Chain Dimensions in Filled Polymers: An Intriguing Problem

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ABSTRACT: Simulations of realistically dense polymer melts filled with randomly distributed solid nanoparticles and calculations performed with various methods for single chains in the presence of filler do not show the large increase of chain dimensions with respect to the unfilled polymer predicted by previous RIS calculations when the chains are larger than the particles. It is concluded that the increased dimensions found in recent SANS experiments for poly(dimethylsiloxane) filled with relatively small polysilicate particles cannot be explained on the basis of simple excluded-volume arguments. It is also shown that simulation studies of polymers in the presence of solid obstacles can only be performed by simulating systems with realistic densities.

The distribution of the end-to-end distance of chain segments between topologically adjacent cross-links plays a fundamental role in molecular theories of rubberlike elasticity.[1−4] With some modifications, these theories have been recently extended to explain one of the most valuable processes in polymer technology, namely, the reinforcement (i.e., the enhanced mechanical properties) of elastomers filled with solid nanoparticles.[5−8]

Utilizing Monte Carlo calculations for simple model systems consisting of a single RIS chain in several possible filler environments, the latter studies have shown that the chain dimensions are modified in the presence of the filler with respect to the unfilled case. In particular, calculations performed for poly(dimethylsiloxane) chains (PDMS) in the presence of a random distribution of fixed spherical impenetrable particles predict a decrease of chain dimensions for large particles and short chains and a considerable increase of chain dimensions for small particles and long chains.[7] For instance, the characteristic ratio of PDMS chains of 200 bonds at 400 K (6.41 in the absence of filler) is calculated to decrease to 5.75 when 20% of the volume is occupied by filler particles of diameter 8.0 nm, while it is calculated to increase to 9.65 when 7.5% of the volume is occupied by filler particles of diameter 4.0 nm.[7]

The behavior predicted on the basis of the RIS calculations could not be compared with experiments until very recently, when the dimensions of poly(dimethylsiloxane) chains filled with polysilicate nanoparticles have been investigated by means of small-angle neutron scattering (SANS).[9] The experimental results indicate a decrease of the root-mean-square radius of gyration (R_g) when the polymer chains are approximately the same size as the filler particles and a substantial increase of R_g (on the order of 20%, or even higher at low filler density) when the polymer chains are much larger than the particles. These findings are explained in ref 9 on the basis of the same excluded-volume arguments used in ref 7 to explain the similar results obtained from single-chain Monte Carlo RIS calculations.

Surprisingly, Monte Carlo simulations of realistically dense polymer melts filled with solid nanoparticles show

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Table 1. Composition of the Simulated Systems[a]

system	cell edge	N_p	N_f	σ_f	φ
M_0	40σ	640			
$M_{4,20}$	40σ	512	196	4σ	0.20
$M_{8,10}$	40σ	576	17	8σ	0.10
$M_{8,20}$	40σ	512	34	8σ	0.20
$M_{8,30}$	40σ	448	50	8σ	0.30
$M_{8,36}$	40σ	410	60	8σ	0.36
$M_{10,36}$	40σ	409	34	10σ	0.36
$M_{16,36}$	40σ	409	9	16σ	0.36

[a] N_p = number of polymer chains of 100 units; N_f = number of spherical filler particles; σ_f = diameter of the particles; φ = volume fraction of filler.

only a moderate decrease of the characteristic ratio and of R_g in the systems studied up to now, although in one of them the chains are larger than the particles.[10] To clarify the situation, this paper compares results obtained from simulations of realistically dense systems with various compositions, including cases in which the particles are much smaller than the chains, with the results of several single-chain calculations performed with different methods.

