Entropic Trapping of Additive Particles at Polymer Surfaces and Interfaces

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Abstract

I consider the possibility that Gaussian random walk statistics are sufficient to trap nanoscopic additives at either a polymer interface or surface. When an additive particle goes to the free surface, two portions of the polymer surface energy behave quite differently. The purely enthalpic contribution increases the overall free energy when the additive protrudes above the level of the polymer matrix. The entropic part of the surface energy arising from constraints that segments near a surface can’t cross it, is partly relaxed when the additive moves to the free surface. These two portions of the polymer surface energy determine the equilibrium wetting angle formed between the additive and the polymer matrix, the measurement of which in an experiment would allow an independent determination of each piece of the polymer surface energy.
1 Introduction

The addition of small, nanoscopic additives to polymer matrices is quite important technologically and scientifically. Even when the particles have no special properties other than hard exclusions of polymer chains, they are useful in improving the toughness of plastic components by preventing large-scale disruptions of the matrix, for instance near a crack tip. They can also pin local interfaces in a phase segregating polymer blend, providing a mechanism for halting the growth of domains and making blends behave more compatibly.

Using polymer patterns as templates for inorganic and metallic depositions is another example involving polymers and hard additive particles. Here, microsegregation or other patterns in a polymer film can be selectively decorated by the evaporation of metal. I am particularly interested in these deposition processes with high surface-energy metal particles that reside at the free surface of a polymer thin film. Usually, patterned films cooled below their glass transition temperatures are used for such purposes, with the goal of keeping the polymer pattern static and allowing the additive particles to decorate the top of an impenetrable polymer layer. The vicinity of the free surface of such patterned films can often have a deep supression of $T_g$, giving the metallic elements a chance to interact with a rubbery or molten polymer layer. However, even materials that would be expected to be wet with polymers in bulk situations at temperatures well above the bulk value of $T_g$ seem upon deposition to remain pinned at the free polymer surface rather than to penetrate to the interior of the films. When a further layer of polymer is floated upon these particles, these trapped polymers are free to diffuse along the film normal. When the floated layer is a different homopolymer, the particles can remain trapped at the interface. When the particles wet neither of the polymer involved, they act as a compatibilizer, replacing polymer-polymer contacts with polymer-particle contacts.

To understand the fundamental physical effects driving these particles toward free surfaces, the basic contributions to the bare polymer surface energy will be crucial to understand. These
contributions have typically two parts, giving partial surface energies usually the same order of magnitude \[14\]. Firstly, there is the enthalpic contribution to the polymer surface energy, arising from short-range dispersion effects, contributing \[\gamma'_p \equiv w_p / \sigma^2\] to the overall polymer surface energy. Roughly speaking, every segment at the interface costs an interaction energy \(w_p\) compared to the reference of pure melt polymer. Here, \(\sigma\) is a typical polymer segment length scale. Another interaction is \(\gamma'_{ps} \equiv w_{ps} / \sigma^2\) as well as \(\gamma'_s \equiv w_s / \sigma^2\), giving the enthalpic contribution to the surface energy between polymer and the sphere, and the sphere and vacuum respectively. Usually, \(w_p \approx w_{ps}\), with both much smaller than the energy scale for sphere-vacuum contacts, \(w_s\). There is a strong thermodynamic driving force keeping the additive particle surrounded with at least a thin skin of polymer segments \[7\] \[8\].

The other main contribution to the polymer surface energy is entirely entropic in nature, and arises from the constraint placed on a random walk polymer configuration in the vicinity of an impenetrable interface \[14\]. Given a polymer segment near an interface, the adjoining polymer segments must avoid crossing the forbidden surface. This constraint can be thought of as an external bias applied to the chain random walks, with the bias energy approximately equal to \(k_B T\) per constrained surface monomer. Here, \(k_B\) is Boltzmann’s constant, and \(T\) is the temperature. Silberberg determined the correct weighting from an ingenious symmetry argument, but the overall effect is entirely entropic, and contributes to the surface energy of \(\gamma_e \equiv k_B T / \sigma^2\). The total polymer surface energy, \(\gamma_p\), is then given by \(\gamma_p = \gamma'_p + \gamma_e\). Typically, \(\gamma'_p \approx \gamma_e\), so that entropic and enthalpic effects are equally important in determining \(\gamma_p\). It may be possible to separate these two effects, using one to drive the creation of new surface area, while using the other to stabilize the particle position. Analyzing how these contributions affect the deposition or evaporation of metallic particles onto a polymer melt is the main goal of this paper.

