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Effects of a nanoscopic filler on the structure and dynamics of a simulated polymer melt and the relationship to ultrathin films

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We perform molecular dynamics simulations of an idealized polymer melt surrounding a nanoscopic filler particle. We show that the glass transition temperature T_g of the melt can be shifted to either higher or lower temperatures by tuning the interactions between polymer and filler. A gradual change of the polymer dynamics approaching the filler surface causes the change in the glass transition. We also find that polymers close to the surface tend to be elongated and flattened. Our findings show a strong similarity to those obtained for ultrathin polymer films.

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Significant enhancements in mechanical, rheological, dielectric, optical, and other properties of polymer materials can be obtained by adding fillers such as carbon black, talc, silica, and other inexpensive materials [1]. Applications of filled polymers are diverse, ranging from automobile tires and bumpers to the rapidly expanding area of microelectronic and nanoelectronic devices [1,2]. The growing ability to design customized nanofillers of arbitrary shape and functionality provides an enormous variety of property modifications by introducing specific heterogeneity at the nanoscale [2–4]. However, a detailed knowledge of the effects of fillers on a polymer melt at the molecular level is lacking due to the difficulty of directly probing the polymer structure and dynamics in the vicinity of the polymer-filler interface. In this regard, molecular simulations provide an ideal opportunity for direct insight into filled materials. Additionally, understanding ultrathin polymer films, which also have many important technological applications (e.g. paints, lubricants, adhesives, and electronic packaging), is a topic of continuing discussion [5–18]; the present results provide a framework in which to interpret experiments on filled polymers, and also possibly polymer thin films, which report both increases and decreases of the glass transition temperature T_g [19] depending on the details of the system studied [1,20–22].

Our findings are based on extensive molecular dynamics simulations of a single nanoscopic filler particle surrounded by a dense polymer melt [Fig. 1(a)]. We simulate 400 chains of 20 monomers each (below the entanglement length). The polymers are modeled as chains of monomers, which interact via a Lennard Jones (LJ) potential. Additionally, bonded monomers are connected via a finitely extensible nonlinear elastic (FENE) anharmonic spring potential $V_{\mathrm{FENE}} = -k(R_0^2/2)\ln(1-(r/R_0)^2)$ [23,24]. For the state points studied, the bond length between monomers is narrowly distributed around an average value of 0.96, and the average radius of gyration $\langle R_g \rangle = 4.72$, with a very weak T dependence (all lengths in units of σ_{mm}. The pure system has been shown to be a good glass former [25,26]. This type of ''coarse-grained'' model is frequently used to study general trends of

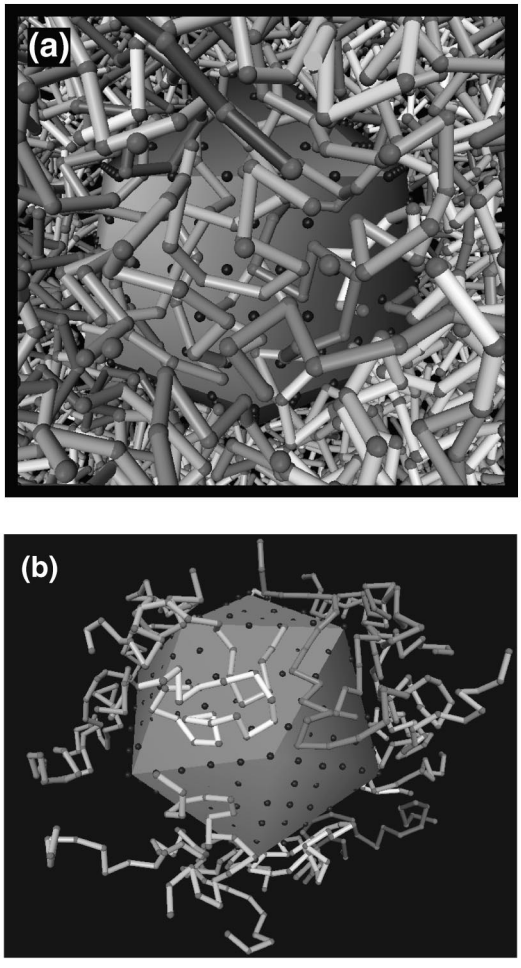

FIG. 1. (a) ''Snapshot'' of our simulation of the filled polymer melt. The bonds between nearest-neighbor monomers along a chain are drawn in various shades of gray for clarity. (b) A few representative polymers that have monomers near the filler surface.

