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Reduction of polymer surface tension by crystallized polymer nanoparticles

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Self-consistent field theory is applied to investigate the effects of crystallized polymer nanoparticles on polymer surface tension. It is predicted that the nanoparticles locate preferentially at the polymer surface and significantly reduce the surface tension, in agreement with experiment. In addition to the reduction of surface tension, the width of the polymer surface is found to narrow. The reduced width and surface tension are due to the smaller spatial extent of the nanoparticles compared to the polymer. This allows the interface to become less diffuse and so reduces the energies of interaction at the surface, which lowers the surface tension. The solubility of the surrounding solvent phase into the polymer melt is mostly unchanged, a very slight decrease being detectable. The solubility is constant because away from the interface, the system is homogeneous and the replacement of polymer with nanoparticles has little effect. © 2010 American Institute of Physics.

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I. INTRODUCTION

Polymer industrial processes often benefit from a knowledge of polymer surface tension. This is true, for example, in polymer foaming, where conditions are sought such that the polymer to be foamed will exhibit a low surface tension. A low surface tension increases the nucleation rate of bubbles in the foam and can result in smaller, more uniform cells in the final product.¹

Surface tension will generally increase as temperature is lowered, the limit of this being the temperature at which the polymer solidifies and melt surface tension measurements no longer have meaning. Although amorphous polymers will behave in this way, reaching a maximum surface tension at low temperatures for a given pressure and then undergoing a glass transition, crystalline polymers can behave differently. Wei *et al.*² conducted the first surface tension measurements on a crystalline polymer through its melting temperature and found that high density polyethylene enters a viscoelastic state before solidifying and that, in the region below the melting point, the surface tension drops a stunning 20% as temperature is reduced over a very small range. The amount of this change of surface tension is surprising as is its direction: normally, one would expect the surface tension to continue to rise as the temperature is lowered.

The appearance of a viscoelastic state below the melting temperature is not in itself surprising. It is expected that small crystal regions will form and grow within a continuous polymer melt. This idea led Wei *et al.* to hypothesize that the small crystals act as nanoparticles that locate at the polymer surface and reduce the surface tension. If one accepts the idea that nanocrystals form, the hypothesis of Wei *et al.* leads

to a number of questions. (1) Would such nanoparticles be preferentially located at the surface? (2) If so, would they indeed reduce the surface tension? (3) If so, what is the mechanism of this reduction?

The purpose of this paper is to test the hypothesis of Wei *et al.* by answering the above three questions. A good way to do this is through theoretical calculations where many complicating factors can be removed. For example, one can compare identical systems with and without particles with no change in temperature; equation of state effects can be removed by assuming a simple incompressibility condition; a random coil (Gaussian chain) model for the polymer can be used; the chemical details of the constituents can be incorporated into a phenomenological Flory–Huggins parameter. Such a coarse-grained theory is not expected to yield quantitatively accurate results, but by using a self-consistent field theory (SCFT) method, the results will be qualitatively correct and even semiquantitative in that order of magnitudes should be credible.³

We will show in the sections that follow that SCFT provides evidence in support of the following results. (1) The nanoparticles locate robustly at the polymer surface, that is, the probability of finding a nanoparticle in the vicinity of the polymer surface is higher than the probability of finding a particle in the bulk. (2) The surface tension is reduced by a significant amount that is consistent with the experimental observations of Wei *et al.* (3) The reason for this reduction in surface tension is the smaller spatial extent of the polymer crystals compared to the noncrystallized polymer. The nanocrystals are calculated to preferentially locate near the surface so as to “buffer” the polymer from the surface. This lets the polymers explore more conformations and lowers the free energy of the system. The crystals, having smaller spa-

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tial extent than noncrystallized polymers, are able to form a narrower boundary with a fluid (in experiments, this fluid may be, for instance, supercritical nitrogen or supercritical carbon dioxide⁴⁻⁷). The narrower surface lowers the internal energy and thus the surface tension. A counterintuitive result is therefore found: a sharper interface with a lower surface tension. In addition, we find that the solubility of the polymer phase is almost unchanged, with only a very slight decrease in solubility being detected. It should be emphasized that all these results, since they are found through SCFT calculations (as shown in the following sections), are equilibrium results; no kinetic factors are included. The importance of this is discussed in Sec. III.