As such, the scenario of evaporating metallic particles onto a polymer film is far from a new one, and has been studied in mean field models \[15\] and interaction-site monte-carlo simulations \[16\]. Melt-particle interactions have been studied in very detailed bead-spring simulations \[17\].
While the constraints placed on polymer conformations are dealt with explicitly in an early mean field theory [15], that theory is most applicable to broad interfaces which dilutes the importance of the segment-swapping contribution to the surface energy, and therefore underestimates the entropic stabilizing effect. Interestingly, this theory does predict that fully wet particles should be stabilized near a polymer free surface at a range of approximately the particle radius. Studies aimed at studying the formation of nanoclusters of metallic particles after being embedded in the upper reaches of a polymer film also show a marked tendency for the growing metallic particles to cluster at the free surface as they grow, but it should be noted that this particular simulation does not treat the polymer conformational entropy well, and therefore a layer of entropically active wetting segments is absent in the equilibrated system. The very through simulations in [17] investigate the interactions of moderately long polymer bead-spring chains with hard additive icosahedral particles. They find that polymer chains in contact with the the surfaces of these particles are indeed aligned along the particle surfaces, indicating that Silberberg’s notion of the entropic contributions to the polymer surface energy are operating.

In a much simpler theory focusing on the Silberberg idea, I consider impenetrable additive particles wetted with polymer segments.[7, 8] The question is *do such particles have an enhanced surface activity?* The quantitative prediction is that generally wetting particles are surface active, and to a degree that will allow the measurement of the relative size of the entropic and enthalpic contributions to the system free energy. I will consider two simple, though related cases. The first is a single spherical wetting particle in the vicinity of the free surface of a polymer melt, as in fig. [1] part C. The second case has a wetting, though partially selective particle near the interface between incompatible polymer melts. Even when the particles are preferentially wet with a single one of the polymers involved, there are indeed situations in which entropic gains keep the particles trapped at the interface. In the special case in which the spherical particles are deposited upon a polymer melt, and then covered with an amorphous layer of the same polymer, the entropic pinning of the single particles is released, driving the particles away from the original interface, as is observed.
Figure 1: The surface of a typical polymer melt. Chains with at least one monomer at the surface are shown as bold lines. Each monomer within the shaded region at the free surface represents a free energy cost of $k_B T$ to maintain the polymer conformations so that they do not cross the free surface. The bold line represents enthalpic, and the shaded region represents entropic, polymer-vacuum contacts. A) bare melt, B) particle in the bulk, and C) particle surface stabilized by entropic contacts.

experimentally [6]. It should be noted that the argument here is entirely equilibrium in character, and does not depend on the presence of any other additive particles. Thus, the effect described here does not depend on bridging interactions between adjacent particles [19].

After describing the effect for a single surface, I will treat the case of a polymer-polymer interface. After a short discussion, I will draw my conclusions.

2 Free Surface

As in fig. I part A a polymer melt surface is characterized by a strong constraint on the conformations of all the polymer segments laying within a polymer segment size, $\sigma$, of the interface. Roughly speaking, for each such segment at the interface, the random walk configuration of its chain must be biased so that both the preceding and the subsequent monomers on the chain are prevented from crossing the interface. In fig. I part A the darkly drawn polymers are those which have at least one monomer segment at the surface. All of the monomer segments within the shaded region represent monomers located at the surface, and each of these incurs an entropic cost of $k_B T$ in order to bias the random walk of its parent chain to respect the interface. Each of the segments at
the free surface also are in contact with vacuum on one side, and an semi-infinite sea of monomer on the other. If the total surface area of the free surface of the melt is $L^2$, then the free energy associated with maintaining this interface is:

$$F_{surf} = \frac{L^2}{\pi \sigma} k_B T \left(1 + \frac{w_p}{k_B T}\right) \equiv L^2 \gamma,$$

(1)
where $w_p$ is the energy to have a single monomer segment in contact with vacuum, and $\gamma$ is the surface energy of the polymer. Clearly

$$\gamma = \gamma_{entropic} + \gamma_{enthalpic},$$

(2)
with

$$\gamma_{entropic} \equiv \gamma_e = \frac{k_B T}{\pi \sigma^2} \quad \text{and} \quad \gamma_{enthalpic} \equiv \gamma'_p = \frac{w_p}{\pi \sigma^2}.$$  

(3)

The free energy involving the presence of the additive particle, a sphere of radius $R$ is:

$$F_{sphere} = \frac{4 \pi R^2}{\pi \sigma^2} k_B T \left(1 + \frac{w_{ps}}{k_B T}\right).$$

(4)
Here, $w_{ps}$ is the energy cost per unit monomer to make a polymer-sphere contact. In principle, there is another energy in the problem, $w_s$, the energy needed to make a vacuum-particle contact for each polymer-segment sized patch of surface. We assume, as is generally the case when the additive particles are metallic [8], that

$$w_p \approx w_{ps} \ll w_s$$

(5)
and the additive particle are always wet with polymer segments.

