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\cite{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 $\sigma_f$. The phantom chains are modeled as unbranched segments of $L_p = 2000$ isodiametric units connected by links of length $\sigma$. If the chain units are considered to be polymethylene isodiametric units (3.5 CH$_2$, $\sigma = 0.45$ nm\cite{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 $E(\theta) = (1/2) k_B \theta^2$ ($\theta$ being the angle between two consecutive links; $\theta = 0$ for collinear links), and values of $\theta$ higher than 150° are forbidden (for details, see ref\cite{10}). The value of $k_B$ 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\cite{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\cite{16}.

The interactions between chain units and filler are evaluated as $E_{uf} = \varepsilon (\sigma r_{uf})^2 - 2(\sigma r_{uf})^6$, where $r_{uf}$ is the distance of the unit from the surface of the closest particle. Values of $r_{uf}$ less than $0.7\sigma$ are forbidden and the interactions are sharply truncated at $r_{uf} = 2\sigma$ (for a discussion, see ref\cite{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 $\varepsilon/RT$ 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 $\varepsilon/RT$ 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 0.8$\sigma$ and 2$\sigma$ 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 $\Omega$ are used to indicate the dense systems with chains of 100 units described in previous papers\cite{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>
<thead>
<tr>
<th>System</th>
<th>Cell edge</th>
<th>$N_f$\textsuperscript{a}</th>
<th>$\sigma_f$\textsuperscript{b}</th>
<th>$\phi$\textsuperscript{c}</th>
<th>$\varepsilon/RT$\textsuperscript{d}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{25.05}$</td>
<td>185.65$\sigma$</td>
<td>25</td>
<td>28$\sigma$</td>
<td>0.05</td>
<td>0.96</td>
</tr>
<tr>
<td>$P_{25.10}$</td>
<td>185.65$\sigma$</td>
<td>50</td>
<td>28$\sigma$</td>
<td>0.10</td>
<td>0.96</td>
</tr>
<tr>
<td>$P_{25.15}$</td>
<td>185.65$\sigma$</td>
<td>75</td>
<td>28$\sigma$</td>
<td>0.15</td>
<td>0.96</td>
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<td>$P_{25.20}$</td>
<td>185.65$\sigma$</td>
<td>100</td>
<td>28$\sigma$</td>
<td>0.20</td>
<td>0.96</td>
</tr>
<tr>
<td>$P_{30.05}$</td>
<td>371.30$\sigma$</td>
<td>36</td>
<td>50$\sigma$</td>
<td>0.05</td>
<td>0.99</td>
</tr>
<tr>
<td>$P_{30.10}$</td>
<td>371.30$\sigma$</td>
<td>72</td>
<td>50$\sigma$</td>
<td>0.10</td>
<td>0.99</td>
</tr>
<tr>
<td>$P_{30.15}$</td>
<td>371.30$\sigma$</td>
<td>108</td>
<td>50$\sigma$</td>
<td>0.15</td>
<td>0.99</td>
</tr>
<tr>
<td>$P_{30.20}$</td>
<td>185.75$\sigma$</td>
<td>18</td>
<td>50$\sigma$</td>
<td>0.20</td>
<td>0.99</td>
</tr>
</tbody>
</table>

\textsuperscript{a} $N_f$ = number of spherical filler particles.
\textsuperscript{b} $\sigma_f$ = diameter of the particles.
\textsuperscript{c} $\phi$ = volume fraction of filler.
\textsuperscript{d} $\varepsilon/RT$ = 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 \(2.5 \times 10^7\) 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 \(\varepsilon/RT\) 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 0.1\(\sigma\) centered on the filler particles for system P\(_{28,20}\) with analogous curves obtained for two other systems, D\(_{28,20}\) and P\(_{28,20}^\prime\). 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 28\(\sigma\) in a periodic cell of edge 40\(\sigma\). 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\(_{28,20}^\prime\) is obtained from an equilibrium configuration of system D\(_{28,20}\) by converting the chains into phantom chains and re-equilibrating.