II. THEORY

Self-consistent field theory (SCFT) uses equilibrium statistical mechanics to describe systems on a molecular level. An effective Hamiltonian that incorporates all the degrees of freedom of a coarse-grained system is used to derive, without approximation, a partition function. A single mean field approximation is then made to give a free energy functional. SCFT is mainly used to describe inhomogeneous polymer systems.^{8,9} In the SCFT free energy functional, local volume fractions $\varphi(\mathbf{r})$ describe amounts of each chemical species of a system as a function of position. Related to these are position dependent fields $w(\mathbf{r})$ that give a mean field representation of all the interactions that the molecules are subject to. The excluded volume is often introduced through a position dependent pressure field $\xi(\mathbf{r})$; this acts as a Lagrange multiplier in the formalism to enforce an incompressibility constraint. (This incompressibility condition is not able to describe nonlocal phenomena such as packing effects.)

SCFT can be used to model an incompressible polymer/solvent system with filler particles of the same chemical species as the polymer. These fillers can represent polymer nanocrystals. Although equation of state effects are quantitatively important in polymer surface tension systems, an incompressible system is chosen here so as to simplify the analysis—recent work has provided evidence that an incompressible system can capture much of the qualitative physics in polymer surface tension phenomena.¹⁰ Similar SCFT representations of polymer/solvent systems, both compressible and incompressible, are described in Refs. 5 and 10. If we modify these SCFT descriptions to include nanofillers, the free energy functional (actually, free energy per volume F/V) for a polymer/solvent/nanofiller system can be written as

$$\begin{aligned} \frac{NF}{\rho_0 k_B T V} = & -\phi_p \ln\left(\frac{Q_p}{V\phi_p}\right) - \frac{\phi_s}{\alpha_s} \ln\left(\frac{Q_s\alpha_s}{V\phi_s}\right) - \frac{\phi_f}{\alpha_f} \ln\left(\frac{Q_f\alpha_f}{V\phi_f}\right) \\ & + \frac{1}{V} \int d\mathbf{r} \{ \chi N \varphi_s(\mathbf{r}) [\varphi_p(\mathbf{r}) + \varphi_f(\mathbf{r})] \\ & - R_f^2 \nabla \varphi_f(\mathbf{r}) \cdot [\nabla \varphi_p(\mathbf{r}) + \nabla \varphi_s(\mathbf{r})] - w_p(\mathbf{r}) \varphi_p(\mathbf{r}) \\ & - w_s(\mathbf{r}) \varphi_s(\mathbf{r}) - w_f(\mathbf{r}) \varphi_f(\mathbf{r}) - \xi(\mathbf{r}) \\ & \times [\varphi_p(\mathbf{r}) + \varphi_s(\mathbf{r}) + \varphi_f(\mathbf{r})] \}, \end{aligned} \quad (1)$$

where α_f and α_s are the ratios of the volumes of filler f and solvent s , respectively, to the contour volume N/ρ_0 of poly-

mer p of polymerization N . The global volume fractions (as opposed to the local, position dependent volume fractions) are given by $\phi_{p,s}$, or f . The length R_f describes the spatial extent of the filler particles due to excluded volume or other interactions—more will be said about this parameter in Sec. III. In principle, there could be different R_f values for the filler interactions with the polymer and the solvent, but for simplicity, they are kept the same in this work. The square gradient expressions follow a common form (see Ref. 11 for example) with $R_f = N^{1/2} \sigma / \sqrt{6}$. The length σ is a gradient expansion coefficient and is the quantity usually defined in other SCFT works. Note the similarity of form with the radius of gyration $R_g = N^{1/2} a / \sqrt{6}$, which gives the spatial extent of the polymer and which will be used as the unit of length in this work. The length a is the average length of one segment of the polymer. The factors $Q_{p,s}$, or f are the partition functions of a polymer, a solvent molecule or a filler particle, respectively, each subject to the corresponding field $w(\mathbf{r})_{p,s}$ or f . (Note that in the absence of particles, Eq. (1) is still strongly nonlocal through the term involving Q_p .) In incompressible SCFT, Flory–Huggins exchange parameters are used to describe molecular interactions, one for each pair of *different* chemical species. Although we have three different moieties in our system (polymer, solvent, and fillers), the polymer and filler are of the same chemical species, leaving just two species (one pair) and thus only one Flory–Huggins parameter χ . The value of χ is chosen based on chemistry and temperature (it is inversely proportional to temperature) and is defined with respect to the polymer segment volume ρ_0^{-1} . In Eq. (1), the free energy per volume F/V is made dimensionless using a factor $N/\rho_0 k_B T$, where k_B is Boltzmann's constant and T is the temperature.