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polymer systems, but does not provide information for a specific polymer.

The filler particle shape is icosahedral. We assign ideal force sites at the vertices, at four equidistant sites along each edge, and at six symmetric sites on the interior of each face of the icosahedron, as shown in the lower panel of Fig. 1(b). We tether a particle to each of these sites by a FENE spring, which maintains a relatively rigid structure but allows for thermalization of the filler [27]; the nonrigid structure also allows for a small degree of surface roughness [28]. We consider a filler particle with an excluded volume interaction only, as well as one with excluded volume plus attractive interactions, to determine which properties are results of the steric constraints imposed by the filler, and which properties are affected by polymer-filler attraction. We choose the same parameters for the interaction potential for all filler force sites. Periodic boundary conditions are used in all directions [31].

Our model filler has several general features typical of a primary carbon black particle (a traditional filler) [1,32], as well as some newer nanofillers [3,4]: (i) it has a size of order 10 nm; and (ii) it is highly faceted, but nearly spherical. The size of the facets is roughly equal to the end-to-end distance R_e of the low molecular weight polymers comprising the surrounding melt. We also consider a pure dense melt for comparison. We simulate the pure system at density $\rho=1.0$ at temperatures ranging from $T=0.37$ to 1.0. We report all values in reduced LJ units. Standard units for T are recovered by multiplying T by $\epsilon_{\rm mm}/k_B$, where k_B is Boltzmann's constant. Time is given by $t^*=(m_{\rm m}\sigma_{\rm mm}^2/\epsilon_{\rm mm})^{1/2}$, and $\epsilon_{\rm mm}$ is the monomer-monomer interaction energy.

We simulate the filled systems in the range $T=0.35$–1.2. Equilibration times range from $5\times10^2 t^*$ at the highest T to $2\times10^4 t^*$ (approximately 40 ns in argon units) at the lowest T; we use the rRESPA multiple time step algorithm to improve simulation speed [33,34]. In order to compare the simulations of the filled system with the pure melt, we choose the box size so that the local density far from the filler deviates at most by 0.2% from the density of the pure melt; such a density difference would cause a change in T_g in this model less than that shown in Fig. 2 [25]. For attractive monomer-filler interactions, a box size $L=20.4$ satisfies this constraint at all T. In the nonattractive case, the characteristic first neighbor distance between the filler sites and monomers is T dependent due to the lack of a unique minimum in the polymer-filler interactions. As a result, at each T a different L is required to achieve the correct ρ at large distance from the filler. The box sizes range from $L=20.49$ at $T=1.0$, to $L=20.6$ at $T=0.4$.

To quantify the effect of the filler on T_g and on dynamic properties, we first calculate the relaxation time τ of the intermediate scattering function

$$F(q,t)\equiv\frac{1}{NS(q)}\left\langle\sum_{j,k=1}^{N} e^{-i\mathbf{q}\cdot[\mathbf{r}_k(t)-\mathbf{r}_j(0)]}\right\rangle. \qquad (1)$$

We define the value of τ by $F(q,\tau)\equiv0.2$ [36]. Relative to the pure system, we find that τ is larger at each T for the attractive system (Fig. 2). This difference grows with decreasing T, and so we expect the attractive filled system to vitrify at higher T than in the pure system (in other words, T_g should increase relative to the pure system). While τ of the nonattractive system is nearly indistinguishable from the pure system at the highest T studied, τ becomes increasingly smaller than the pure system as T decreases; hence we would expect a decreased T_g value for the excluded volume system.

