Polymer brushes with nanoinclusions under shear: A molecular dynamics investigation

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We use molecular dynamics simulations with a dissipative particle dynamics thermostat to study the behavior of nanosized inclusions (colloids) in a polymer brush under shear whereby the solvent is explicitly included in the simulation. The brush is described by a bead-spring model for flexible polymer chains, grafted on a solid substrate, while the polymer-soluble nanoparticles in the solution are taken as soft spheres whose diameter is about three times larger than that of the chain segments and the solvent. We find that the brush number density profile, as well as the density profiles of the nanoinclusions and the solvent, remains insensitive to strong shear although the grafted chains tilt in direction of the flow. The thickness of the penetration layer of nanoinclusions, as well as their average concentration in the brush, stays largely unaffected even at the strongest shear. Our result manifests the remarkable robustness of polymer brushes with embedded nanoparticles under high shear which could be of importance for technological applications. © 2010 American Institute of Physics. [doi:10.1063/1.3396446]

I. INTRODUCTION

The interaction of collapsed proteins with polymer brushes has found longstanding consideration^{1–4} as a model system for biological interfaces. From the theoretical point of view, the detailed chemical structure of the protein is disregarded in this context so that the protein is considered as a compact nanoparticle.¹ In material science similar systems are investigated in different contexts, motivated by the development of novel materials where various kinds of nanoparticles (metallic, semiconducting, or insulating nanoparticles) embedded in suitable soft matrices have found great interest: Varying the chemical character, shape and size, volume fraction, and spatial arrangement of the nanoparticles in the matrix one expects to obtain materials with tunable properties.^{5–26} Bioinspired, smart, multiscale interfacial materials respond to external stimuli, e.g., light, pH, electrical fields, etc.,²⁷ or show switchable adhesion to interacting materials (from sticky to nonsticky surfaces) and wetting with switchable appearance and transparency. They may be used as high tech coatings capable of rapid release of chemicals, superhydrophobic, antifriction, or as self-healing coatings.²⁸ In this context one needs means to suitably manipulate the arrangement of the nanoparticles in the (typically polymeric) matrix, such as a polymer brush,^{29–34} i.e., an end-grafted layer of flexible macromolecules on a solid substrate. The height h of this ultrathin polymeric layer and the average volume fraction $\bar{\phi}_p$ of monomers contained in this layer can be varied easily by varying the chain length N of the macromolecules, their grafting density σ_g on the substrate, and the quality of the solvent in which the system is contained. The arrangement of the nanoparticles in polymer brushes in thermal equilibrium was first treated theoretically by Kim and O’Shaughnessy.^{13,22} Starting from the strong stretching limit (SSL)^{35–38} of the self-consistent field theory of polymers,^{29,30,39–43} they introduced various further approximations, supposed to be useful for the “semidilute”⁴³ regime where the limits $N \rightarrow \infty$ and $\sigma_g \rightarrow 0$ are taken such that $N\sigma_g^{1/3}$

remains finite and nonzero. Although the need for numerous approximations which are hard to control has led to some criticism,²⁵ and also the required SSL is hard to obtain both in experiment³³ and in simulations,^{31,32,44–48} a recent molecular dynamics (MD) study of nanoinclusions in polymer brushes with explicit solvent⁴⁸ has shown that the qualitative predictions on the arrangement of nanoparticles in polymer brushes^{13,22} are very reasonable and do provide a useful guide for the understanding of the equilibrium structure and resulting properties of such systems. Thus, in the present paper we take a further step and ask how can such systems be manipulated: There is the need to bring nanoparticles from the solution into the brush, or to remove them from the brush. It is important to clarify how a brush with embedded nanoparticles responds to mechanical deformation: As is well known, mechanical deformation of polymer brushes by shear affects very strongly friction forces between brushes.^{49–51} Rather weak shear flow deforms the polymer conformations in polymer brushes rather strongly,^{52–55} and hence it is of interest to ask to what extent shear flow may affect the arrangement of nanoparticles embedded in the brushes. In the extreme case, it is conceivable that the shear flow of the solvent even removes the nanoparticles from the brush: Depending on the applications one has in mind, such a “washing out” of the nanoparticles from the brush may either be desirable or undesirable.

