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Phantom Chain Simulations of Polymer−Nanofiller Systems

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ABSTRACT: Phantom chain simulations can be utilized for studying the molecular arrangements in systems of chain molecules filled with randomly distributed solid nanoparticles, provided that the interaction energy between chains and filler is modified in order to counterbalance the intrinsic tendency of the chain segments to avoid the filler surfaces. In fact, all properties of systems containing phantom chains with suitably modified interactions of this kind are found to be in excellent agreement with those previously obtained for dense systems having the same composition. This makes possible to study systems that cannot be simulated at full density (i.e., systems with long chains and/or with large particles and small filling density). Simulations performed for long phantom chains show that the simple rules recently proposed to *predict* the mutual arrangements of particles and chains in the dense systems simulated up to now can be extended to very long chains. However, these rules should be modified in order to be valid also for large particles and small filling density.

Introduction

Simulation studies are developing into an everyday more essential tool for understanding, controlling, and designing the structure and properties of materials. This is specially true for multicomponent systems, in which the relevant properties are mainly determined by the mutual arrangements of the various components at the molecular or supramolecular level. An important example is represented by polymers filled with solid nanoparticles, a broad class of materials extensively utilized in the modern technology for a variety of practical applications. A distinctive and valuable feature of this kind of materials is the fact that their mechanical properties can be easily modified in a wide range by changing the chemical nature of polymer and filler, the size and shape of the filler particles, and the density of filling. However, tailoring the various properties to the needs and tuning them finely require that the mutual arrangements of polymer chains and solid particles be completely understood, while our present knowledge is still mostly empirical. For this reason, polymer−nanofiller systems have been the subject of several simulation studies in the past few years.[1−10]

Simulations have been performed for lattice[1−4] and for out-of-lattice[5−10] model systems. In the first case, the polymer chains are represented as random walks with excluded volume (i.e., multiple occupancy of lattice sites is forbidden) on the two-dimensional square lattice[2,4] or on the cubic lattice,[1,3] while the filler particles are represented by unavailable sites. Calculations of this kind are (relatively) simple and the simulated systems can be rapidly equilibrated, allowing one to gain an insight into complex phenomena such as the phase behavior of filled polymers, polymer mixtures, and copolymers. Of course, they are less well suited for detailed investigations of the molecular arrangements and conformations in these materials. Out-of-lattice models with realistic densities of chain molecules and solid particles have been simulated using Monte Carlo[5−8] (MC) and molecular dynamics[9,10] (MD) methods. Because of obvious limitations, MD calculations have only been performed for systems containing one single solid particle. MC calculations are less limited in this respect, and have been utilized to simulate systems of coarse-grained chains (100 isodiametric units, corresponding to approximately 350 methylene groups if the simulated polymer is considered to be polymethylene) with randomly distributed particles of various sizes (i.e., with diameter from 4 to 28 times the diameter of the chain units) at various densities of filling (from 10% to 50% in volume).

The overall picture emerging from the results of these calculations can be shortly summarized as follows: the chain units in contact with the filler particles are arranged in densely packed and partly ordered shells of width approximately twice the diameter of the chain units; each particle is in contact with many different chains, and each chain visits the interface shell of a number of filler particles (depending on the size of the particles and on the density of filling); the chains can be considered to be sequences of interface segments (chain segments totally running in the interface shell of a given particle), bridge segments (sequences of noninterface units with the two adjoining units in the interface shells of two different particles), and loop segments (similar to bridge segments, but starting and ending in the interface shell of the same particle). The average length and the relative abundance of the various kinds of segments depend on the exact composition of the system under study. A few simple rules allowing one to predict (approximately) at a quantitative level the relevant characteristics of the simulated systems have been recently proposed.[8]

Although the simulations with relatively short chains and small particles performed up to now are inherently interesting, one would also like to use their results for predicting the properties of systems with much longer chains and larger particles. Note that direct MC simulations of nanocomposites with long chains at realistic densities are not feasible, since there are no suitable methods for equilibrating and sampling systems of this kind (the reptation method, utilized in the previous simulations, becomes quite inefficient for dense systems of chains longer than 100−200 units). On the other