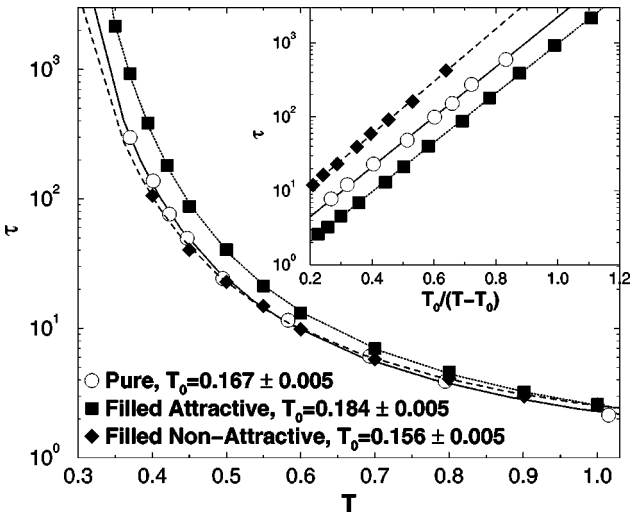

FIG. 2. Temperature dependence of the relaxation time of the collective intermediate scattering function. The lines are a fit to the VFT form. The inset shows the same data plotted against reduced temperature $T_0/(T-T_0)$ to show the quality of the VFT fit. For clarity in the inset, τ of the pure system is multiplied by 2, and τ of the filled nonattractive system is multiplied by 4.

We further test these expectations by fitting to the Vogel-Fulcher-Tammann (VFT) form

$$\tau\sim e^{A/(T-T_0)}, \qquad (2)$$

where T_0 is typically quite close to the experimental T_g value [35]; hence changes in T_g are reflected in T_0. Consistent with the changes in τ relative to the pure melt, we find that T_0 increases in the system with attractive interactions, but clearly decreases in the system with only an excluded volume interaction. Thus the effect of the steric hindrance introduced by the filler particle decreases $\tau(T)$ and T_g, in spite of the fact that monomers have a reduced number of directions in which to move, and hence degrees of freedom that aid in the loss of correlations. The fact that T_g shifts in opposite directions for attractive versus purely excluded volume interactions demonstrates the importance of surface interactions.

To elucidate how the local dynamics of the monomers are influenced by the filler, we examine the relaxation of the self (incoherent) part $F_{\rm self}(q,t)$ of $F(q,t)$ as a function of the monomer distance from the filler. Monomers typically form layers near a surface [11]; we find well-defined monomer layers surrounding the filler, as seen in the density profile of Fig. 3. Hence we split $F_{\rm self}(q,t)$ into contributions from each separate layer. Specifically, we calculate $F_{\rm self}^{\rm layer}(q,t)$ using the monomers located in each layer at $t=0$, such that