Thus, the present work takes a first step toward clarifications of all these questions, extending our previous study where the static equilibrium properties of polymer brushes with embedded nanoparticles were investigated⁴⁸ to include deformation of the brushes caused by shear flow. In Sec. II we describe our model and explain the simulation aspects, while Sec. III describes our results and Sec. IV summarizes a few conclusions.

II. MODEL AND SIMULATION ASPECTS

Following previous studies of coarse-grained models for polymer brushes with MD methods,^{44,47,50,55} polymer chains are represented by the Grest–Kremer⁵⁶ bead-spring model. The interaction potential between solvent-wall, polymer-wall, solvent-solvent, and solvent-polymer particles has been chosen as purely repulsive, that is, we employ the Weeks—Chandler—Anderson potential where one truncates the Lennard-Jones potential in its minimum and shifts it up by the potential depth ϵ , so that it equals and remains zero in its minimum and for distances beyond

$$U_{LJ}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] + \epsilon, & r \leq \sigma \cdot 2^{1/6} \\ 0, & r > \sigma \cdot 2^{1/6}. \end{cases} \quad (1)$$

Scales for length and energy (and temperature) are chosen such that both $\sigma=1$ and $\epsilon=1$ (the Boltzmann constant $k_B=1$).

The spring potential of our bead-spring model is created by adding a finitely extensible nonlinear elastic (FENE) potential⁵⁶

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

with the choice of the constants $k=30$, $R_0=1.5$ as usually done.^{44,47,56} 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 cross either by monomers or solvent particles since both solvent particles and monomers interact with the wall atoms by the purely repulsive potential, Eq. (1), of strength $\epsilon=1$. The lateral linear dimensions L_x, L_y are chosen as 25 and 21.65, respectively. The wall particles are fixed in the plane $z=0$. Our previous study of the degree of nanoparticle penetration in polymer brushes⁴⁸ indicates that larger particles are mostly expelled from the brush at too high grafting density σ_g . Therefore, in this study, we take as a rule the number N_{ch} of end-grafted chains, containing $40 \leq N \leq 80$ effective monomers each, to be $N_{\text{ch}}=36$, corresponding to grafting density $\sigma_g=0.067$, where $(\sigma_g=N_{\text{ch}}/(L_x L_y))$. For comparison, also a polymer brush with

FIG. 1. Snapshots showing a polymer brush with chain length $N=80$ and grafting density $\sigma_g=0.067$ for the case of (a) no shear and for (b) maximal shear $\gamma=0.049$. For clarity, solvent particles are not displayed, and different colors are used for different chains in order to be able to distinguish them.

$N_{\text{ch}}=9$, that is, $\sigma_g=0.017$, has been studied. The latter corresponds to a comparatively loose brush which is nevertheless denser than the so-called “mushroom regime” where neighboring grafted chains hardly touch one another.

The monomers at the grafted chain end are bound with the FENE potential, Eq. (2), to virtual points, located in the plane $z=1$ and also forming a triangular lattice. A closely related model of a polymer brush with explicit solvent but without any nanoparticles has been studied in an earlier work.⁴⁷ Our simulation box contained $N_s=8000$ solvent particles of the same size as the polymer segments. The solvent-solvent, solvent-wall, and solvent-polymer interactions were chosen as purely repulsive, according to Eq. (1). Thus our polymer brush has been studied in the so-called “good solvent” regime. The spherical nanoparticles are characterized by radius $b=1.3\sigma$. The radius of the solvent particles and of the monomers of the polymer brush is the same. Typically we use $N_{\text{nano}}=100$ such nanoparticles which interact with the polymer brush and among themselves by the repulsive potential, Eq. (1). Note that this potential is shifted away from the center of the colloid by a distance r_c defined as $r_c=b-\sigma$.

At a distance of about $z_{\text{wall}}=74, 84$, or 94 , depending on the grafting density σ_g , and on the size of the colloids b , we introduce a second (albeit structureless and massless) wall that acts on both solvent and nanoparticles by the repulsive part of the Lennard-Jones interaction, Eq. (1), and thus serves as a barostat. This wall may be moved up or down in z -direction in order to maintain constant pressure $P=0.67$ in 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. We create shear in the system by a force applied parallel to the grafting wall to all particles in the immediate vicinity of the barostat. By variation in this force we obtain different velocity profiles $v(z)$ in z -direction whereby the slope of these velocity profiles defines our shear rate γ .