Polymer segments near the sphere also endure entropic constraints. Up to terms of order $\sigma/R$ this entropic cost is exactly the same for the polymer free surface, and represents the term in $F_{sphere}$ that scales strictly as $k_B T$, as in eq. [4] Altogether, the total polymer + sphere free energy is:

$$F_{in} = F_{surf} + F_{sphere} = L^2 (\gamma_e + \gamma'_p) + 4 \pi R^2 (\gamma_e + \gamma'_p),$$

(6)
when the sphere is free to explore the interior of the matrix..
Figure 2: (A) Definitions of several quantities in the text are shown here schematically. This height of protrusion, \( h \), the particle radius \( R \) and the wetting angle \( \theta \) are shown. (B) Young’s law as applied at the polymer-metal contact.

Now, consider a situation as in fig. 1 part C, where the sphere protrudes some distance above the level of the polymer matrix. For definiteness, let us suppose that the sphere protrudes a distance \( 0 < h < 2R \) above the polymer matrix, so that the portion of the sphere protruding covers an azimuthal angle \( \theta \) as in fig. 2. When \( \theta = 0 \), the particle has just been brought to contact with the free surface, and \( h = R(1 - \cos \theta) = 0 \). When \( \theta = \pi \), \( h = 2R \), and the particle has been expelled from the matrix. The particle occupies a circular patch at the original interface with a radius equal to \( R \sin \theta \), so the contribution from the surface of the unperturbed polymer matrix is:

\[
F_{\text{surf}} = (L^2 - \pi R^2 \sin^2 \theta)(\gamma_e + \gamma'_p),
\]

or, using elementary trigonometry,

\[
F_{\text{surf}}(h) = (L^2 - \pi 2hR + \pi h^2)(\gamma_e + \gamma'_p).
\]

This represents the entropic and enthalpic contributions from the flat polymer-vacuum interface.

The contribution to the system free energy depending on the presence of the sphere is also easy to estimate. Using the fact that the sphere is still completely wet with polymer segments, and that each of these segments still represents constraints on the chain conformations of \( k_B T \) per monomer, the entropic contribution to the sphere interaction is still exactly the same as if it were completely
immersed in the polymer melt. The polymer-sphere contacts are exactly the same as well, but there are now quite a few more polymer-vacuum contacts to account for. In all:

\[ F_{\text{sphere}}(h) = 4\pi R^2(\gamma_e + \gamma_{\text{ps}}) + 2\pi Rh\gamma_p \]  

Thus, the total free energy is

\[ F_{\text{out}}(h) = F_{\text{surf}}(h) + F_{\text{sphere}}(h), \]

the free energy associated with having the particles a distance \( h \) “out” of the polymer melt.

It only remains to determine the equilibrium value for \( h \), which can be found by minimizing \( \Delta F(h) = F_{\text{in}} - F_{\text{out}}(h) \):

\[ \Delta F(h) = (\gamma_e + \gamma_p)\pi(h^2 - 2hR) + 2\pi Rh\gamma_p. \]

This relation can be essentially read off from the schematic in fig. 1 part C. The dark line at the surface of the polymer melt marks polymer segment-vacuum contacts, and the shaded region represents the volume in which entropic biases are required to keep the chains from crossing a surface. There is less shaded area when the particle protrudes above the melt, but with a cost in more polymer-vacuum contacts.