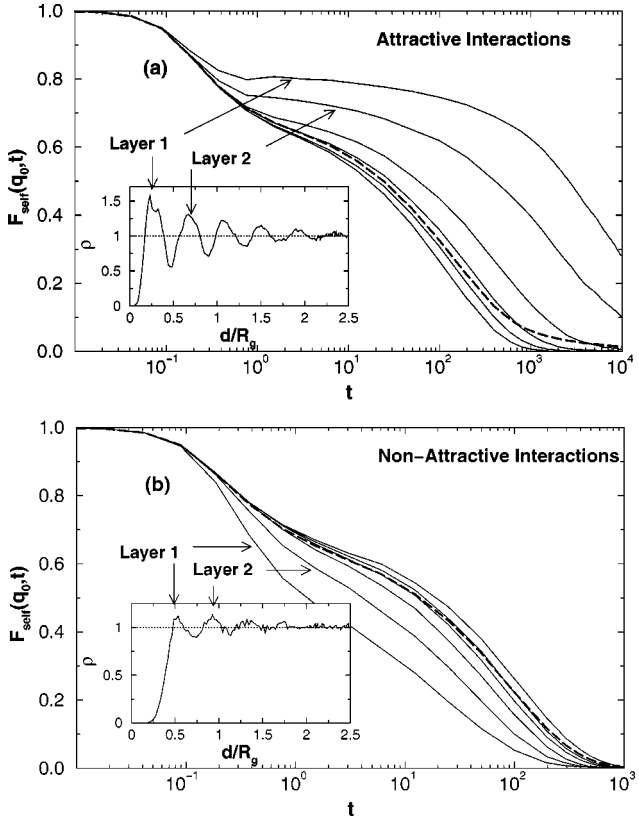

FIG. 3. $F_{\mathrm{self}}(q_0,t)$ for the average of all monomers (dotted line), and decomposed into layers (defined by the distance from the filler surface) for (a) attractive interactions and (b) nonattractive interactions at $T=0.4$. The inset of each figure shows the local density profile $\rho[d/\langle R_g\rangle]$ of monomers as a function of distance from the filler, normalized by $\langle R_g\rangle$ of the melt. We define the distance d from the filler surface as the difference between the radial position of a monomer r_{mon} and the radius of the inscribed sphere of the icosahedral filler particle $r_{\mathrm{icos}}=\frac{1}{12}(42+18\sqrt{5})^{1/2}L$, where L is the length of an edge of the icosahedron. The monomers order in well-defined layers surrounding the filler; we use the minima in $\rho(r)$ to define the boundary between layers. At distances beyond where the layers are clearly observable, we simply split $F_{\mathrm{self}}(q_0,t)$ into shells corresponding to the typical layer thickness. In (a), we see that the relaxation near the filler surface is slowed by roughly two orders of magnitude. In contrast, (b) shows the relaxation of $F_{\mathrm{self}}(q_0,t)$ is enhanced by roughly one order of magnitude near the surface. The relaxation time of the outer most layer in both cases nearly coincides with the relaxation time of the pure system.

$$F_{\mathrm{self}}(q,t)=1/N\sum_{\mathrm{layers}} N_{\mathrm{layer}}F_{\mathrm{self}}^{\mathrm{layer}}(q,t), \tag{3}$$

where N_{layer} is the number of monomers in a given layer. We show $F_{\mathrm{self}}^{\mathrm{layer}}(q_0,t)$, as well as $F_{\mathrm{self}}(q_0,t)$ for one temperature in Fig. 3. In the attractive system, the relaxation of the layers closest to the filler are slowest, consistent with the system dynamics being slowed by the attraction to the filler and the increase in T_g. Conversely, for the nonattractive system, we find that the relaxation of inner layer monomers is significantly enhanced compared to the bulk, consistent with the decrease of T_g. In both attractive and excluded volume cases, the relaxation of monomers near the corners of the filler is slightly faster than other monomers in the first layer; this may be expected, since the corners impose less constraint on the monomer motion than the faces. Preliminary results support the possibility that faster dynamics may also occur with attractive interactions, provided that the polymer-filler attraction is weaker than that of polymer-polymer interactions. The altered dynamics persist for a distance slightly less than $2\langle R_g\rangle$ from the surface. Our results demonstrate that interactions play a key role in controlling T_g and the local dynamics of filled polymers. We expect the role of interactions to be largely the same when many filler particles are present in the melt, but there will be additional effects on dynamic properties due to the more complex geometrical constraints, such as observed near the filler corners.