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Table 1. Composition of Previously Simulated[5−8] Dense Systems Used for Comparison (N_p = Number of Chains of 100 Units; N_f = Number of Spherical Filler Particles; σ_f = Diameter of the Particles; φ = Volume Fraction of Filler), and Values of ϵ^*/RT Used for the Corresponding P* Systems

system	cell edge	N_p	N_f	σ_f	φ	ϵ^*/RT
D_0	40σ	640				
$D_{8,20}$	40σ	512	34	8σ	0.20	0.88
$D_{8,30}$	40σ	448	50	8σ	0.30	0.93
$D_{16,36}$	40σ	409	9	16σ	0.36	0.96
$D_{28,20}$	40σ	512	1	28σ	0.20	0.97

hand, systems characterized by large particles and small filling density contain, when the model chains are only 100 units long, a large proportion of free chains (i.e., chains with no interface units) and of very long terminal segments. Therefore, the results obtained with these systems are of little use for predicting the behavior of longer chains.

The simple idea of solving this problem by studying the behavior of long phantom chains in the environment provided by the filler particles is clearly attractive.[11−14] However, it has been recently shown that phantom chains designed to be a good approximation for the unperturbed chains of a polymer melt cannot be utilized for investigating situations in which the conformational distribution is perturbed by interactions with solids.[6] In fact, chains of this kind tend to avoid the interface with solids for the obvious reason that the conformational freedom of their segments is restricted when these segments are in contact with solid surfaces. As a consequence, phantom chain simulations describe mainly the behavior of chains running far from the particles, unless the force field is modified in such a way that this effect is properly counterbalanced. This paper reports on phantom chain simulations performed with an arbitrary modification of the interaction energy between particles and chain units, compares the results with those of simulations previously performed for dense systems, and extends the calculations to much larger systems with longer chains.

Models and Methods

The composition of some of the dense systems simulated in previous papers and utilized here for comparison is listed in Table 1. They consist of three-dimensionally periodic arrays of cubic cells containing N_f randomly distributed non overlapping spherical filler particles of diameter σ_f and N_p chains, modeled as unbranched sequences of 100 isodiametric units connected by links of length σ. The chain stiffness is 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). Nonbonded interactions between chain 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 chain 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 the 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}. Other details can be found in refs 5−8. System D_0 simulates the reference unfilled melt with a number density of units equal to σ^{-3}. If the units are considered to be polymethylene isodiametric units (3.5 CH_2, $\sigma = 0.45$ nm),[15] this density corresponds to 890 kg/m^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.

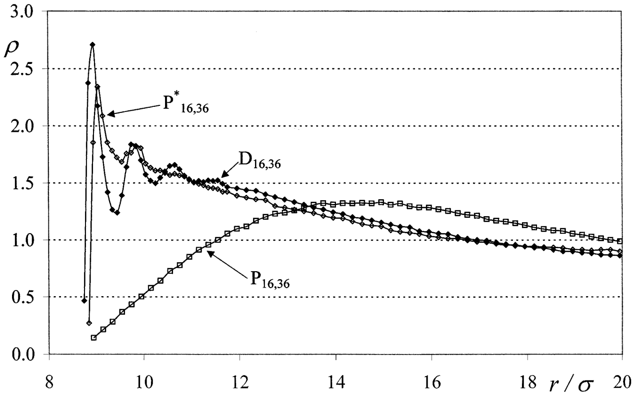

Figure 1. Normalized density of polymer units in spherical shells of radius r and thickness 0.1σ centered on the filler particles in system $D_{16,36}$ and in large systems of phantom chains of 100 units with $\sigma_f = 16\sigma$, $\varphi = 0.36$.

