**Summary:** Phantom chain MC simulations have been performed for realistically sized systems of polymer chains filled with solid nanoparticles. The results of the simulations and simple theoretical considerations are used to rationalize a number of parameters relevant to the characterization of these systems. Even when the average number of nanoparticles in contact with a chain is very small (much less than unity), the nanoparticles are nodes of highly interconnected transient networks bridged by the polymer chains.
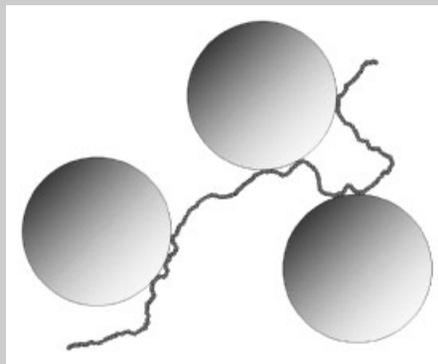
Phantom Chain Simulations of Realistically Sized Polymer-Based Nanocomposites

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Introduction

Direct simulations of systems containing amorphous polymers at proper density are normally restricted to models in which the polymer chains are represented by relatively short oligomers. This is true not only for molecular dynamics (MD) calculations, intrinsically limited by the exceedingly long times required for the overall conformational rearrangements of long chain molecules in dense systems, but it is also true for Monte Carlo (MC) simulations, because none of the available MC methods is well suited for equilibrating and sampling dense systems of long chains. Even when the polymer molecules are approximated by sequences of identical beads, making it possible to use reptation or other simple moves, the calculations are limited to chains of 100–200 beads at most in continuum models and to not much longer chains in lattice models. This is not a severe problem when one is interested in local properties such as the mutual arrangements and the conformations of short segments embedded in the polymer chains, since these properties are scarcely influenced by the presence of a few more chain ends (unless the simulated oligomers are too short). On the other hand,

the properties of systems with long chains can be often extrapolated from those of systems with oligomers of various length.

In some cases, however, simulations of short chain oligomers are of little use for predicting the behavior of real polymers. A recent example of this situation is given by the simulations performed using both MD and MC in order to understand molecular arrangements, conformation, and dynamics in polymer-based nanocomposites.[1−14] Owing to their enhanced mechanical properties, polymer-based composite materials are of vast industrial impact and represent today a significant portion of the polymer market. Furthermore, advances in nanotechnologies will likely lead in the near future to new developments and to still unpredictable applications of these materials. It is then surprising that our physical picture is still rather obscure, and that no one is presently able to guess for a given system fundamental parameters such as the average number of different particles in contact with a given polymer chain or the average length of the polymer segments connecting two different particles.

Although polymers filled with particles of diameter 1–2 nm will play in the future an increasingly important role,

the average diameter of the filler particles in the real polymer-based nanocomposites that are widely used today is normally much larger than the transverse diameter of the chains. Even in the simplifying assumption that the filler can be modeled as a random distribution of spherical entities, direct simulations of nanocomposites with such large particles are not feasible when the polymer is simulated at full density. A base cell with a few particles 50 times larger than the polymer units would also contain more than 10^6 such units for any practical partial volume of filler, irrespective of the chain length. In fact, all simulations of dense systems of this kind have been performed up to now either with small randomly distributed nanoparticles (i.e. with diameter less than 20 times the diameter of the polymer units) or with one single particle in the base cell. Though these simulations have been valuable to enlighten a number of interesting aspects of the problem, their results cannot be extrapolated to realistically long chains and large particles. In particular, simulated systems with particles of diameter larger than 10–15 times the diameter of the chain units at a partial volume of filler less than 30% contain a substantial proportion of free chains (i.e. chains with all units far from the surface of any particle) and of chains with long dangling terminal segments. As a consequence, the results obtained from these simulations cannot be utilized to predict the behavior of systems with long chains.

It has been recently shown[10] that this problem can be circumvented by simulating the behavior of phantom chains in the filler environment, provided that the interaction energy of filler particles and polymer units is properly modified in such a way to counterbalance the entropic tendency of the chain segments to avoid the surface of the particles. In fact, all properties of interest of relatively short phantom chain systems with these properly modified interactions have been found to be practically coincident with those of the same systems simulated at full density. This paper reports on phantom chain simulations of nanocomposites that cannot be simulated at full density, i.e. systems with realistically long chains and large particles at various partial volumes of filler.