Due to the lack of attraction between solvent particles, the solvent in our system is volatile with rather high fluidity. At the maximum shear, generated in our container so that the thermostat is still capable of maintaining a constant temperature $T \approx 1.0$, our estimated Reynolds number $R \approx 65 \pm 5$. The Weissenberg number $We = \gamma\tau_R$ which measures the relative strength between polymer relaxation and the stretching, exerted by the flow, can be estimated using the chain relaxation time τ_R , derived from the autocorrelation function of the polymer’s end-to-end distance⁴⁷ in a state of quiescent solvent. For a tethered chain with $N=80$ we thus get $We \approx 250$, suggesting that a single polymer chain should be substantially stretched by the flow, and it will become elongated.

MD simulations were carried out using the standard velocity-Verlet algorithm,⁵⁷ carrying out typically 3.10^6 time steps with an integration time step $\delta t=0.01t_0$, where t_0 is the corresponding MD unit of time (note that the masses of both monomers, nanoparticles, and solvent particles were chosen equal, $m=1$). Although this choice is not necessarily a realistic one, it is most efficient from the computational point of view. Temperature was held constant at $T=1$ using a standard dissipative particle dynamics thermostat⁵⁸ with a friction constant $\zeta=0.5$ and a step-function-like weight function with cutoff $r_c=1.5\sigma$. This choice of thermostat is advantageous (in comparison to

FIG. 2. Velocity profile $v(z)$ in a slit with polymer brush at grafting density (a) $\sigma_g=0.067$ and $\sigma_g=0.017$. (b) The unperturbed ($\gamma=0.0$) brush monomer density profile $\phi_p(z)$ is presented by a shaded area and magnified 20 times for better visibility. The chain length is $N=80$. Five different shear rates γ are included, as indicated.

the Langevin thermostat originally proposed⁵⁶ and used^{44,55}) since it is compatible with hydrodynamics on large scales, and is therefore suitable to study the dynamical behavior even under nonequilibrium conditions.^{50,51} The friction introduced by the thermostat leads to shear viscosity of our model fluid $\eta_s \approx 0.3$.⁵⁹ Figure 1 displays two representative simulation snapshots of our systems for a polymer brush made of chains with length $N=80$ at $\sigma_g=0.067$ for a case where no nanoparticles are yet present.

III. RESULTS

Before we describe the effect of shear flow in our model system on brushes that contain nanoparticles, it is of interest to make certain that the parameters chosen for our model yield a significant deformation of the polymer brush due to the flow already in the absence of nanoparticles (Figs. 2–4). When one studies the velocity profiles $v(z)$ in our model system, one notes that the flow penetrates only a little bit in the outer region of the brush, while the velocity field $v(z)$ is essentially zero in the inner region of the brush. More precisely, we estimate about a 20 times lower mean velocity of the solvent particles inside the brush for $\sigma_g=0.067$ and approximately ten times drop of mean solvent velocity for grafting density $\sigma_g=0.017$ at the highest shear rate $\gamma=0.049$. Consideration of hydrodynamic effects in the presence of a polymer brush described by self-consistent field theory⁶⁰ has predicted a behavior qualitatively similar to Fig. 2, and these data are also quite compatible with previous simulations.⁶¹ Indeed, for the denser brush with $\sigma_g=0.067$, cf. Fig. 2(a), the brush density profile is not affected by the shear at all, whereas at $\sigma_g=0.017$, Fig. 2(b), the brush profile is visibly changed in comparison to the $\gamma=0$ case, getting more compact and narrow. For the denser brush the velocity profile $v(z)$ outside the brush is to a very

FIG. 3. Probability distribution $P(x-x_0)$ of polymer segment position with regard to the grafting point of the chain x_0 in x -direction parallel to the slit walls for a quiescent fluid, $\gamma=0$ (symbols), and with shear (filled area): Δ —all monomers of the chain, $\circ$ —chain-end monomer. Here $N=80$, and (a) $\gamma=0.024$, $\sigma_g=0.017$, (b) $\gamma=0.049$, $\sigma_g=0.067$. Note that in (a) the chain ends are at distance 25!