Minimizing Eq. (1), we get the SCFT equations

$$w_p(\mathbf{r}) = \chi N \varphi_s(\mathbf{r}) + R_f^2 \nabla^2 \varphi_f(\mathbf{r}) + \xi(\mathbf{r}), \quad (2)$$

$$w_s(\mathbf{r}) = \chi N [\varphi_p(\mathbf{r}) + \varphi_f(\mathbf{r})] + R_f^2 \nabla^2 \varphi_f(\mathbf{r}) + \xi(\mathbf{r}), \quad (3)$$

$$w_f(\mathbf{r}) = \chi N \varphi_s(\mathbf{r}) + \xi(\mathbf{r}), \quad (4)$$

$$1 = \varphi_p(\mathbf{r}) + \varphi_s(\mathbf{r}) + \varphi_f(\mathbf{r}), \quad (5)$$

$$\varphi_p(\mathbf{r}) = \frac{\phi_p V}{Q_p} \int_0^1 ds q(\mathbf{r}, s) q(\mathbf{r}, \alpha_p - s), \quad (6)$$

$$\varphi_s(\mathbf{r}) = \frac{\phi_s V}{Q_s} e^{-\alpha_s w_s(\mathbf{r})}, \quad (7)$$

$$\varphi_f(\mathbf{r}) = \frac{\phi_f V}{Q_f} e^{-\alpha_f w_f(\mathbf{r})}, \quad (8)$$

$$Q_p = \int d\mathbf{r} q(\mathbf{r}, 1), \quad (9)$$

$$Q_s = \int d\mathbf{r} e^{-\alpha_s w_s(\mathbf{r})}, \quad (10)$$

$$Q_f = \int d\mathbf{r} e^{-\alpha_f w_f(\mathbf{r})}, \quad (11)$$

where $q(\mathbf{r}, s)$ is the solution to the modified diffusion equation

$$\frac{\partial}{\partial s} q(\mathbf{r}, s) = \left[\frac{Na^2}{6} \nabla^2 - w_p(\mathbf{r}) \right] q(\mathbf{r}, s), \quad (12)$$

with the initial condition $q(\mathbf{r}, 0) = 1$. In Eqs. (1)–(12), we use definitions and notation similar to those in Ref. 8. Further details on the use and derivation of SCFT can be found in that reference. The equations are solved numerically and self-consistently in one dimension using reflecting boundary conditions. A guess is taken for the fields $w(\mathbf{r})_{p,s}$ and f_s , and from this guess, Eqs. (12) and (6)–(11) are solved. Equations (2)–(4) can be combined using Eq. (5) to give an equation for $w(\mathbf{r})$ in terms of $w(\mathbf{r})_{p,s}$, and f_s , and so one can also find $w(\mathbf{r})$ from the guess of the fields. Having results for all the local volume fractions $\varphi(\mathbf{r})_{p,s}$, and f_s as well as $w(\mathbf{r})$, one can find new values for $w(\mathbf{r})_{p,s}$, and f_s by using Eqs. (2)–(4). The old values and new values of $w(\mathbf{r})_{p,s}$, and f_s are mixed in a ratio that maintains computational stability, and the result is used as a new guess for $w(\mathbf{r})_{p,s}$, and f_s . This process is iterated until the new values of $w(\mathbf{r})_{p,s}$, and f_s deviate from the old values of $w(\mathbf{r})_{p,s}$, and f_s by less than 10^{-10} according to the definition of Thompson *et al.*¹²

In the homogeneous case, the free energy density (1) reduces to

$$\begin{aligned} \frac{NF}{\rho_0 k_B TV} &= \phi_p \ln \phi_p + \frac{\phi_s}{\alpha_s} \ln \left(\frac{\phi_s}{\alpha_s} \right) + \frac{\phi_f}{\alpha_f} \ln \left(\frac{\phi_f}{\alpha_f} \right) \\ &+ \chi N \phi_s (\phi_p + \phi_f). \end{aligned} \quad (13)$$