Models and Methods

The simulated systems consist of three-dimensionally periodic arrays of cubic cells containing N_f randomly distributed non-overlapping spherical filler particles of diameter σ_f. The phantom chains are modeled as unbranched sequences of $L_p = 2\,000$ isodiametric units connected by links of length σ. If the chain units are considered to be polymethylene isodiametric units (3.5 CH_2, $\sigma = 0.45$ nm[15]), the molecular mass of the simulated chains is on the order of 10^5 amu. The distribution of angles between consecutive links is regulated by a bending potential of the form $E(\theta) = (1/2)k_\theta\theta^2$ (θ being the angle

between two consecutive links; $\theta = 0$ for collinear links), and values of θ higher than $150°$ are forbidden (for details, see ref.[10]). The value of k_θ/RT is chosen to be 1.00 rad^{-2}, giving a chain stiffness comparable to that in polymer-based nanocomposites of practical interest. It has been shown[10] that the conformational properties of phantom chains of this kind are nearly coincident with those of the corresponding coarse-grained chains simulated in the polymer melt at full density. In particular, when the chain units are considered to be polymethylene isodiametric units (see before), both conformational distributions coincide with that theoretically predicted for unperturbed polymethylene.[16]

The interactions between chain units and filler are evaluated as $E_{uf} = \varepsilon[(\sigma/r_{uf})^{12} - 2(\sigma/r_{uf})^6]$, where r_{uf} is the distance of the unit from the *surface* of the closest particle. Values of r_{uf} less than 0.7σ are forbidden and the interactions are sharply truncated at $r_{uf} = 2\sigma$ (for a discussion, see ref.[10]) As in the case of systems simulated at proper densities, the phantom chains are equilibrated by standard MC methods using chain reptation. When the parameter ε/RT is given the same value 0.125 utilized for the simulations of dense systems, the scaled density of polymer units near the surface of the particles becomes rapidly very small, due to the entropic tendency of the chain segments to avoid the surface of the particles. The parameter ε/RT is then arbitrarily increased in such a way to restore the average density of polymer units found in all simulated dense systems near the surface of the particles (equal to $1.1\sigma^{-3}$ between 0.8σ and 2σ from the surface). Table 1 lists some relevant parameters of the phantom chain systems studied in this work. The volume fraction of filler is calculated taking into account that the effective diameter of a nanoparticle is $\sigma_f + \sigma$. A similar notation and the symbol D are used to indicate the dense systems with chains of 100 units described in previous papers.[5,8,9] The symbol P′ refers to phantom chain systems with $\varepsilon/RT = 0.125$, while the symbol P″ refers to phantom chain systems obtained

Table 1. Composition of the simulated systems of phantom chains of 2 000 units.

System	Cell edge	N_f[a]	σ_f[b]	φ[c]	ε/RT[d]
P$_{28,05}$	185.65σ	25	28σ	0.05	0.96
P$_{28,10}$	185.65σ	50	28σ	0.10	0.96
P$_{28,15}$	185.65σ	75	28σ	0.15	0.96
P$_{28,20}$	185.65σ	100	28σ	0.20	0.96
P$_{50,05}$	371.30σ	36	50σ	0.05	0.99
P$_{50,10}$	371.30σ	72	50σ	0.10	0.99
P$_{50,15}$	371.30σ	108	50σ	0.15	0.99
P$_{50,20}$	185.75σ	18	50σ	0.20	0.99

a) N_f = number of spherical filler particles.
b) σ_f = diameter of the particles.
c) φ = volume fraction of filler.
d) ε/RT = polymer-particle interaction parameter used in the simulations, see text.

from D systems by converting the coarse-grained chains to phantom chains.

Phantom chain calculations have been performed by adding to the cubic cell containing the randomly distributed non-overlapping nanoparticles 25 independent chains of 2 000 units. Note that, since the chains are phantom chains, this is equivalent to simulate 25 different single chain systems. A MC cycle is defined to consist of $2.5 \cdot 10^7$ reptation attempts. Since more than 99% attempts are successful with phantom chains, all chains are practically renewed in one cycle (i.e., it has been checked that the fraction of chain units having at the end of a cycle the same coordinates of any unit of the same chain at the start of the cycle is quite small), and always totally renewed in two cycles. Calculations have been performed on a battery of PC's equipped with Pentium 4 2.80 GHz CPU's, where each cycle takes approximately 30 min. Following an initial 20 cycle equilibration, all calculation have been continued for 180 more cycles, the resulting system configurations being stored for evaluating the properties studied here and for future uses. Three independent simulations with different placements of the particles have been performed for each system (five for system $P_{50,20}$). Numerical values reported in the following are averages of 540 (900 for system $P_{50,20}$) independent snapshots of the simulated systems, each containing 25 independent chains. Uncertainties, evaluated by dividing these snapshots in subgroups of 60, depend on the property considered. They are usually less than 5%, and never higher than 8%. The fact that the numerical values obtained for the various properties correspond to the equilibrium distribution has been checked by perturbing the simulated systems and then restoring the original conditions. In particular, all properties of a given system are substantially altered when the ε/RT parameter is arbitrarily changed to 0.125 for a few cycles; however, they are rapidly restored to the values before the change when this parameter is restored to the original value listed in Table 1.