It has been shown in ref 6 that the conformational properties of the chains in system D_0 are practically unaffected when the interaction energy between chain units (E_{uu}) is turned off and values of θ higher than 150° are forbidden, indicating that such phantom chains are an excellent model for the unperturbed chains of the reference melt. However, when phantom chains of this kind are studied in filled systems and E_{uf} is used for the interaction energy between chain units and particles, the results are very far from those obtained with properly dense systems. In particular, the fraction of chain units in contact with the filler surfaces turns out to be much smaller for the phantom chains, since the chain segments tend to stay far from the surface of the filler particles. As a consequence of this anomalous distribution, the chain conformations and the mutual arrangements of particles and chains are strongly perturbed. Hopefully, the introduction of an arbitrary attraction between chain units and filler surfaces may restore the original distribution and may give properties approaching those observed in dense systems. To explore this possibility, the simulations of phantom chains reported here have been performed by substituting the interaction energy E_{uf} with a similar term $E^*_{uf} = \epsilon^*[(\sigma/r_{uf})^{12} - 2(\sigma/r_{uf})^6]$, where the energy parameter ϵ^*, different for the various systems, is chosen such that the density of units in the shell between 0.8σ and 2σ from the surface of the filler particles coincides, when properly scaled, with the value found for all dense systems ($1.1\sigma^{-3}$; see ref 8). Also, to avoid an excessive crowding of chain units in regions that are at less than 2σ from two or more filler surfaces, E^*_{uf} is evaluated only for the interaction of each chain unit with the *closest* filler surface. Of course, this modified energy E^*_{uf} has no particular merit other than being simple and giving good results for all systems examined (see later); it is certainly possible that other forms for the interaction energy between particles and chain units, or totally different methods, may give equally good results. For instance, the $0.8-2\sigma$ range is chosen here because the thickness of the interface shells is approximately 2σ, but there are no polymer units at distances less than 0.8σ from the filler surfaces. Since all interactions are truncated at the distance 2σ, any reasonable different choice (for instance, $1-1.5\sigma$, with values of ϵ^* such to give in this range the value of the density observed in the same range for dense systems) would only change the relatively unimportant distribution of units *inside* the interface shells, but would not modify the mutual arrangement of filler particles and chain molecules in the simulated systems (see later, Figure 1). Systems of phantom chains simulated using E_{uf} or E^*_{uf} will be denoted in the following by the symbols P and P*, respectively.

Using phantom chains allows to simulate much larger systems with many more particles. Filled systems containing phantom chains with σ_f and φ identical to the dense systems listed in Table 1 have been simulated by placing 10 times the number of particles in Table 1 in cubic cells of volume 10 times larger (cell edge 86.174σ). Calculations have been first performed for chains of 100 units, to establish suitable values for ϵ^*/RT and to compare the results obtained for the phantom chains with those obtained in dense systems. The value of ϵ^*/RT giving the proper scaled density in the interface shells is found to depend on σ_f and φ (Table 1, last column), ranging from 0.88 for $\sigma_f = 8\sigma$ and $\varphi = 0.20$ to 0.97 for $\sigma_f = 28\sigma$ and $\varphi = 0.20$. The same values of ϵ^*/RT have been then utilized for calculations with longer chains of 500 units in larger cells of edge 185.65σ containing a considerable number of particles (100 times the values of N_p reported in Table 1). In one case ($\sigma_f = 28\sigma$ and $\varphi = 0.20$), this large cell has been also utilized for calculations with chains of 1000 units. The methods used for initializing and equilibrating the systems are practically coincident with those described in refs 5−8.

Results and Discussion

All results obtained from calculations with phantom chains using E_{uf}, instead of E^*_{uf}, are totally inconsistent with the simulations performed for dense systems. This is clearly exemplified in Figure 1, comparing the normalized density of polymer units in spherical shells of radius r and thickness 0.1σ centered on the filler particles in three simulated systems with $\sigma_f = 16\sigma$ and $\varphi = 0.36$. Full symbols refer to the dense system $D_{16,36}$ (Table 1), while open symbols refer to systems $P_{16,36}$ and $P^*_{16,36}$, as indicated. The curve for system $D_{16,36}$ has been previously reported and its peculiar features (a series of maxima and minima superimposed to a large maximum near the filler surface; ρ less than unity at r as high as 20σ) have been discussed and explained.[5] Note that an average value of ρ on the order of 1.7 between 0.8σ and 2σ from the filler surface is consistent with an average density of 1.1σ^{-3} in this region (see before), since ρ is normalized dividing by the average density of chain units in the system (=0.64 σ^{-3}). The behavior of ρ for phantom chains with the unmodified energy E_{uf} (system $P_{16,36}$) is in line with that shown in ref 6 for a different system with smaller particles and lower φ; i.e., the chain units tend to avoid the solid surfaces, with the consequence that all properties are profoundly altered with respect to dense systems. Although simple and totally arbitrary, substituting E_{uf} with E^*_{uf} is seen to be very effective, in the sense that not only do the phantom chains in system $P^*_{16,36}$ show the correct proportion of units in contact with the filler particles but also the overall shape of the $P^*_{16,36}$ curve in Figure 1 is quite similar to that of the $D_{16,36}$ curve. The same is true for all other P* systems studied in this work. Of course, phantom chains can only approximate the behavior of dense systems in proximity of the filler surfaces, since the exact location and intensity of the maxima and minima characterizing these systems are mainly related to packing effects due to intramolecular and intermolecular interactions between neighboring chain units.