To calculate the surface tension, we follow the prescription given in Ref. 5. This involves subtracting the bulk homogeneous free energies from the inhomogeneous free energy (1) to get the excess free energy of the existence of the interface. Dividing by area gives the surface tension. The forms for the dimensionless homogeneous bulk free energy densities \mathcal{F}_i (where $i = p, s$, or f for the polymer, solvent, and fillers) are different from the corresponding equations in Ref. 5 because the system is different. The bulk free energies are now

$$\mathcal{F}_p = \phi_p \ln \phi_p + \frac{\chi N}{2} \phi_p \phi_s, \quad (14)$$

$$\mathcal{F}_s = \frac{\phi_s}{\alpha_s} \ln \left(\frac{\phi_s}{\alpha_s} \right) + \frac{\chi N}{2} \phi_s (\phi_p + \phi_f), \quad (15)$$

$$\mathcal{F}_f = \frac{\phi_f}{\alpha_f} \ln \left(\frac{\phi_f}{\alpha_f} \right) + \frac{\chi N}{2} \phi_f \phi_s. \quad (16)$$

When subtracting these bulk free energies from the inhomogeneous free energy, one must weigh them appropriately as discussed in Ref. 8.

III. RESULTS AND DISCUSSION

We choose $\alpha_s = 0.05$ and $\alpha_f = 2.0$. This makes the solvent molecular volume much smaller than the polymer contour

volume, as it should be, while letting the filler particles have a bigger volume than the polymer contour volume. This also should be the case since the fillers are created through the crystallization of the polymers, which could join together more than one polymer. By taking $\alpha_f = 2.0$, we are choosing to give each nanoparticle crystal a volume equal to the total contour volume of two polymers. Note however that while the crystals have larger *volume* than the contour volume of the polymers, they do not necessarily have a larger spatial extent. Each noncrystallized polymer is an open, random walk structure, whereas the nanoparticles are expected to be more collapsed and confined in size. Whereas the volume ratio between crystals and polymers is given by the parameter α_f , the size ratio, or spatial extent ratio, is given by R_f/R_g , the ratio of crystal size (radius) to the polymer radius of gyration. (Thus, we make a difference between the contour volume of a polymer and the volume in which the polymer gyrates.) We will examine two different values of R_f as discussed below. We take $\chi N = 20.0$ with $\phi_p = 0.35$ and $\phi_f = 0.0$; then, we slowly increase ϕ_f up to 0.1 while decreasing ϕ_p by the same amount.¹³ Since the fillers are crystallized polymers, these choices account for a zero-sum volume fraction of nanoparticles and polymers—we are approximating no volume change upon crystallization. Using these parameters, numerical errors are not visible on the scale of the plots that follow.

We want to test the hypothesis that nanocrystalline particles go to the polymer surface and reduce the surface tension. To this end, we will compare two systems at the same temperature: one with zero percent nanoparticles and one with approximately 30% nanoparticles. [The relevant quantity here is the fraction of polymer that has crystallized: $\phi_f / (\phi_p + \phi_f)$.] We choose 30% as it is high enough to show a dramatic effect but low enough that three phase separation is unlikely. As a reference, Fig. 1(a) shows the concentration profiles of the polymer/solvent system without fillers ($\phi_f = 0.0$). Figure 1(b) shows that the fillers do go robustly to the interface. The interface is observed to become very sharp (narrow) and the surface tension drops enormously (about 50%) as shown by the open circles in Fig. 2. The crystals are predicted to locate preferentially near the interface because they have no configurational entropy and less translational entropy than the polymer. They have less translational entropy because their volume is greater than that of a single polymer. Due to their large sizes, both crystals and polymers will have negligible translational entropy compared with the solvent molecules, so the configurational entropy difference is the more important quantity. Figure 1(d) shows a blow-up of filler profiles for various values of filler-to-polymer volume α_f . Reducing the value of α_f is seen to reduce the migration of fillers to the interface by only very small amounts, and this would be expected to be even less for smaller, more realistic solvent to polymer volume ratios α_s . To cause the particles to distribute uniformly, such as in the experimental results of Gupta *et al.*,¹⁴ one would need a very small value of α_f , but this would mean giving the crystals volumes smaller than single polymers, which would be unphysical in the present case since there is no mechanism to subdivide polymers upon crystallization. Once at the interface, for the