Results and Discussion

Figure 1a compares the normalized density of polymer units (i.e. the density divided by the bulk density) in spherical shells of radius r and thickness 0.1σ centered on the filler particles for system $P_{28,20}$ with analogous curves obtained for two other systems, $D_{28,20}$ and $P''_{28,20}$. System $D_{28,20}$ (named M_{28} in ref.[9]) is a full density system with 512 chains of 100 units and one single filler particle of diameter 28σ in a periodic cell of edge 40σ. Particles of this size are the largest particles that have been simulated at full density. Since the base cell contains only one particle, system $D_{28,20}$ does not correspond to a random distribution of particles, but to a regular distribution at the nodes of a cubic array. System $P''_{28,20}$ is obtained from an equilibrium configuration of system $D_{28,20}$ by converting the chains into phantom chains and re-equilibrating.
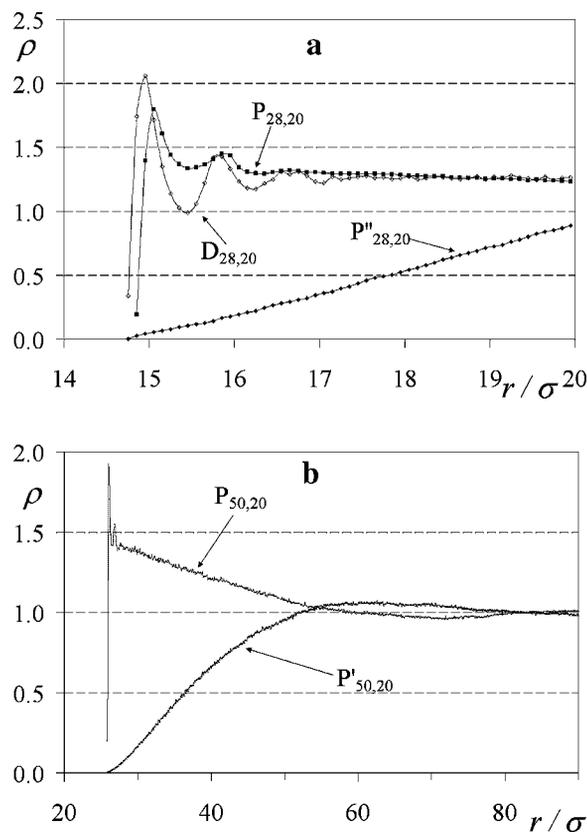

Figure 1. The normalized density of units in spherical shells of radius r and thickness 0.1σ centered on the filler particles in: a) three simulated systems with $\sigma_f = 28\sigma$; b) two simulated systems with $\sigma_f = 50\sigma$.

The $D_{28,20}$ density profile shown in Figure 1a is typical of filled systems simulated at full density. All these profiles are characterized by a series of maxima and minima close to the surface of the particles, due to the formation of well packed and partly ordered shells of chain units of width approximately 2σ, superimposed to broader and longer range features related to the distribution of filler particles.[5,8] When the same systems are re-equilibrated after converting the chains to phantom chains with $\varepsilon/RT = 0.125$, as in the original dense system, the density profiles are profoundly altered, in the sense that the density of units near the surface of the nanoparticles becomes very small (system $P''_{28,20}$). By inspecting various snapshots taken in the first part of the re-equilibration process, it is seen that the chains progressively abandon the interface shells of the particles and tend to concentrate in the largest cavities of the base cell. The curve for system $P_{28,20}$ in Figure 1a shows that this effect is fully compensated by changing the value of ε/RT to that listed in Table 1. Note that systems $D_{28,20}$ and $P_{28,20}$ are substantially different, because the chains in the latter are much longer and the nanoparticles are distributed at random. Not unexpectedly, however, the overall behavior of the density profiles is scarcely sensitive to these

differences. The minor discrepancies observed in the position and intensity of the maxima and minima close to the surface of the particles are obviously due to the fact that these features are dictated in system $D_{28,20}$ by the interactions among adjacent chain units, not included in phantom chain systems. Provided that the density of polymer units in the interface shells is the same, the detailed packing of these units within the interface shells is not expected to have a substantial influence on the overall organization of chains and particles in the model systems.