![Figure 1](Image 303x417 to 519x562)

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 2\(\sigma\), superimposed to broader and longer range features related to the distribution of filler particles.\(^{\text{[15]8}}\) 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\(_{28,20}^\prime\)). 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\(_{28,20}^\prime\) in Figure 1a shows that this effect is fully compensated by changing the value of \(\varepsilon/RT\) 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
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 D28,20 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 P50,20 and P′50,20 (similar to P50,20, but simulated with εRT = 0.125). No comparison can be made with dense systems in this case, since the direct simulation of dense systems with σi = 50σ is out of reach, even using shorter chains. Figure 1b shows, however, that the density profile for system P50,20 is practically as expected on the shorter chains. Figure 1b shows, however, that the density belonging to the same chain and separated by a fraction of filler. System P 

Increasing the value of e/RT produces a moderate 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 polymers17,18 entails approximations of unknown severity.

Table 2 lists the average values of various parameters characterizing the simulated systems. jf is the fraction of interface units (units with center in the interface shells of width 2σ surrounding the filler particles); jf is the fraction of free chains (chains with no interface units); Nf, Nn, and Nf 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; Li, Lb, and Ll are the average lengths of these segments in terms of chain units; Pi is the average number of different interface shells visited by each chain.

Additional parameters utilized in previous papers5,8–10 to describe systems with smaller particles, such as the average number of direct connections per chain (consecutive 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 plots R2/nσ2 vs. n, with R2 the mean square distance of units belonging to the same chain and separated by n links for systems with σf = 28σ and various volume fraction of filler. System P′28,20 is reversibly obtained from system P28,20 by switching εRT from 0.96 to 0.125 and vice versa. The curve for system P28,20 is practically superimposed to the corresponding curve for phantom chains without fillers10 and to theoretical predictions for freely rotating chains with the bending potential E(θ) (R2/nσ2 = (1 + z)(1 − z)−1 − (2z/n)(1 − x)−2 with z = √θ/cosθ; ref.16). Therefore, in both cases the model chains are actually bulk-like and practically unperturbed. Increasing the value of e/RT 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 P28,20 coincides with that obtained for system D28,20, while the results obtained for system P′28,20 are quite different (and rather unusual). Figure 2 shows that the average value of εRT 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 e/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
however, that these simple equations allow to predict the agreement of the values in the first row of Table 2 with those obtained for crowded systems simulated up to now, crowded with relatively small nanoparticles (for the most a fraction of interface units.

The fraction of interface units, $f_1$, is obviously regulated in phantom chain systems by the value of $\sigma/RT$. Since the density of units in a spherical shell between $0.8\sigma$ and $2\sigma$ from the surface of a filler particle is found to be approximately $1.1\sigma^{-3}$, $f_1$ is given in general by $f_1 \approx 1.1(V_s/N_f/V_p)\sigma^{-3}/(1 - \varphi)(f_2 + f_3 + \ldots)$, where $V_s$ is the volume of this shell, $N_f/N_p = \varphi L_s \sigma^{-3}(1 - \varphi)V_p$ is the number ratio of filler particles to polymer chains, $V_p$ is the effective volume of a filler particle (i.e., the volume of a sphere of diameter $\sigma_f + \sigma$) and $f_2$ 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 $f_2 \approx 40\zeta^2$, with $\zeta$ the dimensionless parameter $\zeta = \varphi\sigma/\sigma_f$), while $f_3$ and higher terms are always practically negligible. For the systems simulated here, with $\zeta$ less than 0.01, $f_1$ is then well approximated by $f_1 \approx 1.1(V_s/V_p)\sigma^{-3}/(1 - \varphi)$. Since $\sigma/RT$ 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 $\sigma_f$ and $\varphi$.

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 $\sigma/\sigma_f$ for systems with $\sigma_f$ varying in a wide range (from $4\sigma$ to $50\sigma$) at various $\varphi$. 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 $\sigma/\sigma_f$ is seen to be approximately linear, with $L_i \approx 4.8 - 6.5 \sigma/\sigma_f$ (the minor dependence of $L_i$ on $\varphi$ observed for small particles can be taken into account with a slightly modified equation).