The conformational consequences of substituting E_{uf} with E^*_{uf} are exemplified in Figure 2, plotting $R_n^2/n\sigma^2$ vs n, where R_n^2 is the mean square distance of units belonging to the same chain and separated by n links. Results are shown for the reference system D_0, for phantom chains without filler and for the systems studied in Figure 1. The close similarity of the curves for system D_0 and for phantom chains without filler confirms that these phantom chains are a good model for the unperturbed reference melt.[6] The plot for system $P_{16,36}$ is characteristic of all filled systems simulated with the unmodified energy E_{uf}; i.e., the initial rise is followed by a decrease (more pronounced for more densely filled systems) and then by a subsequent tendency to rise again. This anomalous behavior, quite different from the behavior shown by the dense system $D_{16,36}$, is clearly related to the peculiar shape of the corresponding curve in Figure 1 and reveals that the chain conformation is strongly altered by the tendency of the phantom chains to avoid the surfaces of the filler particles. On the other hand, the curve for system $P^*_{16,36}$ is seen to be very close to the curve for system $D_{16,36}$, indicating that the conformational distribution observed in dense filled systems is properly restored when the simulations are performed for phantom chains with this arbitrarily modified interaction energy. As a consequence, the average dimensions of the phantom chains of 100 units (characteristic ratio between 2.4 and 2.5 and rms radius of gyration between 6.3σ and 6.4σ) are very similar in P* and D systems having the same composition (with a tendency to be slightly on the lower side in P* systems).

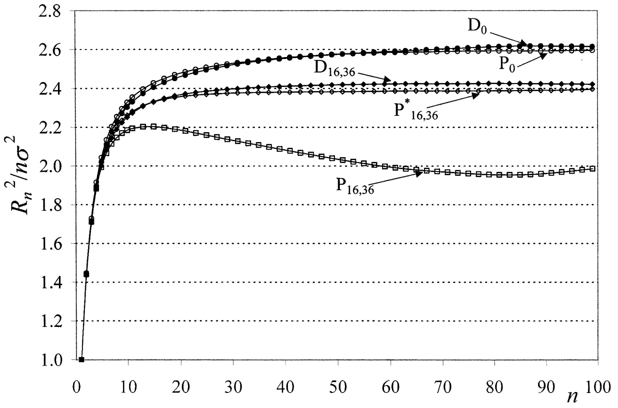

Figure 2. Plots of $C_n = \langle R_n^2\rangle/n\sigma^2$ as a function of n for systems D_0 and $D_{16,36}$ and for large systems of phantom chains of 100 units with $\sigma_f = 16\sigma$, $\varphi = 0.36$.

Table 2. Comparison of Results Obtained for Phantom Chains of 100 Units in Large Systems of Randomly Distributed Spherical Nanoparticles (P* Systems) with Those Obtained for the Smaller Properly Dense Systems Listed in Table 1 (D Systems)[a]