Figure 1b shows on a wider scale the density profiles obtained for systems $P_{50,20}$ and $P'_{50,20}$ (similar to $P_{50,20}$, but simulated with $\varepsilon/RT = 0.125$). No comparison can be made with dense systems in this case, since the direct simulation of dense systems with $\sigma_f = 50\sigma$ is out of reach, even using shorter chains. Figure 1b shows, however, that the density profile for system $P_{50,20}$ is practically as expected on the basis of the results obtained for systems $D_{28,20}$ and $P_{28,20}$. Therefore, one can assume that the distribution of chain units in system $P_{50,20}$, as well as in all other simulated systems, is similar to that in the corresponding dense systems.

Figure 2 plots $R_n^2/n\sigma^2$ vs. n, with R_n^2 the mean square distance of units belonging to the same chain and separated by n links for systems with $\sigma_f = 28\sigma$ and various volume fraction of filler. System $P'_{28,20}$ is reversibly obtained from system $P_{28,20}$ by switching ε/RT from 0.96 to 0.125 and vice versa. The curve for system $P_{28,05}$ is practically super-imposed to the corresponding curve for phantom chains without filler[10] and to theoretical predictions for freely rotating chains with the bending potential $E(\theta)$ ($R_n^2/n\sigma^2 = (1+\alpha)(1-\alpha)^{-1} - (2\alpha/n)(1-\alpha^n)(1-\alpha)^{-2}$ with $\alpha = \langle\cos\theta\rangle$; ref.[16]). Therefore, in both cases the model chains are actually bulk-like and practically unperturbed. Increasing the value of φ produces a moderate decrease of chain dimensions similar to that found in all dense systems studied up to now. Remarkably, the first part ($1 < n < 100$) of the curve for system $P_{28,20}$ coincides with that obtained for system $D_{28,20}$, while the results obtained for system $P'_{28,20}$ are quite different (and rather unusual). Figure 2 shows that the same value of ε/RT giving the proper
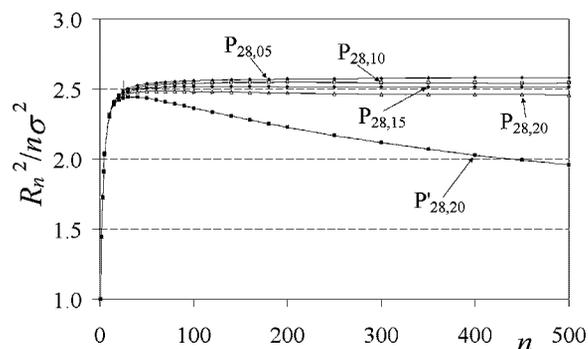
distribution of chain units in the simulated systems (Figure 1a) also gives a conformational distribution of the phantom chains in agreement with that found in dense systems. It is concluded that phantom chains simulations with well tailored values of ε/RT can be confidently used to study the mutual arrangements of chains and particles in polymer-based nanocomposites that cannot be simulated at full density.

MC calculations on single chains have been also performed in recent years by sequentially generating Rotational Isomeric State (RIS) chains in the presence of nanoparticles and discarding conformations in which chains and particles overlap ([17,18] and references therein). These calculations predict a decrease of chain dimension for large particles and short chains, and an increase in the opposite case. The same behavior was not observed in other RIS calculations, showing a small decrease of chain dimensions irrespective of the relative size of chains and particles.[7] Although the calculation methods are different in the two cases, the origin of the discrepancy is still unclear. On the other hand, single chain calculations of this kind are better suited to describe distribution of matter and chain conformation in very dilute polymer solutions containing suspended nanoparticles, rather than in filled polymers. In fact, when the tendency of the polymer units to avoid the surface of the nanoparticles is not properly compensated, both distribution of matter and chain conformation are strongly altered with respect to those in filled polymers simulated at full density (see Figure 1 and 2 and refs.[7,10]). Therefore, using the results of these single chain RIS calculations in the frame of theories of the elasticity of reinforced polymers[17,18] entails approximations of unknown severity.

Table 2 lists the average values of various parameters characterizing the simulated systems. f_I is the fraction of interface units (units with center in the interface shells of width 2σ surrounding the filler particles); f_f is the fraction of free chains (chains with no interface units); N_i, N_b and N_l are the average number per chain of interface segments (chain segments running in the interface shell of a given particle), bridge segments (sequences of non-interface 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), respectively; L_i, L_b and L_t are the average lengths of these segments in terms of chain units; P_c is the average number of different interface shells visited by each chain.