The dense systems (Table 1) have been simulated as previously described.[10] In brief, the polymer chains are modeled as sequences of 100 isodiametric units connected by links of length σ, with the chain stiffness regulated by a bending potential of the form $E(\theta) = (1/2)k_\theta\theta^2$ (θ being the angle between consecutive links; $\theta = 0$ for collinear links). N_p such chains are added to a cubic cell of edge 40σ containing N_f nonoverlapping spherical particles of diameter σ_f placed at random. Nonbonded interactions between polymer units are evaluated as $E_{uu} = \epsilon[(\sigma/r_{uu})^{12} - 2(\sigma/r_{uu})^6]$, with r_{uu} the distance between the units; interactions between polymer units and filler particles are evaluated as $E_{uf} = \epsilon[(\sigma/r_{uf})^{12} - 2(\sigma/r_{uf})^6]$, with r_{uf} the distance of the unit from the *surface* of the particle ($r_{uu,min} = r_{uf,min} = 0.7\sigma$). All interactions are truncated at a distance 2σ, where they are practically negligible. The systems are equilibrated in the NVT ensemble by standard Monte Carlo methods using chain reptation. Calculations are performed with $\epsilon/RT = 0.125$ and $k_\theta/RT = 1.00$ rad^{-2}. Details on the force field used, on the equilibration methods, and on the efficiency of the reptation technique have been reported in ref 10. All simulations are long enough that the rms displacement of the centers of mass
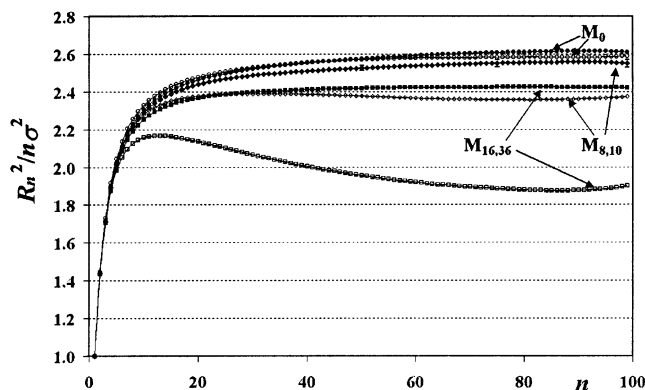
Figure 1. Behavior of $C_n = \langle R_n^2 \rangle / n\sigma^2$ as a function of n for systems M_0, $M_{8,10}$, and $M_{16,36}$ with E_{uu} (full symbols) and without E_{uu} (open symbols).

Table 2. Average Chain Dimensions in Systems Simulated with E_{uu} and without E_{uu}[a]

system	with E_{uu}		without E_{uu}	
	C	Σ/σ	C	Σ/σ
M_0	2.61(2)	13.02(6)	2.59(2)	13.00(5)
$M_{4,20}$	2.59(2)	13.00(5)	1.81(3)	11.16(6)
$M_{8,10}$	2.55(2)	12.92(5)	2.37(2)	12.56(6)
$M_{8,20}$	2.53(2)	12.88(5)	2.09(2)	11.90(6)
$M_{8,30}$	2.52(2)	12.86(5)	1.80(2)	11.18(6)
$M_{8,36}$	2.52(2)	12.87(5)	1.55(2)	10.52(6)
$M_{10,36}$	2.46(2)	12.68(5)	1.69(3)	10.88(6)
$M_{16,36}$	2.42(2)	12.64(5)	1.90(3)	11.48(6)

[a] C = characteristic ratio of the chains; $\Sigma = 2R_g$.

of the chains is at least 4 times their rms radius of gyration (i.e., more than half the width of the base cell).

System M_0 simulates the reference polymer melt with a number density of units equal to σ^{-3}. In filled systems, the first layer of chain units in contact with the filler surfaces is found at $r_{uf} \approx \sigma$, such that the effective diameter of the particles is close to $\sigma_f + \sigma$; the volume fraction of filler (φ in Table 1) is calculated on this basis. The number of chains in the various systems is regulated such that the number density of units in the space left empty by the filler is equal to σ^{-3}. If the units are considered to be polymethylene isodiametric units (3.5 CH_2, $\sigma = 0.45$ nm),[11] this density corresponds to 890 kg/m³.