	$P^*_{8,20}$	$D_{8,20}$	$P^*_{8,30}$	$D_{8,30}$	$P^*_{16,36}$	$D_{16,36}$	$P^*_{28,20}$	$D_{28,20}$
f_1	0.28	0.29	0.47	0.46	0.32	0.33	0.08 (0.08)	0.08
f_2	0.01	0.02	0.04	0.02	0.01	0.01	0 (0)	0
f_f	0.007	0.009	0	0	0.005	0.005	0.5 (0.4)	0.4
N_i	7.8	7.4	13	12	7.7	7.3	1.9 (1.8)	1.6
L_i	3.7	4.0	3.7	3.8	4.1	4.5	4.4 (4.4)	4.8
N_b	2.9	2.6	5.0	4.4	2.4	2.4	0.2 (0.06)	0.05
L_b	11	12	6.4	7.3	11	12	16 (42)	42
N_l	2.8	2.4	3.3	2.8	3.3	3.1	1.2 (1.2)	1.0
L_l	5.4	5.6	3.9	4.2	5.8	5.7	8.3 (9.0)	9.7
N_t	1.3	1.4	1.0	1.0	1.3	1.3	0.9 (1)	1
L_t	17	18	8	9	17	16	36 (38)	39
N_d	1.1	1.5	3.4	4.0	1.0	0.7	0 (0)	0
P_c	3.4	3.3	5.2	5.2	2.7	2.7	0.6 (0.6)	0.6
C_p	50	50	50	50	120	120	320 (320)	290

[a] The data in parentheses for system $P^*_{28,20}$ refer to particles arranged at the nodes of a cubic lattice. All parameters are defined in the text.

Table 2 reports a number of parameters chosen such to describe the mutual arrangements of particles and chains in filled systems.[7,8] Values obtained for P* systems with chains of 100 units are compared with those obtained from the corresponding dense systems. The various parameters are defined as follows: f_1 is the fraction of interface units (interface units are units with center in the interface shells; interface shells are shells of width 2σ surrounding the filler particles), while f_2 is

Table 3. Comparison of Results Obtained for Phantom Chains of 500 Units with Those Extrapolated from the Results Reported in Table 2 for Phantom Chains of 100 Units (in Parentheses) and with Those Predicted a Priori According to the Approximate Rules Described in the Text (Third Column, for Each System)

	$P^*_{8,20}$			$P^*_{8,30}$			$P^*_{16,36}$			$P^*_{28,20}$		
f_1	0.29	(0.28)	0.29	0.48	(0.47)	0.49	0.33	(0.32)	0.33	0.08	(0.08)	0.08
f_2	0.01	(0.01)	0.03	0.04	(0.04)	0.06	0.01	(0.01)	0.01	0	(0)	0
f_f	0	(0)		0	(0)		0	(0)		0.09	(?)	
N_i	38	(39)	36	63	(65)	62	38	(39)	34	9.3	(9.5)	7.9
L_i	3.8	(3.7)	4.0	3.8	(3.7)	3.9	4.2	(4.1)	4.4	4.5	(4.4)	4.7
N_b	17	(15)	17	27	(25)	30	15	(12)	16	1.5	(1.0)	3
L_b	14	(11)	11	6.7	(6.4)	7.3	14	(11)	12	70	(16)	39
N_l	15	(14)	11	18	(17)	13	18	(17)	11	6.8	(6.0)	3.5
L_l	6.1	(5.4)	5.5	4.1	(3.9)	3.7	6.4	(5.8)	6.1	16	(8.3)	19
N_t	1.4	(1.3)		1.0	(1.0)		1.3	(1.3)		1.6	(0.9)	
L_t	17	(17)		7.6	(8)		18	(17)		124	(36)	
N_d	5.4	(5.5)	7.6	17	(17)	18	5	(5.0)	5.5	0.1	(0)	0.5
P_c	12		13	17		20	7.5		6.4	1.8		1.5
C_p	35		37	31		30	70		69	180		184

the fractions of units in the overlapping regions of interface shells of adjacent particles; f_f is the fraction of free chains (i.e., chains with no interface units); N_i, N_b, N_l, and N_t are the average number of interface, bridge, loop, and terminal segments per chain, respectively (the various kinds of segments are defined in the Introduction), while L_i, L_b, L_l, and L_t are their average length in terms of chain units; N_d is the average number of direct connections per chain (direct connections are two consecutive interface segments belonging to the interface shells of adjacent particles, without an intermediate bridge segment); P_c is the average number of different interface shells visited by each chain, and C_p is the number of different chains having at least one unit in the interface shell of a given particle.