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%.

<table>
<thead>
<tr>
<th>$P_{28,05}$</th>
<th>$P_{28,10}$</th>
<th>$P_{28,15}$</th>
<th>$P_{28,20}$</th>
<th>$P_{50,05}$</th>
<th>$P_{50,10}$</th>
<th>$P_{50,15}$</th>
<th>$P_{50,20}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_1^{a)}$</td>
<td>$0.017$</td>
<td>$0.035$</td>
<td>$0.054$</td>
<td>$0.075$</td>
<td>$0.010$</td>
<td>$0.020$</td>
<td>$0.030$</td>
</tr>
<tr>
<td>$L_i^{a)}$</td>
<td>$4.5$</td>
<td>$4.5$</td>
<td>$4.5$</td>
<td>$4.5$</td>
<td>$4.7$</td>
<td>$4.7$</td>
<td>$4.7$</td>
</tr>
<tr>
<td>$N_f^{a)}$</td>
<td>$7.6$</td>
<td>$15$</td>
<td>$24$</td>
<td>$33$</td>
<td>$4.1$</td>
<td>$8.4$</td>
<td>$13$</td>
</tr>
<tr>
<td>$P^{b)}$</td>
<td>$1.1$</td>
<td>$2.3$</td>
<td>$3.5$</td>
<td>$4.7$</td>
<td>$0.48$</td>
<td>$0.98$</td>
<td>$1.5$</td>
</tr>
<tr>
<td>$P^{c)}$</td>
<td>$0.31$</td>
<td>$0.07$</td>
<td>$0.007$</td>
<td>$0.001$</td>
<td>$0.061$</td>
<td>$0.32$</td>
<td>$0.15$</td>
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<tr>
<td>$N_f^{d)}$</td>
<td>$0.66$</td>
<td>$2.0$</td>
<td>$4.1$</td>
<td>$6.6$</td>
<td>$0.13$</td>
<td>$0.44$</td>
<td>$0.98$</td>
</tr>
<tr>
<td>$P_{28,10}$</td>
<td>$350$</td>
<td>$290$</td>
<td>$200$</td>
<td>$145$</td>
<td>$400$</td>
<td>$410$</td>
<td>$350$</td>
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<tr>
<td>$N_f^{d)}$</td>
<td>$6.2$</td>
<td>$12$</td>
<td>$19$</td>
<td>$25$</td>
<td>$3.6$</td>
<td>$7.3$</td>
<td>$11$</td>
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<tr>
<td>$L_i^{d)}$</td>
<td>$35$</td>
<td>$30$</td>
<td>$25$</td>
<td>$22$</td>
<td>$41$</td>
<td>$38$</td>
<td>$35$</td>
</tr>
</tbody>
</table>

$a)$ $f_1$ = fraction of interface units.
$b)$ $f_2$ = fraction of free chains.
$c)$ $N_f, N_b$ and $N_l$ = average number per chain of interface, bridge and loop segments, respectively.
$d)$ $L_i, L_{28}$ and $L_i$ = average lengths of interface, bridge and loop segments in terms of chain units.
$e)$ $P_i$ = average number of different interface shells visited by each chain.

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. Since the length of the interface segments is known for a given system, the average number of interface segments per chain is obviously given by $N_i \approx f_1 L_i/N_f$. The good agreement of predicted and found values of $f_1$ and $N_i$ is evident 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...
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 2000 units.