FIG. 4. (a) Average bond orientation in z -direction perpendicular to the grafting wall for a quiescent brush with $N=80$ and at maximum shear $\gamma=0.049$ for a dense $\sigma_g=0.067$ and a loose $\sigma_g=0.017$ brush. (b) Average bond orientation against successive bond number for the same cases as in (a).

good approximation linear, $v(z)=V_{\text{wall}}(z-h)/(z_{\text{wall}}-h)$ for $h < z < z_{\text{wall}}$, whereas for the loose brush [Fig. 2(b)] the nonlinearity of the profile $v(z)$ in the vicinity of the brush end indicates that the flow is perturbed and stirred by the chain ends considerably.

The expulsion of the flow from the brush seen in Fig. 2 should not be misinterpreted to conclude that the brush stays unaffected by the flow, however. In fact, the particular hydrodynamic screening of the flow stays in marked contrast with respect to the changes in brush structure due to shear.

Figure 3 shows that the distribution of the lateral coordinate x of the free chain end, $P(x_0 - x)$, which in a quiescent fluid ($\gamma=0$) is trivially symmetric around the grafting site x_0 of the grafted chain end, $P(x-x_0)=P(x_0-x)$, becomes strongly asymmetric for nonzero shear rates, such as $\gamma=0.049$. Also analogous distributions for the coordinates of all monomers develop a corresponding asymmetry. The effect is especially pronounced for the case of loosest brush made of long ($N=80$) polymer chains, Fig. 3(a), where the chains tilt so strongly that they entirely lay over their neighboring chains. One can observe even a maximum in the probability distribution of chain ends above the anchoring sites of the neighboring chains. Nonetheless, as we shall demonstrate below, even in this case the flow velocity of nanoinclusions in the brush does not differ from that of the much smaller solvent particles—Fig. 6(a). The stretching of the chains along the flow direction can be also clearly detected from an analysis of $P_2(\cos \theta)$, where θ denotes the angle between a bond and the normal to the grafting plane. Figure 4(a) shows the degree of bond orientation, $P_2(\cos \theta)$, whereby the average bond orientation in z -direction is shown as a function of the distance z from the surface, at which the midpoint of the bond is located. Both data for loose $\sigma_g=0.017$ and denser brush $\sigma_g=0.067$ are compared for quiescent flow and maximum shear rate γ . While for small z $P_2(\cos \theta)$ is positive, indicating that the orientation of the bond perpendicular

FIG. 5. (a) Comparison of number density profiles (normalized to unity) of chain segments $\phi_p(z)$, solvent particles $\phi_s(z)$, and nanoparticles of diameter $b=1.3$ without shear (shaded area, dashed lines) and at maximum shear $\gamma=0.049$ (full lines). Here (a) $\sigma_g=0.067$ and (b) $\sigma_g=0.017$.

FIG. 6. (a) Velocity profiles of nano-inclusions and solvent at rest, $\gamma=0$, and at maximal shear $\gamma=0.049$, demonstrating virtually no difference between both. (b) Comparison of mobility (short time diffusion coefficient) of nano-inclusions and solvent particles in a quiescent solvent. The number density profiles (normalized to unity) of chain segments for brushes with grafting density $\sigma_g=0.017$ (yellow) and $\sigma_g=0.067$ (gray shaded) are shown as a reference.

to the surface is prevailing, for large z , in contrast, $P_2(\cos \Theta)$ is predominantly slightly negative; this means that for such bonds the orientation is more likely parallel to the grafting wall rather than perpendicular to it. However, when one studies how $P_2(\cos \Theta)$ varies with the index n of the bond (from the grafting site to the next monomer we have $n=1$, while the bond ending at the free end is $n=N-1$), one finds that $P_2(\cos \Theta)$ stays uniformly positive, and decays to zero for large n , and this decrease is slightly faster when γ is large. From Fig. 4 it is evident that the grafting density has a strong impact on the average bond orientation (brush tilting) when shear is applied—at $\sigma_g=0.017$ the “orientation parameter” $P_2(\cos \Theta)$ lies almost entirely in the negative region—an indication that most of the bonds orient predominantly parallel to the substrate. One might expect, therefore, that such shear induced restructuring of the polymer brush could influence the distribution of nano-inclusions.