Additional parameters utilized in previous papers[5,8–10] to describe systems with smaller particles, such as the average number of direct connections per chain (consec-utive interface segments belonging to the interface shells of adjacent particles, without an intermediate bridge segment) or the fraction of units in the overlapping regions of interface shells of adjacent particles, are not listed in Table 2

Figure 2. $R_n^2/n\sigma^2$ vs. n, with R_n^2 the mean square distance of units belonging to the same chain and separated by n links.

Table 2. Average values of various parameters characterizing the simulated systems as defined in the text. Uncertainties are normally less than 5% and never higher than 8%.

	$P_{28,05}$	$P_{28,10}$	$P_{28,15}$	$P_{28,20}$	$P_{50,05}$	$P_{50,10}$	$P_{50,15}$	$P_{50,20}$
f_I[a)]	0.017	0.035	0.054	0.075	0.010	0.020	0.030	0.042
L_i[d)]	4.5	4.5	4.5	4.5	4.7	4.7	4.7	4.6
N_i[c)]	7.6	15	24	33	4.1	8.4	13	18
P_c[e)]	1.1	2.3	3.5	4.7	0.48	0.98	1.5	2.0
f_f[b)]	0.31	0.07	0.007	0.001	0.61	0.32	0.15	0.07
N_b[c)]	0.66	2.0	4.1	6.6	0.13	0.44	0.98	1.8
L_b[d)]	350	290	200	145	400	410	350	275
N_l[c)]	6.2	12	19	25	3.6	7.3	11	16
L_l[d)]	35	30	25	22	41	38	35	31

[a)] f_I = fraction of interface units.
[b)] f_f = fraction of free chains.
[c)] N_i, N_b and N_l = average number per chain of interface, bridge and loop segments, respectively.
[d)] L_i, L_b and L_l = average lengths of interface, bridge and loop segments in terms of chain units.
[e)] P_c = average number of different interface shells visited by each chain.

because they are practically negligible for the large particles considered here.

The fraction of interface units, f_I, is obviously regulated in phantom chain systems by the value of ε/RT. Since 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 $1.1\sigma^{-3}$, f_1 is given in general by $f_1 \approx 1.1V_sN_f/N_pL_p\sigma^3 - (f_2 + f_3 + \ldots) \approx 1.1(V_s/V_f)\varphi/(1 - \varphi) - (f_2 + f_3 + \ldots)$, where V_s is the volume of this shell, $N_f/N_p = \varphi L_p\sigma^3/(1 - \varphi)V_f$ is the number ratio of filler particles to polymer chains, V_f is the effective volume of a filler particle (i.e. the volume of a sphere of diameter $\sigma_f + \sigma$) and f_k is the fraction of units that are simultaneously in the interface shells of k or more different particles. As expected, f_2 is significantly different from zero only for systems crowded with relatively small nanoparticles (for the most crowded systems simulated up to now, f_2 is approximately given by $f_2 \approx 40\xi^2$, with ξ the dimensionless parameter $\xi = \varphi\sigma/\sigma_f$), while f_3 and higher terms are always practically negligible. For the systems simulated here, with ξ less than 0.01, f_1 is then well approximated by $f_1 \approx 1.1(V_s/V_f)\varphi/(1 - \varphi)$. Since ε/RT has been suitably chosen, the good agreement of the values in the first row of Table 2 with those predicted by the latter equation is not a surprise. Note, however, that these simple equations allow to predict f_1 for any given values of σ_f and φ.

When a polymer chain enters the interface shell of a nanoparticle, the length of the interface segment is expected to depend mainly on the chain stiffness and on the curvature of the interface shell. For chains of the simulated stiffness (comparable to that in most practical systems), the average value of this length (L_i in Table 2) is between 3.5 units for very small particles and nearly 5 units near planar surfaces. Figure 3 plots L_i as a function of σ/σ_f for systems with σ_f varying in a wide range (from 4σ to 50σ) at various φ. The full points refer to chains of 100 units in dense systems, while the open squares refer to phantom chains of 500 or

2000 units. The dependence of L_i on σ/σ_f is seen to be approximately linear, with $L_i \approx 4.8 - 6.5\sigma/\sigma_f$ (the minor dependence of L_i on φ observed for small particles can be taken into account with a slightly modified equation).