Table 2 shows that the agreement between the results of phantom chain simulations and those obtained for dense systems having the same composition is truly remarkable. In fact, all parameters characterizing the mutual arrangements of particles and chains are practically coincident in the two cases (with one exception, see later). Consider for instance a system crowded with relatively small particles like $D_{8,30}$. The two different calculations agree that an average chain of 100 units consists of this case of 12−13 interface segments of length approximately four units, of four to five bridge segments of length six to seven units, of three loop segments of length four units and of one terminal segment of length height to nine units, with three or four direct connections between consecutive interface segments; the average chain is in contact with five different particles, and each particle is in contact with about 50 different chains. A similar good agreement is found for the other systems studied, with the single exception of the bridge segment length in systems with $\sigma_f = 28\sigma$ and $\varphi = 0.20$, found to be 42 units in system $D_{28,20}$ and only 16 units for the corresponding phantom chains. The reason for this discrepancy is rather obvious, when it is considered that the base cell of system $D_{28,20}$ contains only one single filler particle. Therefore, this system does not correspond to a random arrangement of particles, but to a regular arrangement at the nodes of a cubic lattice with lattice spacing 40σ. The phantom chain calculations have been then repeated for a cubic arrangement of eight particles with $\sigma_f = 28\sigma$ in a cell of edge 80σ. The results (in parentheses) indicate that these calculations are also quite sensitive to the exact arrangement of the particles, and that nearly identical results are obtained for a given arrangement with phantom chain and in dense systems simulations. When it is considered that the systems described in Table 2 are largely different for density of filling and size of the filler particles, it is apparent that phantom chains with a properly modified interaction energy between chain units and particles can be confidently utilized to study the behavior of these complex systems in cases that cannot be directly simulated at full density. It is also concluded that the exact form of the modified interaction energy is relatively unimportant, as far as the scaled density of units between 0.8σ and 2σ from the surface of the particles is forced to correspond to the value ($1.1\sigma^{-3}$) found in dense systems.

Extrapolating to longer chains the results obtained for the relatively short chains of 100 units simulated up to now is far from being straightforward. For systems in which the chains of 100 units are in contact with several filler particles (i.e., systems with small particles and high density of filling), one expects that the values of f_1 and f_2 and the average length of the various kinds of segments remain practically unchanged when the chain length is increased, while N_i, N_b, N_l, and N_d are expected to increase proportionally to the chain length. This is obviously not true for P_c (and for the related quantity C_p), since the number of different particles in contact with a given chain is a complex function of the radius of gyration of the chains[8] (see later). When the particles are large and the density of filling is small, however, the chains of 100 units are too short to show a behavior indicative of the behavior of long chains. For instance, systems of this kind contain a large proportion of free chains and of chains that, being in contact with a single filler particle, have long terminal segments. Free chains and terminal segments are partly converted in bridges when the chain length is increased, with the consequence that both the number and the length of these segments in long chains cannot be extrapolated on the basis of the values obtained for shorter chains.

This is well seen in Table 3, where the results of simulations performed for phantom chains of 500 units are compared with those extrapolated from the results obtained for phantom chains of 100 units (in parentheses) assuming that the length of the various kinds of segments is unchanged and that N_i, N_b, N_l, and N_d are proportional to the chain length. All values found for the chains of 500 units are approximately as anticipated, except for the length of the bridge, loop and terminal segments in systems with $\sigma_f = 28\sigma$ and $\varphi = 0.20$. This is obviously due to the fact that nearly half the chains are free chains when the chain length is 100 units (Table 2). On the other hand, even when the chains are as long as 500 units, the system still contains 10% of free chains. For this particular case, calculations have been also performed with chains of 1000 units, giving $L_b = 100$, $L_l = 18$, and $L_t = 160$ (to be compared with 70, 16 and 124, respectively, for chains of 500 units). All other results are practically as expected, but the system still contains 2% of free chains. Therefore, the properties of long chain polymers with large particles and low content of filler can be only studied by simulating phantom chains of appropriate length. Though feasible, calculations of this kind with chains longer than 500 units are quite slow, since the number of accepted reptation moves required to regenerate the chains increases with the square of the chain length.