The central findings of our study concerning the nanoparticles in sheared polymer brushes are collected in Fig. 5: Not surprisingly, the number density profiles of the nano-inclusions (as well as the density profile of both brush monomers and solvent particles) are hardly affected by the shear, except in the case of rather small grafting density $\sigma_g=0.017$. In this latter case the brush profile is considerably deformed by the shear which in turn leads to significant reduction in the concentration of nanoparticles penetrating the polymer coating. As mentioned above, however, even in this case of stronger brush distortion, one finds that the nanoparticles inside the brush flow with the same velocity as the solvent itself—Fig. 6(a).

Eventually, we examine the short time diffusion⁶² (mobility) of nanoparticles in a brush immersed in a quiescent solvent, Fig. 6, and compare it with that of the solvent particles themselves for two grafting densities, $\sigma_g=0.017; 0.067$. According to Fig. 6, one finds that the mobility of nano-inclusions (in direction parallel to grafting plane) is generally about three times lower than that of the solvent particles both outside and inside the polymer brush. Given that our nanoparticles are larger than the solvent atoms by the same amount, this observation appears as a simple manifestation of Stokes law. The difference in grafting density in the brush coatings leads then additionally to a mobility decrease by about 20% in the denser brush both for nano-inclusions as well as for solvent particles.

IV. CONCLUSIONS

In the present paper, the effect of shear on a polymer brush with embedded nanoparticles was studied by MD simulations of a coarse grained model whereby the solvent particles were explicitly included in the simulation. We have assumed good solvent conditions as well as short-range repulsive forces between effective monomers of the polymer chains and the nanoparticles. Being interested in generic features of the problem, no particular chemical effects are ascribed to the nanoparticles which could even be a crude model for globular proteins.

As is evident both from configuration snapshots (Fig. 1) and suitable distribution functions (Fig. 3) shear flow does affect the polymer conformations in a brush significantly. The chains get inclined into the flow direction, in spite of the fact that the brush monomer density profile (and hence the brush height) display more or less significant changes only for rather small grafting density of the polymer brush. Such findings have already been reported by several other authors for various related models,^{60,61} but it is important in the present context that this selective action of the shear flow on the brush is also true for the present study.

We present evidence for the much stronger statement that also the density profile of the nanoinclusions changes rather insignificantly when shear flow is acting on the system (Fig. 5). Since the velocity profile of the flowing solvent inside the brush is strongly screened (Fig. 2), a noticeable flow can only be detected in the immediate vicinity of the outermost region of the brush close to $z=h$. Remarkably, inside the brush no difference between nanoparticles and solvent can be detected in flow velocity.

The average velocity of the nanoparticles in the brush is typically about a factor of 10–20 smaller than the average velocity of the nanoparticles in the adjacent solvent region. This small value of the nanoparticle velocity arises from three factors. (i) The solvent velocity inside the brush is very strongly screened (Fig. 2). (ii) For the chosen radius of the nanoparticles, there occurs still a significant fraction of nanoparticles deeply inside the brush, which do not move at all when shear is applied [Fig. 6(a)]. (iii) Due to the larger size of the nanoparticles (in comparison to the solvent particles) they experience larger friction forces from the monomers when moving in the outer regions of the brush [note that the short-time diffusion coefficient of the nanoparticles typically is a factor of 3–4 smaller than the diffusion coefficient of the solvent particles, Fig. 6(b)].

The present results imply that shear flow can remove nanoparticles at best from the outermost region of polymer brushes but not from the inner region, and hence is not a suitable means for washing out of nanoparticles from such ultrathin polymeric layers.