Note that the good alignment of the data points in Figure 3 for dense systems and phantom chains is far from being obvious, since the packing of the polymer units in the interface shells is profoundly different in the two cases. It confirms that L_i is mainly regulated by chain stiffness and curvature of the interface shells. Once the length of the interface segments is known for a given system, the average number of interface segments per chain is obviously given by $N_i \approx f_1L_p/L_i$. The good agreement of predicted and found values of f_1 and N_i is evidenced in Table 3 for several dense and phantom chain systems with widely different compositions. One has to emphasize, on the other hand, that numerical values obtained from coarse-grained models on short distance scales (such as those of L_i) are clearly unphysical, and can be only taken as indicative of general trends. In particular, the length of the interface segments for
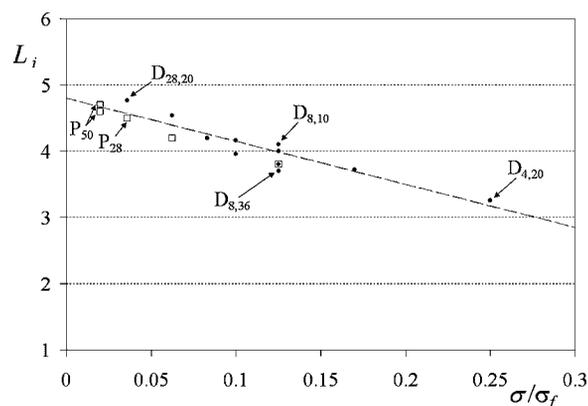

Figure 3. The average length of the interface segments as a function of σ/σ_f for various simulated systems (full points: dense systems; open squares: phantom chain systems).

Table 3. Comparison of values found for dense and phantom chain systems with those predicted according to the equations in the text (in parentheses). Data for D systems refer to chains of 100 units, while data for P systems refer to chains of 2 000 units.

	f_I[a]	N_i[b]	P_c[c]	f_f[d]
$D_{6,20}$	0.41 (0.41)	11 (11)	5.2 (5.4)	0.00 (0.00)
$D_{8,10}$	0.14 (0.14)	3.3 (3.5)	1.5 (1.7)	0.22 (0.14)
$D_{8,20}$	0.29 (0.29)	7.3 (7.3)	3.3 (3.4)	0.01 (0.01)
$D_{10,36}$	0.51 (0.50)	13 (12)	4.9 (4.3)	0.00 (0.00)
$P_{28,05}$	0.017 (0.016)	7.6 (7.0)	1.1 (1.1)	0.31 (0.30)
$P_{28,20}$	0.075 (0.075)	33 (33)	4.7 (4.4)	0.00 (0.00)
$P_{50,05}$	0.010 (0.009)	4.1 (3.9)	0.48 (0.42)	0.61 (0.64)
$P_{50,20}$	0.042 (0.041)	18 (18)	2.0 (1.7)	0.07 (0.09)

[a] f_I = fraction of interface units.
[b] N_i = average number of interface segments per chain.
[c] P_c = average number of different interface shells visited by each chain.
[d] f_f = fraction of free chains.

a given real polymer depends on conformational characteristics that are not included in these idealized models.

The average number P_c of interface shells of different filler particles visited by each polymer chain is a fundamental parameter for describing the molecular arrangements in the nanocomposites under study. If a polymer molecule is simply considered to be on average a spherical distribution of matter with radius proportional to the chain root mean square (rms) radius of gyration, P_c can be calculated as 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. Though this view is patently naive, P_c has been found to be fairly well approximated for all dense systems simulated up to now 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 $R_g \approx 0.65 L_p^{1/2}$ for chains of the given stiffness. The last column in Table 3 shows that this is also true for very long chains and large particles. A correspondingly good agreement is found for the number C_p of different chains visiting the interface shell of a given nanoparticle; on the other hand, C_p is related to P_c by $C_p = P_c N_p/N_f = P_c(1-\varphi)V_f/(\varphi L_p \sigma^3)$.