Minimizing \( \Delta F \) with respect to \( h \) yields the equilibrium value for \( h \):

\[ h_{\text{eq}} = R \frac{\gamma_e}{\gamma_e + \gamma_p}. \]

The wetting angle that the particle makes with the polymer matrix is simply \( \theta \), with an equilibrium value of:

\[ \cos \theta_{\text{eq}} = \frac{\gamma_p}{\gamma_e + \gamma_p}, \]

specifying the usual equilibrium contact angle. Thus, the polymer coated particle acts just as Young’s Law says it should, as applied to the effective three-component interface consisting of the polymer melt (with surface tension \( \gamma_1 = \gamma_p + \gamma_e \)), the portion of the particle immersed in the melt with an effective surface tension \( \gamma_2 = \gamma_{\text{ps}} + \gamma_e \) and the portion of the particle protruding from the
surface of the melt with a surface tension of $\gamma_3 = \gamma_p' + \gamma_e + \gamma_{ps}$. According to Young’s law, the wetting angle $\theta$ obeys:

$$\cos \theta = \frac{\gamma_2 - \gamma_3}{\gamma_1}, \quad (14)$$

agreeing with the result in eq. [13].

Thus, measurements of $h$ and $R$ and $\gamma$ disentangle the two contributions to the bare polymer surface energy, and allows us to resolve its two parts. In terms of the measurable quantities, we have

$$\gamma_p' = \frac{h}{R} \quad \text{(enthalpic), and} \quad (15)$$

$$\gamma_e = \gamma (1 - \frac{h}{R}) \quad \text{(entropic).} \quad (16)$$

Indeed, in the system of [7], the protrusion of silver nanoparticles indicates that the $\gamma_e/\gamma_p'$ is on the order of 2. From the form of eq. [16], a number of interesting predictions are possible. First, the observable range of $h$ is $0 < h < R$, so that the additive particle can either truly wet with the polymer, and have virtually no surface activity ($h = 0, \theta = 0$) up to $h = R, \theta = \pi/2$. The most dewetting configuration possible here is when $\gamma_p = 0$ so that there is no enthalpic penalty for increasing $h$. In this limit, we see that the additive particles act effectively as neutrally wetting particles.

For nonzero $h$, the amount of free energy pinning the particles to the free surface can be estimated:

$$F_{\text{pin}} = \Delta F(h_{eq}) = -\pi R^2 \gamma \left| \frac{\gamma_e}{\gamma} \right|^2 = -\pi R^2 \gamma (1 - \mu)^2. \quad (17)$$

Clearly, when the enthalpic contribution to $\gamma$ dominates and $\gamma_e \ll \gamma$, (so that $\mu \approx 1$) the energy pinning the spheres to the free surface can become quite small, so that particle can readily leave the surface and explore the interior of the melt. If the melt is a film with thickness $H$, the translational entropy gained by the sphere when it leaves the surface and enters the films is

$$F_{\text{trans}} \approx \ln \frac{H}{R}. \quad (18)$$
so that the fraction of bound spheres vs. interior spheres can be calculated for any given $H$ through:

$$N_{\text{surf}} = N_{\text{tot}} \frac{\lambda^2}{1 + \lambda^2}$$

$$N_{\text{free}} \sim N_{\text{tot}} \frac{1}{1 + \lambda^2},$$

where

$$\lambda = \frac{H}{R} \exp\left(-\frac{F_{\text{pin}}}{k_B T}\right),$$

and $N_{\text{tot}}$ is the total number of deposited particles in the system. In the discussion, below, I describe the basic sizes of these effects. It should be kept in mind, however, that these particle are driven toward the interface by an entirely entropic effect, which would be removed if the vacuum above the sample were replaced with an identical layer of molten polymer. Also, it should be kept in mind that I am interested here in the ultimate equilibrium situation, and this argument completely ignores how long this equilibrium might take to be effected. Long-lived metastable states can change the experimentally observable phenomena (for example, the situation in which polymer segments have not yet had enough time to envelop the additive particle which is initially placed on the surface). Also, this is a single-particle argument. Interactions between the additives can lead to further surface-active effects that have been discussed elsewhere \[\text{[18]}\].

### 3 Interface

Now, I shall turn to the complimentary situation in which the additive particle is placed at the interface between incompatible polymer melts, $A$ and $B$. The surface energy between these two polymers is $\gamma_{AB}$. The bare particle surface energy is not relevant in this case, but we now have two interactions between polymers and the particle: $\gamma_{As}$ is the surface energy between polymer $A$ and the particle, and likewise for $B$. This energy has entropic and enthalpic parts as well:

$$\gamma_{As} = \frac{k_B T}{\sigma^2} + \frac{w_{As}}{\sigma^2} = \gamma_e + \gamma_{As}$$

Similar quantities can be defined for $B$ polymer, and for the $AB$ interfacial tension.
There are two physically distinct situations to consider, the case in which the particle wets completely with, say $B$ type monomers, and protrudes slightly into the upper $A$ region, and the more usual case in which the particle is partially wet with both $A$ and $B$ monomers. To determine which is the case requires a simple comparison of free energies.