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- ¹A. Halperin, G. Fragneto, A. Schollier, and M. Sferrazza, *Langmuir* **23**, 10603 (2007).
- ²E. P. K. Currie, J. van der Gucht, O. V. Borisov, and M. A. Cohen Stuart, *Pure Appl. Chem.* **71**, 1227 (1999).
- ³W. T. E. Bosker, P. A. Iakovlev, W. Norde, and M. A. Cohen Stuart, *J. Colloid Interface Sci.* **286**, 496 (2005).
- ⁴W. T. E. Bosker, K. Patzsch, M. A. Cohen Stuart, and W. Norde, *Soft Matter* **3**, 754 (2007).
- ⁵D. E. Fogg, L. H. Radzilowski, R. Blanski, R. R. Schrock, and E. L. Thomas, *Macromolecules* **30**, 8433 (1997).
- ⁶A. B. R. Mayer and J. E. Mark, *J. Polym. Sci. A* **35**, 3151 (1997).
- ⁷V. Z. H. Chan, J. Hoffmann, V. Y. Lee, H. Iatrou, A. Avgeropoulos, and N. Hadjichristidis, *Science* **286**, 1716 (1999).
- ⁸T. Thurn-Albrecht, J. Schotter, G. A. Kästle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, and T. P. Russell, *Science* **290**, 2126 (2000).
- ⁹C. I. Black, C. B. Murray, R. L. Sandstrom, and S. Sung, *Science* **290**, 11131 (2000).
- ¹⁰M. Alexandre and P. Dubois, *Mater. Sci. Eng. R.* **28**, 1 (2000).
- ¹¹D. Schmidt, D. Shah, and E. P. Grannelis, *Curr. Opin. Solid State Mater. Sci.* **6**, 205 (2002).
- ¹²Z. Liu, K. Pappacena, J. Cerise, J. Kim, C. J. Durning, and B. O’Shaughnessy, *Nano Lett.* **2**, 219 (2002).
- ¹³J. U. Kim and B. O’Shaughnessy, *Phys. Rev. Lett.* **89**, 238301 (2002).
- ¹⁴J. Y. Lee, R. B. Thompson, D. Jasnow, and A. C. Balasz, *Macromolecules* **35**, 4855 (2002).
- ¹⁵R. B. Thompson, V. V. Ginzburg, M. W. Matsen, and A. C. Balasz, *Macromolecules* **35**, 1060 (2002).
- ¹⁶C. Park, J. Yoon, and E. L. Thomas, *Polymer* **44**, 6725 (2003).
- ¹⁷S. Förster, *Top. Curr. Chem.* **226**, 1 (2003).
- ¹⁸M. R. Bockstaller, Y. Lapernikov, S. Margel, and E. L. Thomas, *J. Am. Chem. Soc.* **125**, 5276 (2003).
- ¹⁹E. Reister and G. H. Fredrickson, *Macromolecules* **37**, 4718 (2004).
- ²⁰E. Reister and G. H. Fredrickson, *J. Chem. Phys.* **123**, 214903 (2005).
- ²¹M. R. Bockstaller, R. A. Mickiewicz, and E. Thomas, *Adv. Mater. (Weinheim, Ger.)* **17**, 1331 (2005).
- ²²J. U. Kim and B. O’Shaughnessy, *Macromolecules* **39**, 413 (2006).
- ²³M. Ballauff and Y. Lu, *Polymer* **48**, 1815 (2007).
- ²⁴A. Halperin, *Langmuir* **15**, 2525 (1999).
- ²⁵J. U. Kim and M. W. Matsen, *Macromolecules* **41**, 246 (2008).
- ²⁶A. Milchev, D. I. Dimitrov, and K. Binder, *Polymer* **49**, 3611 (2008).
- ²⁷F. Xia and L. Jiang, *Adv. Mater. (Weinheim, Ger.)* **20**, 2842 (2008).
- ²⁸M. A. Cohen Stuart, W. T. S. Huck, J. Genzer, M. Müller, C. Ober, M. Stamm, G. B. Sukhorukov, I. Szleifer, V. V.