The data reported in Table 2 are averages over all chains present in the system, including free chains. For instance, the value $P_c = 0.48$ for system $P_{50,05}$ is the average of zero for 61% of the chains ($f_f = 0.61$ in this case) and of 1.2 for the remaining chains. Keeping with the previous approximation, the fraction f_f of free chains corresponds to the probability that there are no filler particles centered inside a sphere of volume V^* around the center of mass of a chain, i.e. the probability of finding in the system of nanoparticles an empty sphere of volume V^*. It can be approximately evaluated from first principles considering a large system of total volume V containing N randomly distributed particles of volume V_f such that $NV_f/V = \varphi$. The probability p_1 that one of the N particles has its center outside a sphere of volume V^* surrounding a given point in the system is given by $p_1 = (V - NV_f/\beta - V^*)/(V - NV_f/\beta) = 1 - [(\beta\varphi/(\beta - \varphi))(V^*/V_f)(1/N)]$, where β is a constant between 0.64 and 0.74 (i.e. V_f/β is the volume excluded by each filler particle to the other filler particles). The overall probability that all filler particles have their center outside V^* is then the N-th power of p_1, equal to $\exp[-\beta\varphi(V^*/V_f)/(\beta - \varphi)]$. In conclusion, the fraction f_f of free chains is expected to be approximately given by $f_f = \exp[-\beta\phi(V^*/V_f)/(\beta - \varphi)]$. The agreement with the data obtained from phantom chain systems is very good (see for instance Table 3, last column). The agreement is also generally quite good for D systems, with sporadic exceptions such as in the case of system $D_{8,10}$. This is not surprising because D systems have been often simulated with a relatively small number of filler particles in the unit cell, such that the simulated value of f_f may depend on the particular distribution of these particles. Note that the predicted values in Table 3 have been evaluated with $\beta = 0.64$; however, any value of β in the range [0.64, 0.74] gives practically the same results; also, the results obtained without the β factor (i.e. with $\beta = 1$) are not substantially different.

The dependence on L_p, σ_f and φ of the other parameters listed in Table 2, i.e. the number and length of loop and bridge segments, is the result of a complex interplay of several factors. Consider for instance the number N_b of bridge segments per chain. Obviously, one expects that N_b increases with increasing chain length for given values of σ_f and φ. The increase is expected to be nearly linear for systems crowded with small particles, in which free chains and long dangling terminal segments are practically absent. In all other cases, free chains and terminal segments are progressively converted in bridges and loops with increasing chain length, the conversion rate depending on the exact values of σ_f and φ. On the other hand, longer chains may also form longer bridges, which is relevant for systems with large particles at usual filling densities. When it is considered that systems with particles of diameter 50σ or larger at practical filling densities contain a large fraction of free chains even with chains as long as 2 000 units, and that most of the remaining chains have very long terminal segments (many of them are in contact with only one particle), it is clear that the behavior of N_b and L_b in realistically sized systems cannot be predicted on simple grounds. In practice, it is not difficult to write semiempirical equations relating these properties to σ_f and φ for a given chain length. However, the form of these equations changes with changing the chain length, in such a way that the simultaneous dependence on L_p, σ_f and φ is quite complicated and cannot be put in a simple form.

It is important to point out, however, that in all simulated systems, including those with large particles and low filling density, chains and particles do form a highly interconnected transient network extended in three dimensions. Consider for instance system $P_{50,05}$, i.e. the less crowded

between those that have been simulated. More than 60% of the chains are free chains and a large proportion of the remaining chains have no bridges (the average number of bridges per chain is as low as 0.13). This is a consequence of the low filling density and of the large size of the particles. However, large particles are in contact with many chains (nearly 300 different chains in this case), such that the number of bridge segments involving a given particle is anyway considerable. As a matter of fact, the average number of bridge segments departing from each filler particle is given by $2N_bN_p/N_f = 2N_b(1 - \varphi)V_f/(\varphi L_p \sigma^3)$, and is approximately equal to 170, 270, 390 and 500 for systems $P_{50,05}$, $P_{50,10}$, $P_{50,15}$ and $P_{50,20}$, respectively. The corresponding numbers for systems $P_{28,05}$, $P_{28,10}$, $P_{28,15}$ and $P_{28,20}$, are 160, 230, 300 and 340, respectively. Note that these large numbers are not in contrast with the low values of N_b listed in several cases in Table 2. For instance, $N_b = 0.13$ for system $P_{50,05}$, is the average of zero for the free chains (61% in this system) and of 0.33 for those chains that are in contact with one or more particles. Considering that each particle is in contact with 300 different chains, the number of bridges departing from a particle is expected to be on the order of 100 at least (it is actually higher, because long chains can form more than one bridge between the same two neighboring particles, specially when these are large). A detailed characterization of the particle-chains networks and the calculation of their elastic properties are beyond the scope of this study. It will be apparent, on the other hand, that important properties characterizing a network (the cycle rank, for instance, and all other properties related to the mutual arrangement of several chains) can be roughly inferred, but not directly determined from phantom chain simulations.

Conclusion

Full density simulations of polymer-based nanocomposites with realistically long chains and large particles are presently out of reach. Also, a number of parameters essential for characterizing these systems cannot be extrapolated from those of the systems with short chain and small particles that can be presently simulated. This paper shows that the problem can be solved by simulating phantom chains with properly modified interaction energy between filler particles and polymer units.