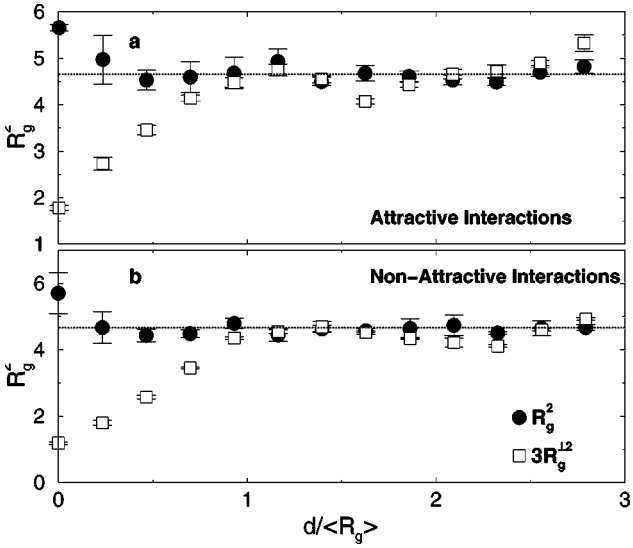

FIG. 4. Radius of gyration R_g of the polymer chains as a function of distance $d/\langle R_g\rangle$ of the center of mass of a chain from the filler surface for $T=0.4$. We normalize d by the $\langle R_g\rangle$ of all chains. We also resolve the component perpendicular to the surface, which we label by $R_g^{\perp}$. We show results for (a) attractive and (b) nonattractive interactions. The dotted line shows $\langle R_g^2\rangle$ for the pure system. The increase of R_g, coupled with the decrease of $R_g^{\perp}$, indicates that the chains become increasingly elongated and ''flattened'' as the surface of the filler is approached. The effect appears largely independent of the temperature and numerical values of the potential parameters.

We next turn our attention to any structural effect the filler has on the melt. The pair distribution function, $\langle R_g\rangle$,$\langle R_e\rangle$, and the distribution of bond lengths and angles show no significant deviations from the pure system. However, by focusing on the dependence of R_g (or R_e) on the distance d from the filler surface, we find a change in the overall polymer structure near the surface. In Fig. 4, we show R_g^2, as well as the radial component from the filler center $R_g^{\perp 2}$ (approximately the component perpendicular to the filler surface) for both attractive and nonattractive polymer-filler interactions at one temperature. R_g^2 increases by about 30% on approaching the filler surface; at the same time $R_g^{\perp 2}$ decreases by slightly more than a factor of 2 for both attractive and nonattractive systems.

The combination of these results indicates that the polymers become slightly elongated near the surface, and flatten significantly. Note that not all monomers belonging to a given ''surface polymer'' are located in the first surface layer, as depicted in Fig. 1(b). We also point out that the chains retain a Gaussian conformation near the filler surface [37]. We find that the range of the flattening effect roughly spans a distance $\langle R_g \rangle$ from the surface, and the results depend only weakly on T. We performed an additional simulation with double the attraction strength between the filler and polymers, and did not find any further significant effect on the chain structure. The independence of the chain structure on the interaction suggests that the altered shape of the polymers is primarily due to geometric constraints of packing the chains close ($d \lesssim \langle R_g \rangle$) to the surface. For significantly stronger interactions, an alteration of the chain structure is expected on theoretical grounds [38,39]. Intuitively, if the monomer-filler interactions were stronger and longer ranged, this would dominate packing considerations. Thus, for a repulsive interaction, the chains would be elongated *perpendicular* to the surface, not unlike a polymer brush; for an attractive interaction, the effect of chain flattening would be more pronounced.