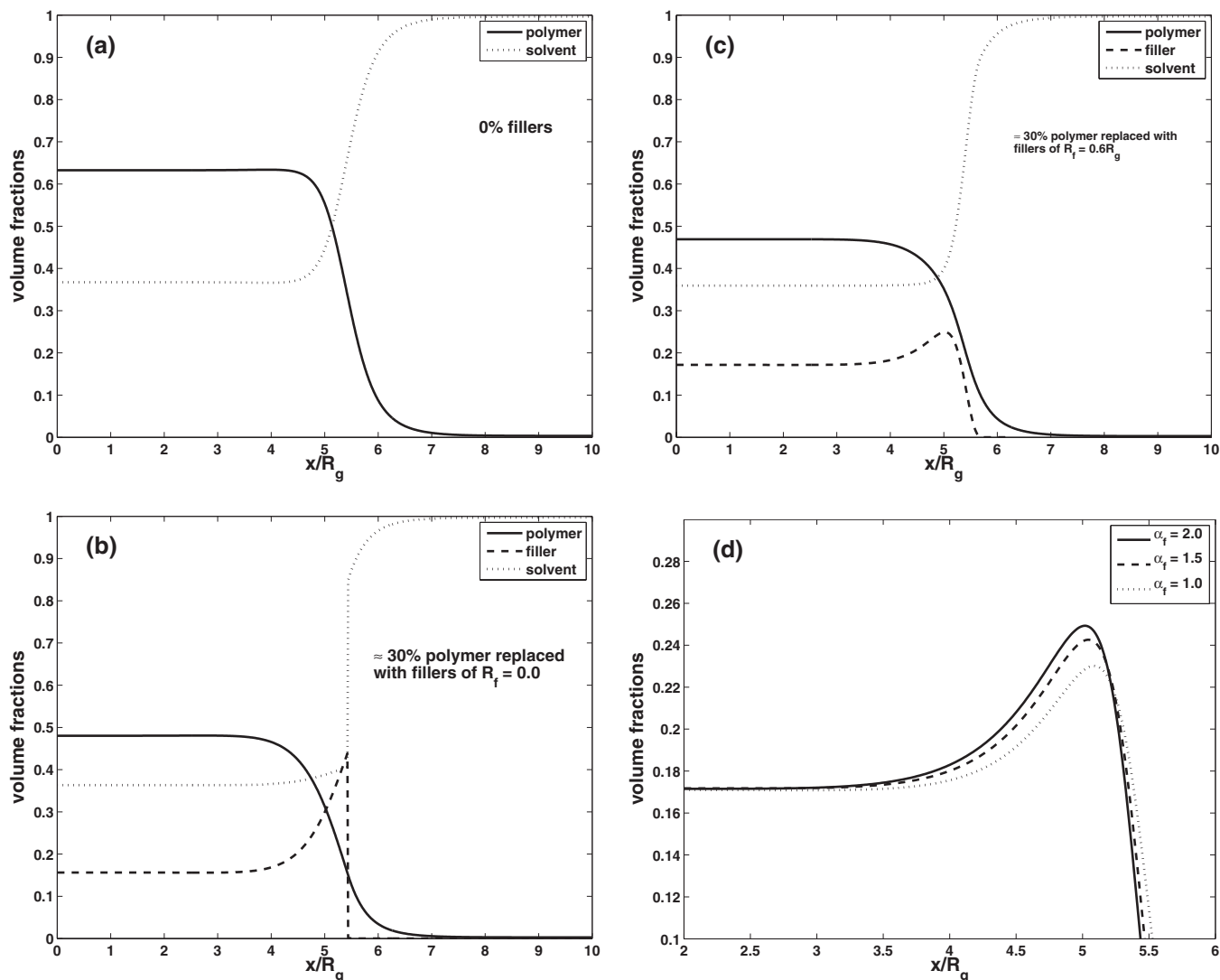


FIG. 1. (a) Concentration profiles for a polymer/solvent interface with no nanofillers. (b) Concentration profiles for a polymer/solvent interface with approximately 30% fillers present and $R_f=0.0R_g$. (c) Concentration profiles for a polymer/solvent interface with approximately 30% fillers present and $R_f=0.6R_g$. (d) Blow-up of concentration profiles for fillers with different values of filler to polymer volume ratio α_f .