The curves with full symbols in Figure 1 plot the behavior of $C_n = \langle R_n^2 \rangle / n\sigma^2$ ($\langle R_n^2 \rangle$ being the mean-square distance of two units in the same chain separated by n links) as a function of n for systems M_0, $M_{8,10}$, and $M_{16,36}$. Curves for all other systems are intermediate. Values of C (the characteristic ratio of the chains) and of $\Sigma = 2R_g$ for all simulated systems are listed in Table 2 (first two columns). The curve for system M_0 is nicely coincident with theoretical predictions for freely rotating chains with the bending potential $E(\theta)$,[12] showing that the polymer molecules in this system are actually unperturbed. Adding the filler particles leads to a decrease of chain dimensions in all cases, including those in which the particles are much smaller than the chains. The decrease depends on filler size and partial volume of filler but is always relatively small (7% for C, 3% for Σ at most). The preliminary results of simulations performed for systems with a fixed value of φ (0.20) and various σ_f (from 4σ to 12σ) are in full agreement with these findings. It is concluded that computer models of filled polymers at proper densities do not show increased chain dimensions when $\Sigma_0/\sigma_f <$

Table 3. Average Dimensions of RIS Chains of 300 Backbone Atoms at 400 K[a]

φ	σ_f/nm	PE		PDMS	
		C	Σ/nm	C	Σ/nm
0		6.87(2)	5.570(3)	6.39(2)	5.795(3)
0.05	1.5	6.14(4)	5.304(4)	5.97(2)	5.628(3)
0.05	2.0	6.48(2)	5.438(3)	5.99(2)	5.642(3)
0.05	4.0	6.61(2)	5.488(3)	6.15(3)	5.709(6)
0.10	1.5	6.13(3)	5.301(4)	5.59(5)	5.475(4)
0.10	2.0	6.16(2)	5.314(3)	5.61(2)	5.481(3)
0.10	4.0	6.34(2)	5.397(3)	5.86(2)	5.599(3)
0.20	2.0	5.56(2)	5.077(3)	4.91(4)	5.168(8)
0.20	4.0	5.75(2)	5.183(3)	5.23(3)	5.345(3)
0.20	8.0	6.23(2)	5.366(4)	5.75(2)	5.571(3)

[a] C = characteristic ratio of the chains; $\Sigma = 2R_g$.

3, with Σ_0 the value of Σ for the unfilled polymer. Simulations performed with several different methods for systems of chain molecules at the interface with solids lead to the same conclusion, since significant changes of R_g with respect to $R_{g,bulk}$ are only observed for nearly two-dimensional chains having center of mass at less than $R_{g,bulk}/2$ from the solid surfaces.[12−17] Placements of this kind are obviously quite infrequent,[12] unless the chains are very short or unusually stiff. The predicted behavior is then in excellent agreement with the outcome of SANS experiments on polystyrene thin films, showing that R_g assumes approximately its bulk value in films of thickness $R_{g,bulk}/2$.[18] As a result, one expects nearly unperturbed chain dimensions in filled polymers with large particles and small φ. The present calculations indicate that this is also approximately true with small particles and higher values of φ, that is, when the chains are simultaneously in contact with several filler particles.

To investigate the origin of the different results obtained in single-chain calculations, showing a large increase of chain dimensions for $\Sigma_0/\sigma_f \approx 1.2$,[7] the simulations in Table 1 have been continued by turning off the interaction potential between polymer units, E_{uu} (i.e., the chains behave now as single chains, and their units interact only with the filler surfaces; values of θ higher than 150° are forbidden, in such a way to balance approximately the effects of the 1−3 intrachain interactions active in systems with full density). Plots of C_n vs n for systems M_0, $M_{8,10}$, and $M_{16,36}$ are shown in this case by the open symbols in Figure 1, while C and Σ are listed in the last two columns of Table 2. Compared with calculations including E_{uu}, the chain dimensions in system M_0 are practically unaffected, indicating that single chains of this kind are an excellent model for the unperturbed chains of the reference polymer melt. The situation is different in the presence of filler, since single chains in this case are more compact than in filled systems with proper density. This behavior is confirmed by other calculations performed for longer chains in larger periodic cells. For instance, a system of chains of 300 units (without E_{uu}) in a cell of edge 100σ filled with 531 particles of diameter 8σ ($\varphi = 0.2$) gives $C = 1.96$ and $\Sigma = 20.2\sigma$, to be compared with 2.61 and 22.6σ in the absence of filler, respectively. No increased chain dimensions with respect to the unfilled polymer have been found in the numerous simulations performed for systems without E_{uu}, irrespective of particle size and partial volume of filler.

