driven.

We also confirm the finding of previous lattice<sup>25</sup> and off-lattice<sup>26</sup> models, both using no explicit solvent, that for a rather low grafting density and bad solvent conditions the brush becomes laterally inhomogeneous due to “dimple formation.” However, all the changes of the state of the brush as a function of the Flory-Huggins  $\chi$  parameter that quantifies the solvent quality are very gradual, Fig. 5; so we are not able to delineate a “phase diagram” where these brush states are sharply distinguished.

In the good solvent regime, the grafted chains cause a strong reduction of surface tension (Fig. 3). This reduction varies much stronger than linear with  $\sigma_g$  [roughly we have  $|\gamma(\sigma_g) - \gamma(\sigma_g=0)| \propto \sigma_g^{\zeta}$  with  $\zeta \approx 2.2 \pm 0.1$ ] throughout the good solvent regime. Of course, no such reduction of the surface tension occurs for very bad solvents and not too large  $\sigma_g$ : When  $\gamma(\sigma_g) > \gamma(0)$ , it is then plausible that it is energetically preferable to form dimples because in the regions where there are hardly any monomers close to the wall, the surface free energy cost of the wall (due to the wall-solvent repulsion) is lower than the solvent-brush surface tension  $\gamma_{\text{int}}$ .

It also is interesting to note that the force acting on the

first monomer adjacent to the grafting site increases with  $\chi$  in the good solvent regime but also increases steeply with  $-\chi$  in the bad solvent regime, so that a minimum near  $\chi=0$  occurs (Fig. 8). While the increase with  $\chi$  in the good solvent regime is attributed to the effect of the stretching of the chains away from the grafting surface, and hence this stretching force is of entropic origin, for  $\chi < 0$ , the stretching force probably is due to monomer-monomer attractions. This competition between enthalpic and entropic effects is presumably responsible for the minimum near  $\chi=0$ . We are not aware of any previous studies of this effect in the literature.

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#### APPENDIX: ESTIMATION OF THE THETA POINT FOR THE PRESENT MODEL

In order to clarify for which values of  $\chi$  we have good or poor solvent conditions, respectively, for the present model that includes explicit solvent molecules, we have carried out simulations of a single chain in a box containing  $N_s=8500$  solvent particles. The size of the box significantly extended the end-to-end distance. In addition,  $N_s$  had to be chosen such that a density  $\rho_s=0.32$  of solvent particles was maintained throughout, in order to make the results comparable to our brush simulations. Since most of the computing effort is needed for the solvent particles, it is very difficult to obtain

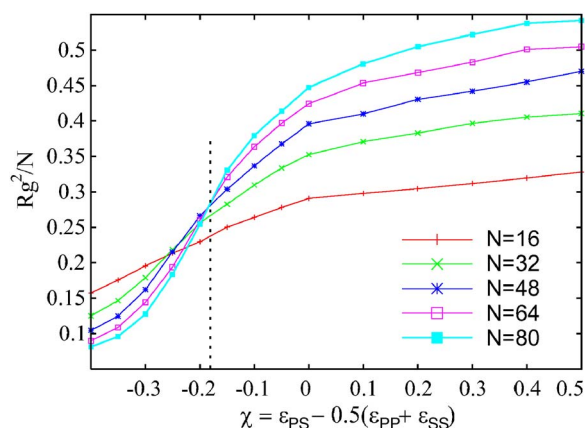


FIG. 11. (Color online) Average normalized mean square gyration radius  $\langle R_g^2 \rangle/N$  of a single free chain in dilute solution plotted vs  $\chi$  for various  $N$ , as indicated in the figure. The vertical broken line highlights our estimate for the theta point,  $\chi_\theta = -0.17 \pm 0.02$ . Data were taken for a  $L \times L \times L$  box with periodic boundary conditions, containing  $N_s=8400$  solvent particles. The linear dimension  $L$  of the box was adjusted to maintain a solvent density  $\rho_s=0.32$ , as in the simulation of the brushes (Fig. 2).

good accuracy for the mean square gyration radius  $\langle R_0^2 \rangle$  of the polymers. This problem prevented us from studying chains longer than  $N=80$ , respectively.

Since under good solvent conditions  $\langle R_0^2 \rangle \propto N^{2\nu}$  with  $\nu \approx 0.59$ ,<sup>29</sup> while at the theta point (disregarding logarithmic corrections)  $\langle R_g^2 \rangle \propto N$  and in the bad solvent conditions  $\langle R_g^2 \rangle \propto N^{2/3}$  [because the chain form compact globules of nonzero density  $\rho_{\text{mon}} = N/(\langle R_g^2 \rangle)^{3/2}$  of the monomers<sup>29</sup>], the standard recipe is to plot  $\langle R_g^2 \rangle/N$  vs  $\chi$  for various  $N$ , looking for a common intersection point.<sup>77</sup> Although the accuracy of this procedure is rather problematic,<sup>78</sup> we have nevertheless attempted to use it (Fig. 11). While the curve for  $N=16$  clearly is off, for larger  $N$  we can estimate, very roughly, that the interaction of the curves occurs for  $\chi = -0.17 \pm 0.02$ . This value hence is taken as our estimate for the theta point.

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