case of $R_f=0.0R_g$, the interface becomes near step-function-like because the polymer, which is now away from the interface, is no longer present to provide a measure of spatial extent to the interface. The sharp interface means that the solvent and crystals have minimal contact, and therefore there is little interaction energy and the surface tension is reduced. In effect, we are approaching the idealized case of two uniform bulk phases separated by a step function. Such an ideal case, for a completely local free energy functional, would have zero surface tension since both sides of the step interface are bulk right up to the interface.¹⁵ Subtracting off the free energy of these bulks leaves zero excess free energy for the interface and thus a zero surface tension.¹⁶

This situation arises because in the vicinity of the interface, there is no longer anything contributing nonlocality, that is, a measure of spatial extent: both the solvent and crystals are unphysically pointlike. Nonlocality arises due to a finite range of interactions, and the biggest contribution is expected to be from excluded volume. The excluded volume contribution to nonlocality has only been enforced in an average way through incompressibility. This subtle point is dis-

cussed at greater length elsewhere.¹⁷ To include the spatial extent due to excluded volume, one can certainly use a classical density functional theory approach.¹⁸ This normally assumes the objects are completely hard, bare, perfect spheres, which they are not likely to be in the present case. The crystals might have some loose polymer extending from them and could take on a variety of shapes and sizes. It does not make sense to put in a specific form of excluded volume since it is not known the nature of the crystals. Although density functional theory would still capture the physics, it would be much more complicated and not improve results compared to what is probably the simplest and most generic mathematical form of nonlocality: that of a square gradient in the free energy functional. This was originally suggested by van der Waals in the 19th century.¹⁶ In the interest of simplicity again, we let the fillers have spherical symmetry, although they are certainly not bare, hard, perfect spheres. In Eq. (1), we use the form given by Hong and Noolandi,¹¹ which is derived through a gradient expansion of the potential. We will not place limits on the size of the R_f parameter, however, since we are treating the terms in a phenomeno-

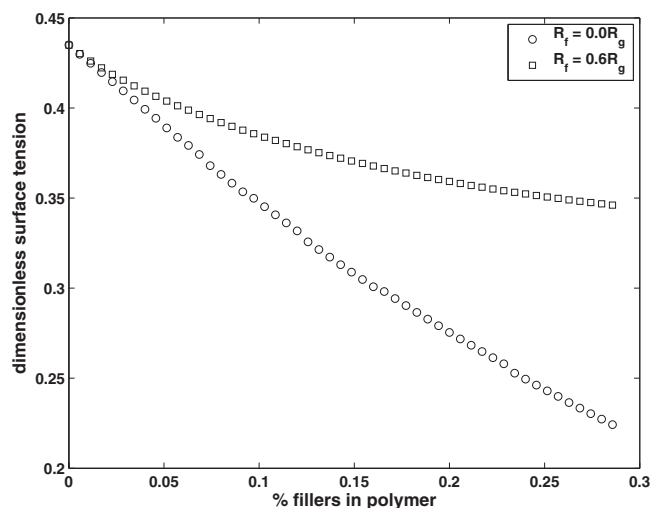


FIG. 2. Surface tension as a function of filler fraction.

logical way. The gradient terms in the free energy give rise to Laplacian terms in the chemical potential fields (2) and (3), which incorporate the nonlocal interactions in the internal potentials of the system. The spatial extent of the crystals can now be “turned on” by adopting a nonzero value of R_f . We take a value of $R_f=0.6R_g$ because this is large enough to have an effect while small enough to not disrupt the stability of the numerical algorithm. Concentration profiles for this case where approximately 30% of the polymer by volume is replaced by fillers are shown in Fig. 1(c). The open squares in Fig. 2 show that nonlocality moderates the effect of the fillers on the surface tension but does not eliminate it. In the present example, there is still a 20% drop in surface tension due to the presence of the fillers. This is consistent with the 20% drop observed experimentally,² although this agreement is fortuitous since we have arbitrarily chosen a representative volume of the crystals and a convenient value of R_f . Nonetheless, these numbers from Fig. 2 demonstrate that a crystal nanoparticle formation mechanism is easily able to, by itself, account for the experimentally observed drop in surface tension.