Similar results are also obtained from Monte Carlo calculations with single RIS chains. Table 3 shows data for polyethylene (PE) and PDMS RIS chains of 300

backbone atoms at 400 K in various filler environments generated as before (σ_f = hard particle diameter). The chains are started in random positions and orientations, and their conformations are weighted according to the RIS models of ref 19 for PE and of ref 20 for PDMS. Chains with backbone atoms overlapping with filler particles are excluded. Taking into account the obvious differences of the models, the data in Table 3 are in good agreement with those in the last two columns of Table 2 and with those obtained by Sharaf et al.[8] for PE with spherical particles. On the other hand, the results for PDMS are significantly at odds with those reported in ref 7. In particular, there is no trace of increased chain dimensions, even when the particles are quite small with respect to the chains.

In conclusion, calculations performed with various methods and with different models do not show increased chain dimensions when Σ_0/σ_f is less than 3. The dissimilar conclusions of ref 7 are likely a consequence of the peculiar setup of the model, in which the chains were always started in a fixed position at the center of a sphere containing the filler. It is then possible that a particular distribution of filler particles in the neighborhood of this center forced most of the accepted chains to run along a limited number of allowed paths. In fact, erratic results (with increased chain dimensions in some cases) are observed when the simulations in Table 3 are repeated with chains starting at fixed locations and with fixed orientations of the first bonds.

In one case ($\varphi = 0.05$, $\sigma_f = 2.0$ nm), the RIS calculations have been also performed for longer PDMS chains, giving $C = 5.91$ for chains of 450 atoms and $C = 5.82$ for chains of 600 atoms. Therefore, the large increase of chain dimensions found for PDMS chains of approximately 2000 atoms in SANS experiments with similar values of φ and σ_f cannot be explained on the basis of simple excluded-volume arguments.[9] This behavior is then to be attributed to effects that are presently not understood. One could obviously invoke the existence of unexpectedly strong preferential interactions between PDMS and the polysilicate nanoparticles used in the experiments. However, the reason that interactions of this kind should lead to a large increase of chain dimensions is far from being obvious. The same is true if one assumes a nonrandom distribution of the filler, in the sense that it is not clear why any particular distribution should increase the average dimensions of the chains. More experiments with various polymers and fillers are undoubtedly needed in order to clarify this point, which appears to be central for rationalizing the behavior of these complex systems.

Figure 1 and Table 2 require further comments, since they show that single-chain simulations are a good approximation for the reference polymer melt but not for filled systems. This is explained in Figure 2, plotting the normalized density of polymer units in spherical shells of radius r and thickness 0.1σ centered on the filler particles in system $M_{8,10}$ with E_{uu} (full symbols) and without E_{uu} (open symbols). It is seen that the two distributions are significantly different and that the density of polymer units near the surface of the filler is practically negligible in calculations without E_{uu}. Sequential snapshots of the various systems show that when E_{uu} is turned off the chains, initially distributed such to occupy all regions left free by the filler, migrate preferentially to the largest cavities delimited by the
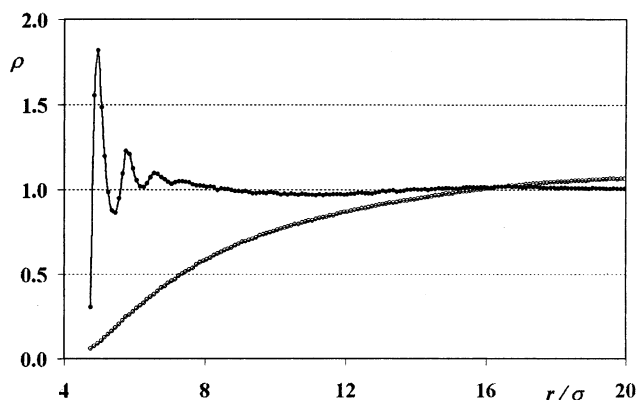

Figure 2. Normalized density of polymer units in spherical shells of radius r and thickness 0.1σ centered on the filler particles in system $M_{8,10}$ with E_{uu} (full symbols) and without E_{uu} (open symbols).

filler particles. This finding is in good agreement with the observation that polymer chains in dilute solutions tend to avoid solid surfaces[21] and implies that single-chain simulations describe mainly the behavior of chains running far from the particles, which are of minor interest in studies of filled polymers. Therefore, these studies (as well as all simulation studies of polymers in the presence of solid obstacles) can only be performed by simulating systems with realistic densities.

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