<table>
<thead>
<tr>
<th></th>
<th>( f_i^{a,b} )</th>
<th>( N_i^{b,c} )</th>
<th>( P_c^{e,f} )</th>
<th>( f_f^{a,d} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{8,20} )</td>
<td>0.41 (0.41)</td>
<td>11 (11)</td>
<td>5.2 (5.4)</td>
<td>0.00 (0.00)</td>
</tr>
<tr>
<td>( D_{8,10} )</td>
<td>0.14 (0.14)</td>
<td>3.3 (3.5)</td>
<td>1.5 (1.7)</td>
<td>0.22 (0.14)</td>
</tr>
<tr>
<td>( D_{6,20} )</td>
<td>0.29 (0.29)</td>
<td>7.3 (7.3)</td>
<td>3.3 (3.4)</td>
<td>0.01 (0.01)</td>
</tr>
<tr>
<td>( D_{10,20} )</td>
<td>0.51 (0.50)</td>
<td>13 (12)</td>
<td>4.9 (4.3)</td>
<td>0.00 (0.00)</td>
</tr>
<tr>
<td>( P_{50,20} )</td>
<td>0.017 (0.016)</td>
<td>7.6 (7.0)</td>
<td>1.1 (1.1)</td>
<td>0.31 (0.30)</td>
</tr>
<tr>
<td>( P_{50,20} )</td>
<td>0.075 (0.075)</td>
<td>33 (33)</td>
<td>4.7 (4.4)</td>
<td>0.00 (0.00)</td>
</tr>
<tr>
<td>( P_{50,05} )</td>
<td>0.010 (0.009)</td>
<td>14 (18)</td>
<td>0.48 (0.42)</td>
<td>0.61 (0.64)</td>
</tr>
<tr>
<td>( P_{50,20} )</td>
<td>0.042 (0.041)</td>
<td>18 (18)</td>
<td>2.0 (1.7)</td>
<td>0.07 (0.09)</td>
</tr>
</tbody>
</table>

\( f_i^{a} \) = fraction of interface units.
\( N_i^{b} \) = average number of interface segments per chain.
\( P_c^{c} \) = average number of different interface shells visited by each chain.
\( f_f^{a} \) = 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 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 \( x_R + \sigma f + 4\sigma \), where \( x_R \) is the rms radius of gyration of the chains and \( x \) 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 \( P_c \propto \varphi V/V_f \), where \( V \) is the volume of a sphere of diameter \( 1.7R_x + \sigma f \) (i.e. \( x = 1.7 \)) and \( R_x \approx 0.65L_p^{1/2} \) for chains of the given stiffness. The last column in Table 3 shows that this is also true for very long chains and 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 \( C_p = P_c / N_f = P_c (1 - \varphi V_f / \varphi L_p) \).

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 \( (f_f = 0.61 \text{ in this case}) \) 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 \( V_p \) such that \( NV/V = \varphi \). 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 \( p_1 = (V - NV/V) / V = 1 - (\beta / \varphi (\beta - \varphi)) (V'/V)(1/N) \), where \( \beta \) is a constant between 0.64 and 0.74 (i.e. \( V/\beta \) 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 \( \exp[-(\beta / \varphi (\beta - \varphi)) (V'/V)] \). In conclusion, the fraction \( f_f \) of free chains is expected to be approximately given by \( f_f = \exp[-(\beta / \varphi (\beta - \varphi)) (V'/V)] \). 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 \( \beta \) in the range [0.64, 0.74] gives practically the same results; also, the results obtained without the \( \beta \) factor (i.e. with \( \beta = 1 \)) are not substantially different.

The dependence on \( L_p, \sigma_f \) and \( \varphi \) 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 \( \sigma_f \) and \( \varphi \). 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 \( \sigma_f \) and \( \varphi \). 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 50 or larger at practical filling densities contain a large fraction of free chains even with chains as long as 2000 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 \( \sigma_f \) and \( \varphi \) 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 \( L_p, \sigma_f \) and \( \varphi \) 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.
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
\[
\frac{2N_bN_f}{N_f} = 2N_b(1 - \varphi)V_f/(\varphi L_p \sigma^3),
\]
and is approximately equal to 170, 270, 390 and 500 for systems
P50,05, P50,10, P50,15 and P50,20, respectively. The corre-

sponding numbers for systems P28,05, P28,10, P28,15 and
P28,20, 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 P50,05, 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.

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