Using the more physical value of $R_f=0.6R_g$, we can observe that the interface still becomes narrower, although not steplike, with the creation of the crystal nanoparticles. This is shown in Fig. 3 where the interfacial width w_l is plotted as a function of filler fraction. For this plot, we use the definition of interfacial width given in Ref. 8, which is inversely related to the slope at the center of the polymer+crystal (or solvent) profile. A narrowing of the interface would usually be identified with a rise in surface tension; however, here the opposite is observed. This counterintuitive result comes about since the system is changing; we can no longer use the width of the interface as an indicator of relative surface tension if we are comparing a polymer system with a polymer/nanoparticle system.

Another parameter related to surface tension is the solubility of the fluid phase into the polymer melt. Still using $R_f=0.6R_g$, the solubility, taken to be the amount of solvent in the bulk polymer phase, is seen to remain very close to constant, a very slight decrease being detectable in Fig. 4. One

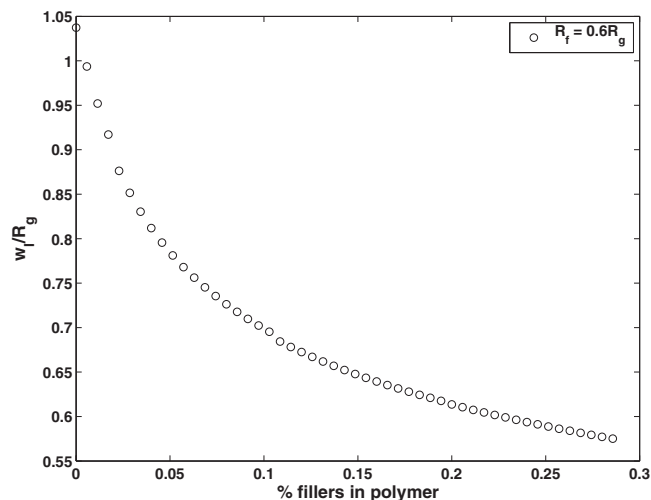


FIG. 3. Interfacial width as a function of filler fraction.

would normally expect a difference in solubility for systems with very different surface tensions, but here we find effectively no change. This is not surprising since in the homogeneous regions away from the interface, the architectural differences between the crystals and polymer have no effect within the SCFT formalism; the diffusion equation for the polymer becomes trivial, and the square gradient terms for the nanoparticles vanish. Only the difference in translational entropy due to the larger volume of the nanoparticles has any influence, and this is quite small.

Since nonlocality of the particles reduces the magnitude of the drop in surface tension, the question can be raised as to whether the surface tension reduction can be completely eliminated if the nonlocality of the fillers is large enough. Figure 5 shows the surface tension as a function of R_f for approximately 30% fillers in the polymer matrix. The plot is made against $R_f^{3/4}$ since this produces a reasonably straight line that allows a rough extrapolation.¹⁹ The extrapolated surface tension crosses the value of polymer surface tension at 0% fillers (dashed horizontal line in Fig. 5) at a value of

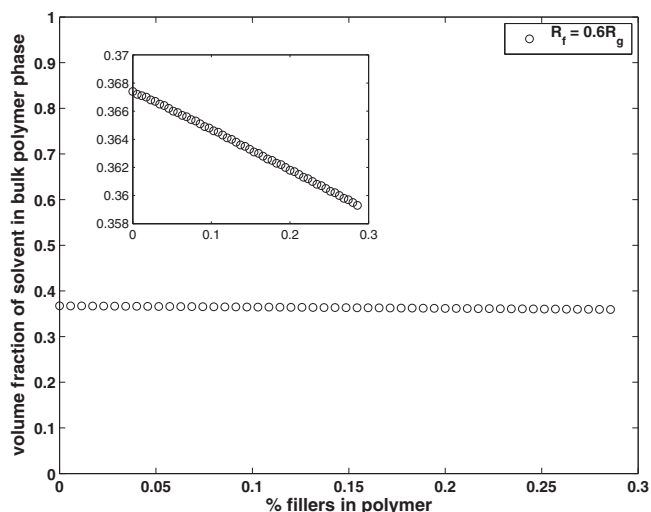


FIG. 4. Solubility, as shown by the volume fraction of solvent in the bulk polymer phase, as a function of filler fraction. The inset shows finer detail along the solubility axis.