We next consider the implications that our results may have for studies of ultrathin polymer films (thickness $\lesssim 100$ nm), where there is long standing debate on the role of interactions versus confinement on T_g shifts [5,12,13], local melt dynamics [5,14–18], and melt structure [5–11]. Our simulations allow us to address the effects of interactions with a surface, without the additional complication of confinement effects present in thin films. It is largely agreed that ultrathin films with strongly attractive substrates increase T_g, while weak substrate interactions (or no substrate, as in freely standing films) lead to a downward shift of T_g; this is consistent with our results. This consistency is reasonable for fillers which have facets that are relatively smooth and large compared to $\langle R_g \rangle$; for nanoscopic fillers, such as we study, it is surprising that a correspondence occurs even for $\langle R_g \rangle$ close to the filler size. Such a similarity implies that the surface interactions play a more important role in the dynamics than the geometrical differences between the systems; we again caution that for more dramatic changes in surface geometry, interactions may not dominate. Not surprisingly, the magnitude of the shifts we observe depends on the relative quantities of polymer and filler; a greater filler concentration would have a more dramatic effect (as observed experimentally in Refs. [20–22]). Insofar as the magnitude of effects depends only on the ratio of the surface to bulk monomers, the thickness of the film is analogous to the inverse of the concentration of the filler. This is consistent with the experimental observation that T_g shifts are more pronounced as the film thickness decreases. Recently there have been several experiments on segmental motion in both freely standing and supported ultrathin films [5,14,15]. The observed segmental dynamics is consistent with a decreased T_g found in calorimetric measurements [5,12,13]. At this time, it is not clear whether a model with layers of different mobility is applicable to understand T_g shifts of thin films [5]; however, the parallel behavior we observe between the thin films and our simulations of a filled melt support this viewpoint. Finally, the elongation and flattening of polymers we observe near the filler has been observed in thin-film simulations [8–11] as well as recent experiments [6,7]; the range of the effect found in Ref. [6] is quantitatively consistent with our results, which show the effect only for a range of roughly $\langle R_g \rangle$, while the results of Ref. [7] observed flattening for film thicknesses $\lesssim 6\langle R_g \rangle$. We also found, as in Ref. [6], that the chains retain a Gaussian structure near the surface. Thus our findings demonstrate that confinement is not a necessary ingredient for the observed changes in the dynamics and structure of polymers near surfaces. While our results provide strong support for interpreting the results for filled melts and ultrathin films in the same framework, it is obvious that much care must be used when analyzing specific systems.

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[1] G. Wypych, *Handbook of Fillers* (ChemTec Publishing, Toronto, 1999).
[2] *Nanotechnology Research Directions: IWGN Workshop Report Vision for Nanotechnology in the Next Decade*, edited by M.C. Roco, S. Williams, and P. Alivisatos (Kluwer, Dordrecht, 2000).
[3] J.J. Schwab and J.D. Lichtenhan, Appl. Organomet. Chem. **12**, 707 (1998).
[4] F.J. Feher, D. Soulivong, A.G. Eklund, and K.D. Wyndham, Chem. Commun. (Cambridge) **13**, 1185 (1997).
[5] J. A. Forrest and R.A.L. Jones, *Polymer Surfaces, Interfaces, and Thin Films*, edited by A. Karim and S. Kumar (World Scientific, Singapore, 2000), p. 251.
[6] R.L. Jones, S.K. Kumar, D.L. Ho, R.M. Briber, and T.P. Russell, Nature (London) **400**, 146 (2000).
[7] J. Kraus, P. Müller-Buschbaum, T. Kuhlmann, D.W. Schubert, and M. Stamm, Europhys. Lett. **49**, 210 (2000).
[8] D.N. Theodorou, Macromolecules **21**, 1400 (1988).
[9] S.K. Kumar, M. Vacatello, and D.Y. Yoon, J. Chem. Phys. **89**, 5206 (1989).
[10] S.K. Kumar, M. Vacatello, and D.Y. Yoon, Macromolecules **23**, 2189 (1990).
[11] J.-S. Wang and K. Binder, J. Phys. I **1**, 1583 (1991).
[12] J.H. van Zanten, W.E. Wallace, and W.L. Wu, Phys. Rev. E **53**, 2053 (1996).
[13] W.E. Wallace, J.H. van Zanten, and W.L. Wu, Phys. Rev. E **52**, 3329 (1995).
[14] J.A. Forrest, K. Dalnoki-Veress, and J.R. Dutcher, Phys. Rev. E **56**, 5705 (1997).
[15] J.A. Forrest *et al.*, Phys. Rev. E **58**, 1226 (1998).
[16] E.K. Lin, R. Kolb, S.K. Satija, and W.L. Wu, Macromolecules **32**, 3753 (1999).