When the polymer chains of a dense system are converted to phantom chains, the density of polymer units near the surface of the particles decreases rapidly and the chains migrate preferentially to regions less crowded with particles. This is fairly obvious, because the number of different orientations and conformations available to a long chain molecule in contact with an impenetrable surface is quite small with respect to the same chain far from the surface. In all cases examined up to now, this is also associated with a strong perturbation of the conformational distribution of the phantom chains with respect to systems simulated at full density. Phantom chain calculations are then of little use for studying polymer-based nanocomposites (or, in general, polymer systems containing obstacles of any kind), unless something is done to restore the distribution of polymer units characteristic of dense systems. It is shown here that one of the possible ways to solve the problem consists in an arbitrary increase of the short range attractive interactions between polymer units and particles. When this is done, the same value of the interaction parameter that restores the proper distribution of polymer units also restores the conformational distribution found in dense systems. Also, all parameters characterizing the mutual arrangements of chains and particles in phantom chain systems with properly modified interactions come out to be practically coincident with those in dense systems having the same composition. It is concluded that these modified phantom chains can be used to study systems that cannot be presently simulated at full density, such as those with long chains and large particles. The same method could be applied to other systems containing polymers in the presence of solid objects of various nature.

The results obtained for nanocomposites with realistically long chains and a random distribution of large nanoparticles show that some of the fundamental parameters characterizing these systems (fraction of interface units, length of interface segments, number of different particles in contact with a given chain and number of different chains in contact with a given particle, fraction of free chains) can be predicted on the basis of simple considerations. Other parameters, such as the average length of the bridge and loop segments and their number per chain, depend on the exact composition of the system in a much less predictable way. In particular, simple semiempirical equations relating these properties to particle size and filling density can be easily written for a given chain length, but their form is different for different chain lengths. More simulations of phantom chain systems with various compositions are then required in order to describe the complex behavior of the latter properties. The simulations reported here, however, are sufficient to show that even when the filling density is quite small (5 vol.-%) and the particles are large, the particles are nodes of highly interconnected transient networks bridged by the polymer chains.

[1] E. J. Meijer, D. Frenkel, *J. Chem. Phys.* **1994**, *100*, 6873.
[2] G. J. A. Sevink, A. V. Zvelindovsky, B. A. C. van Vlimmeren, N. M. Maurits, J. G. E. M. Fraaije, *J. Chem. Phys.* **1999**, *110*, 2250.
[3] J. Huh, V. V. Ginzburg, A. C. Balazs, *Macromolecules* **2000**, *33*, 8085.

[4] A. C. Balazs, V. V. Ginzburg, F. Qiu, G. Peng, D. Jasnow, *J. Chem. Phys.* **2000**, *104*, 3411.

[5] M. Vacatello, *Macromolecules* **2001**, *34*, 1946.

[6] F. W. Starr, T. B. Schroeder, S. C. Glotzer, *Macromolecules* **2002**, *35*, 4481.

[7] M. Vacatello, *Macromolecules* **2002**, *35*, 8191.

[8] M. Vacatello, *Macromol. Theory Simul.* **2002**, *11*, 757.

[9] M. Vacatello, *Macromol. Theory Simul.* **2003**, *12*, 86.

[10] M. Vacatello, *Macromolecules* **2003**, *36*, 3411.

[11] D. Brown, P. Mélé, S. Marceau, N. D. Albérola, *Macromolecules* **2003**, *36*, 1395.

[12] M. S. Ozmusul, C. R. Picu, S. S. Sternstein, S. K. Kumar, *Macromolecules* **2005**, *38*, 4495.

[13] P. J. Dionne, R. Ozisik, C. L. Picu, *Macromolecules* **2005**, *38*, 9351.

[14] H. Lin, F. Erguney, W. L. Mattice, *Polymer* **2005**, *46*, 6154.

[15] P. J. Flory, D. Y. Yoon, K. A. Dill, *Macromolecules* **1984**, *17*, 862.

[16] P. J. Flory, ''*Statistical Mechanics of Chain Molecules*'', Hanser, München 1989.

[17] J. E. Mark, R. Abou-Hussein, T. Z. Sen, A. Kloczkowski, *Polymer* **2005**, *46*, 8894.

[18] M. A. Sharaf, A. Kloczkowski, T. Z. Sen, K. I. Jacob, J. E. Mark, *Eur. Polym. J.* **2006**, *42*, 796.