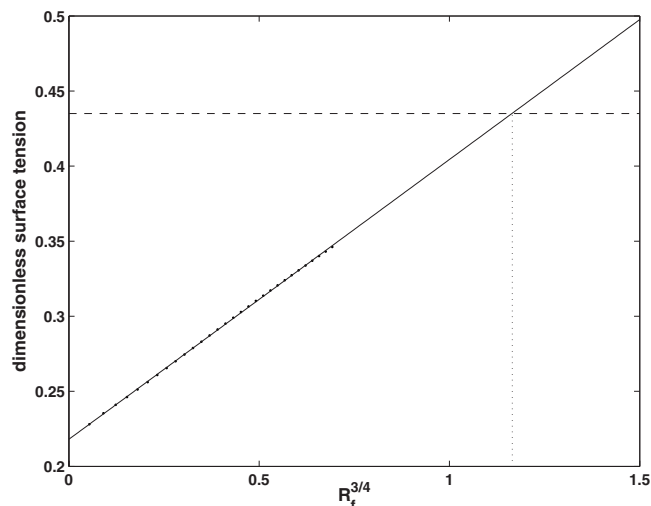


FIG. 5. Surface tension as a function of $R_f^{3/4}$ for approximately 30% crystal fillers. The solid line is a linear fit to the data points, and the dashed horizontal line is the surface tension value of the polymer with no fillers.

$R_f^{3/4} = 1.2(R_g)^{3/4}$, that is, $R_f \approx 1.3R_g$. Beyond this, the surface tension due to the presence of fillers might be expected to be larger than the surface tension of the plain polymer system. Thus, according to our model, the spatial extent of the crystals should not be too much larger than the spatial extent of an unperturbed polymer if the surface tension reduction mechanism is to be expected to operate. Furthermore, for such large crystals, it is possible that complete crystallization might have set in, transforming the sample into a solid.

Another situation where one would not expect crystal nanoparticles to reduce the surface tension is when the crystallization results in a particle that has too many noncrystallized polymer strands extending from it. This would be an *in situ* formed sterically stabilized nanoparticle. As such, it would be expected to disperse more uniformly in the polymer melt²⁰ and would be better modeled as a star polymer or at least a linear polymer with greater contour volume (longer) than the host polymer (it should be of equal or greater contour volume since the crystallization could join several polymers together). The groups of Russell,²¹ Fredrickson,²² Archer,^{23,24} and Sauer²⁵ have discussed theoretical and experimental results for polydisperse polymer melts and linear/star mixtures. In such cases, these authors have shown that the longer polymers (here representing loosely crystallized particles) would avoid the surface and, since the average molecular weight would be higher than a monodisperse polymer system (noncrystallized system), the surface tension would increase rather than decrease.¹⁰ This makes sense since in this picture the “particles” (longer polymers or star polymers) would have *more* conformational entropy than the noncrystallized polymers—they would have fewer free ends after crystallizing together. It is known that the architecture of a polymer affects its localization with respect to a surface with molecules having fewer free ends avoiding the surface,^{21–26} free ends have less configurational entropy to lose near a surface. The experimental situation of Wei *et al.*² is modeled in this paper by nanoparticles that are an extreme limit of this effect: a single segment “polymer” that is purely an end-segment and that therefore has a strong

entropic affinity to the surface. Overall, then, if the mechanism of reduction in surface tension observed experimentally in Ref. 2 is indeed due to the formation of crystallized nanoparticles, we can set some limits on the nature of the particles. They should have a spatial extent that is smaller or of the same order of magnitude as the polymer and they should be reasonably crystallized to avoid the effects of steric stabilization.

We have provided evidence in support of various phenomena associated with crystal nanoparticles locating at the polymer surface, but this evidence is in the form of SCFT calculations, which are equilibrium results.²⁷ It is therefore not clear from this work how nanoparticles would get to the surface; it is only clear that they would be thermodynamically preferred there. It is unlikely that they could form and then migrate to the surface. It may be possible that since, in equilibrium, they are more likely to be found near the surface and that this translates into a higher probability of the particles forming there. This will require further research. For the present, although kinetic factors may be important in this system, they are beyond the scope of this work.

IV. CONCLUSIONS

The hypothesis that nanoparticles formed through crystallization in the polymer melt should locate preferentially at the polymer surface where they reduce the surface tension is shown to be possible and thermodynamically preferred. The particle spatial extent should not be much greater than the unperturbed polymer size, or there would not be a significant reduction of surface tension. If they are large enough, there could even be an increase in surface tension. The particles should not have too much stray polymer “fur” hanging off them, or, again, there may not be a reduction of surface tension and there could be an increase of surface tension.

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