When the particle partially wets with $A$ and $B$ monomers, I again define $h$ to be the distance the particle protrudes into the $A$ region. The free energy of the partially wetting particle is:

$$F_{\text{partial}}(h) = (\gamma'_{AB} + \gamma_e)\pi(h^2 - hR) + 4\pi R^2 \gamma_e + 2\pi h \gamma'_{As} + (4\pi R^2 - 2\pi hR)\gamma'_{Bs}. \quad (23)$$

These terms correspond to the contribution from the $AB$ interface occupied by the particle, the entropic surface energy of the particle, the $A$-particle and $B$-particle surface contacts. The equilibrium position of the particle, $h$, is found from minimizing $F_{\text{partial}}(h)$:

$$h_{eq} = R \frac{\gamma'_{AB} - \gamma'_A + \gamma'_B + \gamma''_A}{\gamma'_{AB} + \gamma_e} = R \frac{\gamma_{AB} - \gamma_{As} + \gamma_{Bs}}{\gamma_{AB}}, \quad (24)$$

again a manifestation of Young’s Law. As usual, we can define a wetting parameter,

$$\varepsilon = \frac{\gamma_A - \gamma_B}{\gamma_{AB}} \quad (25)$$

so that $h_{eq} = (1 - \varepsilon)R$. The free energy for this partially wetting case is thus:

$$F_{\text{partial}} = -\pi R^2 \gamma_{AB}(1 - \varepsilon)^2 + 4\pi R^2 \gamma_{Bs}. \quad (26)$$

Now, assume that the particles are wet with $B$-type fluid. The free energy to maintain the particle protruding a distance $h$ into the upper $A$ fluid is:

$$F_{\text{B-wet}}(h) = \gamma_{AB}\pi(h^2 - Rh) + 4\pi R^2 \gamma_{Bs} + 2\pi h \gamma'_{As}. \quad (27)$$

This represents exactly the same physical situation as is present in Section 2, with the $A$ polymer playing the role of the vacuum. Immediately, then, we have:

$$h_{eq} = R \frac{\gamma_e}{\gamma'_{AB} + \gamma_e}. \quad (28)$$
The equilibrium free energy in this case is therefore:

\[ F_{B\text{-}wet} = -\pi R^2 \gamma_{AB}(1 - \mu)^2 + 4\pi R^2 \gamma_{BS} \]  

(29)

where the appropriate wetting parameter here is

\[ \mu = \frac{\gamma'_s}{\gamma'_s + \gamma_e}. \]  

(30)

Thus, there is a transition between the wetting and non-wetting situations when

\[(\varepsilon - 1)^2 = (\mu - 1)^2, \]  

(31)

the only relevant root of which is \( \mu = \varepsilon \). That is, as long as \( 0 < \varepsilon < \mu \), the particle will be partially wet, and \( \mu < \varepsilon < 1 \) will cause the particle to wet with \( B \) monomers, although it is still confined to the \( AB \) interface by the entropic effect. Clearly, when \( \varepsilon = 0 \), the equilibrium situation is that of neutrally wetting particles, half covered with \( A \) monomers, half covered with \( B \) monomers, exactly straddling the \( AB \) interface. As \( \varepsilon \) is increased, the particle moves toward the \( B \) domain with \( h < R \), until a transition to the particle wet with \( B \) monomers is achieved, when the requirement of eq. 31 is met. As in the case of particles residing at a free surface, an estimate can be made of the equilibrium density of particles at the interface vs. the equilibrium density of particles dispersed into the \( B \) domain. When \( \varepsilon < 0 \), the situation is exactly the same, except the transition is toward the particle wetting with \( A \) monomers, with \( \gamma_{BS} \rightarrow \gamma_{AS} \) in the reference energy. The situation is shown schematically in fig. 3.