- Tsukruk, M. Urban, F. Winnik, S. Zauscher, I. Luzinov, and S. Minko, *Nature Mater.* **9**, 101 (2010).
- ²⁹ S. T. Milner, *Science* **251**, 905 (1991).
- ³⁰ A. Halperin, M. Tirrell, and T. P. Lodge, *Adv. Polym. Sci.* **100**, 31 (1991).
- ³¹ G. S. Grest and M. Murat, in *Monte Carlo and Molecular Dynamics Simulations in Polymer Science*, edited by K. Binder (Oxford University Press, New York, 1995), p. 476.
- ³² I. Szleifer and M. Carignano, *Adv. Chem. Phys.* **94**, 165 (1996).
- ³³ R. C. Advincula, W. J. Brittain, K. C. Carter, and J. Ruehe, *Polymer Brushes* (Wiley, New York, 2004).
- ³⁴ A. N. Semenov, *Sov. Phys. JETP* **61**, 733 (1985).
- ³⁵ S. T. Milner, T. A. Witten, and M. E. Cates, *Europhys. Lett.* **5**, 413 (1988).
- ³⁶ S. T. Milner, T. A. Witten, and M. E. Cates, *Macromolecules* **21**, 2610 (1988).
- ³⁷ E. B. Zhulina, O. V. Borisov, V. A. Pryamitsin, and T. M. Birshtein, *Macromolecules* **24**, 140 (1991).
- ³⁸ M. D. Whitmore and J. Noolandi, *Macromolecules* **23**, 3321 (1990).
- ³⁹ R. R. Netz and M. Schick, *Europhys. Lett.* **38**, 37 (1997).
- ⁴⁰ M. W. Matsen, in *Soft Matter*, edited by G. Gompper and M. Schick (Wiley, New York, 2006), Sec. 2.
- ⁴¹ G. H. Fredrickson, *Equilibrium Theory of Inhomogeneous Polymers* (Clarendon, Oxford, 2006).
- ⁴² J. U. Kim and M. W. Matsen, *Eur. Phys. J. E* **23**, 135 (2007).
- ⁴³ P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
- ⁴⁴ M. Murat and G. S. Grest, *Phys. Rev. Lett.* **63**, 1074 (1989).
- ⁴⁵ P. Y. Lai and K. Binder, *J. Chem. Phys.* **95**, 9288 (1991).
- ⁴⁶ J. Wittmer, A. Johner, J.-F. Joanny, and K. Binder, *J. Chem. Phys.* **101**, 4379 (1994).
- ⁴⁷ D. I. Dimitrov, A. Milchev, and K. Binder, *J. Chem. Phys.* **127**, 084905 (2007).
- ⁴⁸ J. Yaneva, D. I. Dimitrov, A. Milchev, and K. Binder, *J. Colloid Interface Sci.* **336**, 51 (2009).
- ⁴⁹ J. Klein, D. Perahia, and S. Warburg, *Nature (London)* **352**, 143 (1991).
- ⁵⁰ C. Pastorino, K. Binder, T. Kreer, and M. J. Müller, *J. Chem. Phys.* **124**, 064902 (2006).
- ⁵¹ C. Pastorino, T. Kreer, M. Müller, and K. Binder, *Phys. Rev. E* **76**, 026706 (2007).
- ⁵² Y. Rabin and S. Alexander, *Europhys. Lett.* **13**, 49 (1990).
- ⁵³ J. L. Barrat, *Macromolecules* **25**, 832 (1992).
- ⁵⁴ P.-Y. Lai and K. Binder, *J. Chem. Phys.* **98**, 2366 (1993).
- ⁵⁵ G. S. Grest, *Adv. Polym. Sci.* **138**, 149 (1999).
- ⁵⁶ G. S. Grest and K. Kremer, *Phys. Rev. A* **33**, 3628 (1986).
- ⁵⁷ M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1987).
- ⁵⁸ T. Soddemann, B. Dünweg, and K. Kremer, *Phys. Rev. E* **68**, 046702 (2003).
- ⁵⁹ D. Dimitrov, A. Milchev, and K. Binder, *Macromol. Theory Simul.* **17**, 313 (2008).
- ⁶⁰ S. T. Milner, *Macromolecules* **24**, 3704 (1991).
- ⁶¹ G. S. Grest, in *Dynamics in Small Confined Systems III*, edited by J. M. Drake, J. Klafter, and R. Kopelman (Materials Research Society, Pittsburgh, 1997), Vol. 464, p. 71.
- ⁶² J. K. G. Dhont, *An Introduction to Dynamics of Colloids* (Elsevier, New York, 1996), Sec. 6, p. 335.