[17] F. Varnik, J. Baschnagel, and K. Binder, J. Phys. IV **10**, 239 (2000).
[18] S.H. Anastasiadis *et al.*, Phys. Rev. Lett. **84**, 915 (2000).
[19] C.A. Angell, Science **267**, 1924 (1995).
[20] P. Cousin and P. Smith, J. Polym. Sci., Part B: Polym. Phys. **32**, 459 (1994).
[21] G. Tsagaropoulos and A. Eisenberg, Macromolecules **28**, 6067 (1995).
[22] N. Sombatsompop, J. Appl. Polym. Sci. **74**, 1129 (1999).
[23] R.B. Bird, C.F. Curtiss, R.C. Armstrong, and O. Hassager, *Dynamics of Polymeric Liquids: Kinetic Theory* (Wiley, New York, 1987), Vol. 2.
[24] J.W. Rudisill and P.T. Cummings, Rheol. Acta **30**, 33 (1991).
[25] C. Bennemann, W. Paul, J. Baschnagel, and K. Binder, J. Phys.: Condens. Matter **11**, 2179 (1999).
[26] C. Bennemann, C. Donati, J. Baschnagel, and S.C. Glotzer, Nature (London) **399**, 246 (1999).
[27] Relative to a monomer, the mass of a filler site is $m_f = 2m_m$, the spring stiffness is $k_f = 1.5k_m$, and the bond parameter $R_0^f = 2/3R_0^m$. We choose a stiffer spring, a larger mass, and a smaller bond parameter than used for the polymers to reduce the fluctuation of filler sites. In order to avoid any spurious effects that might be induced by a large cavity inside the filler particle, a replica of the particle with three sites on an edge and one with only sites at the vertices are layered inside the outer icosahedron, reminiscent of a ''Russian doll.'' This yields a total 356 force sites associated with the filler. For the attractive case, we use a LJ particle with an interaction strength between filler sites $\epsilon_{\mathrm{ff}} = 2.0\epsilon_{\mathrm{mm}}$. We use the Lorentz-Berthelot [31] mixing rules for the monomer-filler interactions, and take $\epsilon_{\mathrm{mf}} = \sqrt{\epsilon_{mm}\epsilon_{ff}}$. For the nonattractive case, we drop the attractive r^6 term in the LJ potential for monomer-filler interactions and retain only the r^{12} term, accounting for excluded volume.
[28] Studies of confined systems have shown that smooth walls show effects like those observed here, where the surface roughness is dynamic and relatively small [29]. For static roughness adapted to the melt structure, monomers can be trapped by ''pockets'' of surface roughness due to dispersion, etc. [29,30]. Such effects will be particularly important for the many filler case, where complex geometries arise, but are beyond the scope of the present study.
[29] C. Mischler, J. Baschnagel, and K. Binder, e-print cond-mat/0012277.
[30] Z.T. Németh and H. Löwen, Phys. Rev. E **59**, 6824 (1999).
[31] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Oxford University Press, Oxford, 1987).
[32] *Carbon Black: Science and Technology*, edited by J.-B. Donnet, R.C. Bansal, and M.-J. Wang (Marcel Dekker, New York, 1993).
[33] M. Tuckerman, B.J. Berne, and G.J. Martyna, J. Chem. Phys. **97**, 1990 (1992).
[34] The temperature is adjusted using the Andersen method [31]; for production runs, the temperature is weakly coupled to the Berendsen thermostat [31] to prevent a drift in the total energy due to the accumulation of round-off error expected for long simulation times.
[35] P.G. Debenedetti, *Metastable Liquids* (Princeton University Press, Princeton, 1996).
[36] The exact choice for the definition of τ does not significantly change the temperature dependence of our results. We focus our attention on the magnitude of wave vector $q_0 \approx 7.08$, the location of the first maximum in $S(q)$.
[37] The chains retain a Gaussian confirmation in the sense that $R_e^2 = 6R_g^2$; however, the probability distribution of the monomer coordinates is not symmetric in all directions.
[38] J.F. Douglas, A.M. Nemirovsky, and K.F. Freed, Macromolecules **19**, 2041 (1986).
[39] P.K. Brazhnik, K.F. Freed, and H. Tang, J. Chem. Phys. **101**, 9143 (1994); K.F. Freed, *ibid.* **105**, 10 572 (1996).