Thus, the sequence of events is as follows. When high surface energy particles are evaporated or deposited on the surface of a polymer melt, they will first decorate themselves with a mass of restricted monomer, creating a skin of \( B \) monomer, say. If the monomer-particle interaction is not strong (so that the entropic energy dominates the equilibrium) the particles will be essentially trapped at the surface, even upon annealing. If more \( B \) monomer is spun onto the system in a thick blanket, or if a thin film is floated onto the existing \( B \) surface, the entropic stabilization of the
Figure 3: Given the entropic wetting parameter $\mu \equiv \cos \theta$ for the fully-B wet sphere, if the partial wetting parameter $\varepsilon$ satisfies $|\varepsilon| < |\mu|$, then the particle partially wets. Otherwise, and any further increase in $|\varepsilon|$ is irrelevant for determining the energy binding the particle to the interface.
particles toward the interface will disappear, and the particles will start to engage in restricted diffusion normal to the original interface (at possibly a very small rate, as the particles in equilibrium resemble a star polymer, with many protruding loops and long arms of bound polymer). If, on the other hand, a different type of monomer is deposited on the surface, the particles may or may not still be trapped at the surface. Very incompatible polymers (γ_{AB} is very large) that neutrally wet the particles (γ_{As} ≈ γ_{Bs}) will be entropically trapped at the interface. The particles act as compatibilizers. This state of affairs can continue up to and even past the point where the particle wets with B polymer.

4 Discussion

The scale of the energy trapping a typical particle at the free surface could easily lead to practical trapping of even wetted particles. The basic scale of the effect is \( R^2 \gamma_{AB} \). For a \( R = 10\text{nm} \) gold sphere at a free polystyrene surface, this energy scale is \( R^2 \gamma_{PS} \approx (10\text{nm})^2 k_B T / (1\text{nm})^2 \), or approximately \( 100k_B T \). Therefore, a particle is stabilized by a factor of \( 100k_B T (1 - \varepsilon)^2 \). For a typical flexible polymer, \( \gamma_e \approx \gamma_p \), so that \( \varepsilon \approx 1/2 \). Such a particle is therefore trapped by an energy of approximately \( 25k_B T \) per particle, and they protrude approximately \( h = 1/2R = 5\text{nm} \) above the polystyrene surface. Under normal circumstances, it would be virtually impossible to observe such a particle leave the A surface. The particles are thus, for all intents, irreversibly attached to the free surface, although their lateral motion is unrestricted. As mentioned above, coating the sphere-polymer system with another polystyrene layer will result in the particle being freed from the surface, and engaging in diffusive motion along the film normal.

However, if a different polymer is spread on the surface of the metal polymer system, we have to compare the wetting parameter, \( \varepsilon \) for the A – B particle system to the entropic wetting parameter \( \mu \) for the AB interface. Ideal conditions for unpinning of the spheres from the AB interface would require \( \varepsilon \approx \mu \approx 1 \), and we can expect such conditions to occur regularly for very selective interactions that are dominated by \( w_{AS} \) and \( w_{BS} \). Note that the critical element here has nothing to do with
the incompatibility of the A and B fluids per-se, but is sensitive to the interactions of the polymer with the embedded sphere.

The entropic effect here stabilizing the particles at the interface can be thought of an as extreme form of the depletion attraction of colloidal systems [20]. In that case, a solid sphere excludes the colloids from a spherical shell of size $r$ around the sphere of radius $R$, where the colloid radius is $r$. When two such spheres approach, the overlap of their exclusion shells results in fewer constraints that need to be maintained in the system. In the current context, the colloidal particles are represented by the polymer segments at the interfaces. The particles sitting at the interface remove a circular patch of constraints that would otherwise have to be enforced, at the expense of making energetically unfavorable contacts. Thus, we can expect that spheres that have managed to escape the surface and explore the interior of the film will be attracted by an effective potential potential with range $\approx \sigma$ which counts up effectively the number of redundant constraints when two spheres are in contact. The size of the attraction is therefore

$$ F_{\text{attract}} \approx \sqrt{\frac{R}{\sigma}} k_B T. $$

(32)

Thus, for the 10nm gold spheres considered above, the size of the attraction is approximately $k_B T$, resulting in moderately sized clusters of particles, or indeed a much weaker adsorption of these particles at a solid-polymer interface.

The basic assumption here is that the polymer segments have sufficient time to envelop a particle deposited atop a polymer film [7,8]. Even when the film itself is glassy, the segregation of free ends in the melt [21] and the extra free volume expected at a free surface can result in a significant reduction in both the glass transition temperature and the effects of polymer chain topology [22].

## 5 Conclusion

I have demonstrated an entropic attraction resulting from constrained chain trajectories in the presence of a hard surface which can result in the trapping of polymer particles at both a free surface
and at a polymer-polymer interface. The size of the effect can easily be several tens of $k_B T$ per particle for nanoscopic particles, and can even result in a few $k_B T$ attractive short-ranged contact interaction between particles wholly within the polymer matrix.

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