The third column in Table 3 shows the values of the various parameters that can be predicted a priori for each system using the set of simple approximate rules described in ref 8. These rules are roughly valid for all dense systems simulated up to now, with the exception of extreme cases (systems very crowded with small particles or systems containing a large proportion of free chains). They are based on the following considerations:

(a) The density of units in a spherical shell between 0.8σ and 2σ from the surface of a filler particle is found for all dense systems to be approximately $1.1\sigma^{-3}$; therefore, the fraction of interface units is $f_1 \approx 1.1V_sN_f/N_pL_p - (f_2 + f_3 + ...) \approx 1.1(V_s/V_f)\varphi/(1 - \varphi) - (f_2 + f_3 + ...)$, where V_s is the volume of this shell, L_p is the chain length, V_f is the effective volume of a filler particle and f_k is the fraction of units in the interface shells of k or more different particles; for all systems of practical interest, f_3 and higher terms are negligible, while f_2 is usually small (<0.05) and is approximately given by $f_2 \approx 40\xi^2$, the dimensionless parameter $\xi = \varphi\sigma/\sigma_f$ being a measure of how crowded the filler particles are in the system (for a given value of φ, the surfaces of adjacent particles are closer when the particles are smaller).

(b) The length of the interface segments depends mainly on the stiffness of the chains and on the size of the filler particles and only slightly on the value of φ; for chains of the simulated stiffness (comparable to that in most practical systems), L_i is between 3.5 units for very small particles and five units for very large particles, and is approximately given by $L_i \approx 5.0 - 6.5\xi(1 + \varphi)/\varphi$; once L_i is known, the number of interface segments per chain is given by $N_i \approx f_1L_p/L_i$.

(c) P_c corresponds to the number of filler particles having their center in a sphere of diameter $\alpha R_g + \sigma_f + 4\sigma$, where R_g is the rms radius of gyration of the chains and α is a constant; in fact, for the dense systems studied in refs 5−8, P_c is quite well approximated by $P_c \approx \varphi V^*/V_f$, where V^* is the volume of a sphere of diameter $1.7R_g + \sigma_f + 4\sigma$ (i.e., $\alpha = 1.7$) and R_g for the chains simulated is given by $R_g \approx 0.65L_p^{1/2}$; on the other hand, C_p is related to P_c by $C_p = P_cN_p/N_f = P_c(1 - \varphi)V_f/\varphi L_p$.[7,8]

(d) The number of direct connections per chain is obviously higher in systems where the filler particles are more crowded, and is found to be roughly given by $N_d \approx 100(N_i - 1)\xi^2/f_1$; since on the average in the dense systems simulated in refs 5−8 the contact of a chain with a given particle consists of two interface segments (separated by a loop or by two consecutive direct connections),[8] the number of bridge segments per chain is approximately $N_b \approx N_i/2 - 1$; therefore, the number of loop segments per chain can be evaluated as $N_l = N_i - 1 - N_d - N_b$.

(e) As expected, the length of the bridge segments increases with increasing σ_f for a given φ and decreases with increasing φ for a given σ_f (in practice, $L_b \approx 0.275/\xi$); on the other hand, the relative lengths of bridge and loop segments have to be related, since the probability that a chain segment circles back to form a long loop is higher when the particles are far apart, i.e., when the bridges are longer (provided that L_b is not too high; see later); as a matter of fact, for the dense systems simulated up to now, in which L_b is less than 20 units, the length of the loop segments is found to be approximately half the length of the bridge segments ($L_l \approx L_b/2$).

Table 3 indicates that these simple rules, deduced from simulations of dense systems of chains of 100 units and shown to be valid for these systems when σ_f and φ are within the range specified above,[8] can be extended without modifications to approximate the behavior of longer chains. For instance, chains of 500 units in systems with $\sigma_f = 8\sigma$ and $\varphi = 0.20$ (i.e., systems with small particles and intermediate filling density; $\xi = 0.025$) are predicted to consist of 36 interface segments of length four units (found: 38 segments of average length 3.8), of 17 bridges of length 11 units (found: 17 bridges of average length 14) and of 11 loops of length six units (found: 15 loops of average length 6.1), with eight direct connections between interface segments (found: 5.4); each chain is predicted to be in contact with 13 different particles (found: 12), and each particle is predicted to be in contact with 37 different chains (found: 35). For the same particles at higher filling density ($\varphi = 0.30$; $\xi = 0.038$), the chains are predicted to consist of as many as 62 interface segments of length four units (found: 63 segments of average length 3.8), of 30 bridges of length seven units (found: 27 bridges of average length 6.7) and of 13 loops of length four units (found: 18 loops of average length 4.1), with 18 direct connections between interface segments (found: 17); each chain is predicted to be in contact with 20 different particles (found: 17), and each particle is predicted to be in contact with 30 different chains (found: 31). When it is considered that these predictions are totally a priori (i.e., they are made starting only from the values of σ_f and φ), their approximate good agreement with the simulation results can be considered to be quite successful.

On the other hand, Table 3 also shows that the same rules are inadequate for systems with large particles at low filling density. In particular, when $\sigma_f = 28\sigma$ and $\varphi = 0.20$ ($\xi = 0.007$), it is seen that L_l is much less than $L_b/2$ (as also confirmed from calculations with chains of 1000 units). This is not unexpected, since the bridge length is mainly regulated by the average distance between the surfaces of adjacent particles (one can have quite long bridge segments when the particles are large and the filling density is small), while the probability that a chain segment circles back to form a long loop is expected to decrease with increasing the length of the segment. One has to remark that the systems under study, although idealized with respect to real filled polymers, are far from being simple. The predictive rules reported here are based on the results obtained for the few dense systems with relatively short chains and small particles that have been simulated up to now. Therefore, they are only (approximately) valid for these systems, and are obviously open to modifications when new data become available. Unfortunately, simulations of dense systems with large randomly distributed particles are not feasible today, irrespective of the chain length (a cell containing only 20 particles with $\sigma_f = 28\sigma$ and $\varphi = 0.20$ would also contain more than 10^6 chain units). However, if one assumes that the molecular arrangements in these systems are well approximated by phantom chains with the appropriate parameter ϵ^*, the results of phantom chain calculations can be used to modify the rules and to extend their range of validity. A study of this kind, requiring simulations of numerous large systems with various compositions and quite long chains, is currently in progress, and the results will be reported in a forthcoming paper.

Conclusions

MC simulations of polymers filled with randomly distributed solid nanoparticles are limited to systems with (relatively) short chains and small particles. In fact, even when the chain structure is simply approximated by a sequence of identical isodiametric units, there are no good methods for equilibrating and sampling realistically dense systems of chain molecules longer than 100−200 units. On the other hand, when the particles are much larger than the transverse diameter of the chains, meaningful simulations cannot be performed, irrespective of the chain length, because the size of the systems to be simulated grows out of proportion. This paper shows that studies of this kind can be performed using phantom chains, provided that the interaction energy between chain units and filler particles is properly modified in order to counterbalance the intrinsic tendency of the chain segments to avoid the filler surfaces.

Although the modified interaction energy used here is very simple and totally arbitrary, all results obtained for systems of phantom chains of 100 units in P* systems correspond quite closely to those found for dense systems with identical composition. In particular, this is true for the spatial distribution of the units, for the chain conformations and for the mutual arrangements of chains and particles. One is then led to conclude that similar phantom chain calculations can be utilized to study systems that cannot be directly simulated at full density.

In fact, all properties of filled systems with phantom chains of 500 units are practically as expected on the basis of the results obtained for chains of 100 units, with the exception of systems containing large particles at small filling density, where chains of 100 units are too short to show properties indicative of those of longer chains. On one side, this confirms that phantom chain calculations can be used to study the molecular arrangements in polymer-based nanocomposites with various compositions. On the other side, it shows that long chain polymers with large particles and small filling density can be studied only by simulating phantom chains of appropriate length.

The properties of systems with relatively short chains (100 units), small particles and high filling density (ξ in the range 0.02−0.04) can be approximately predicted using a few simple rules based on the results obtained in the simulations of dense systems performed up to now. Phantom chain simulations performed for systems with chains of 500 units, that cannot be simulated at full density, indicate that these rules can be extended to long chains without modifications when ξ is in the range 0.02−004. However, not unexpectedly, they also indicate that the rules should be modified in order to predict the molecular arrangements when the particles are large and the filling density is small ($\xi < 0.02$). Phantom chain simulations with very long chains, large particles, and various filling densities are currently underway. The possibility that similar methods can be profitably used for other systems in which the relevant properties are mainly determined by the presence of polymer/solid interfaces is also under investigation.

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