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Stabilizing grafted colloids in a polymer melt: Favorable enthalpic interactions

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The interactions between spherical colloids covered with end-grafted polymers (brushes) immersed in a polymer melt are studied theoretically. We show that attractive enthalpic interactions between the two polymer species, characterized by a negative Flory parameter ($\chi<0$), can stabilize the colloidal dispersion. The stabilizing mechanism is a result of a structural change from a dry brush, where the melt chains do not penetrate deeply into the brush, to a wet brush, where the free chains penetrate the brush and force the grafted chains to extend into the melt.

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INTRODUCTION

Mixtures of colloids and polymers provide an important class of advanced materials with a wide range of mechanical, adhesive, and optical properties. In many applications polymer chains are end-grafted to the colloid surface, forming what is usually referred to as a *polymer brush* [1–3]. When the grafted particles are immersed in solution steric interactions acting between the grafted chains stabilize the colloidal suspension against attractive van der Waals interactions. Unfortunately, when the embedding medium is a polymer melt this mechanism does not always work. Due to subtle entropic effects the melt chains are expelled from the grafted layer, even if they are chemically identical to the grafted chains [2,4–8], and the intercolloidal interactions become attractive [9]. This attraction limits our ability to produce new materials where the contrast between the colloidal and polymeric properties might have advantageous implications. The aim of this Rapid Communication is to put forward a simple mechanism of stabilizing the grafted colloids in the surrounding polymer melt by means of a favorable enthalpic attraction between the grafted and free chains. A number of such systems exists, e.g., poly(methyl methacrylate) (PMMA) and poly(vinyl chloride) (PVC), poly(styrene) (PS), and poly(2,6-dimethyl-1,4-phenylene oxide) (PXE), etc. In practice, these specific interactions have been used, for example, in the design of impact modifiers. Here, we quantify this effect and provide simple criteria for predicting the intercolloidal interactions.

Colloidal systems are not the only example where enthalpic interactions compete with entropy in determining the structure of the material. Similar behavior can be also observed in mixtures of homopolymers and diblock copolymers [10]. Block copolymer chains are formed from two (or more) different polymers that are tethered together at a single point. For example, an AB diblock copolymer consists of a sequence of A monomers followed by a sequence of B monomers. Depending on the incompatibility of the two blocks these systems have a tendency to segregate into A-rich and B-rich mesophases [11]. The resulting phases include lamellar structures of alternating A-rich and B-rich stripes, hexagonal phases of cylindrical domains, cubic phases of spherical domains, etc. Triblock copolymers (e.g., ABA or ABC) exhibit an even larger variety of phases [11]. When homopolymers are mixed with copolymers the mixture may exhibit very interesting physical properties (e.g., mechanical, optical, etc.) and can be used as, e.g., super tough materials or photonic devices [12]. Many of these properties depend crucially on the special mesostructure of the material, and we would like to be able to determine under what conditions homopolymers can be added without destabilizing the structure.

Our model system consists of two grafted spheres immersed in a polymer melt [Fig. 1(a)]. Typically, the radii R of the colloids is of the order of microns while the attractive interactions appear at separations w of order of 1 to 10 nm. Such a separation of length scales allows us to study first a simpler case of two flat surfaces at a distance w from each other [Fig. 1(b)] and only then include curvature effects. Each surface carries a dense layer of σ/a^2 end-grafted chains per unit area, a being the effective size of a single monomer. The surfaces are immersed in a melt of mobile polymer chains, the indices of polymerization of the grafted and free chains denoted N and P, respectively. In the present study we restrict the discussion to the limit of long free chains $P\gtrsim N$ and to high grafting densities, while the more general case

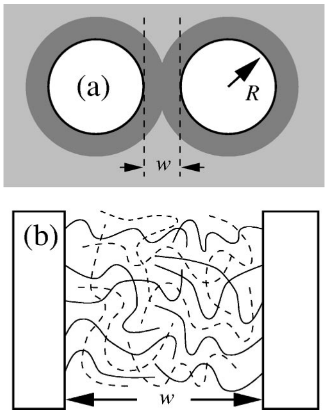

FIG. 1. Schematic views of (a) two grafted colloids immersed in a polymer melt and (b) two interacting flat surfaces in a polymer melt. The solid (dashed) lines are the grafted (free) chains.

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*Present address: Department of Chemistry and Biochemistry, UCLA, 607 C. Young Dr. East, Los Angeles, CA 90095-1569. Email: itamar@chem.ucla.edu will be discussed elsewhere [13]. For simplicity we assume that the different monomer species are all of the same size. We further assume that the different monomers have the same volume a^3, so that the incompressibility of the polymer melt can be expressed as $\phi_N + \phi_P = 1$, where $\phi_N(x)$ and $\phi_P(x)$ are the local volume fractions of grafted and free chains, respectively. The enthalpic interaction between the different monomer species (in units of the thermal energy $k_B T$) is characterized by the Flory interaction parameter χ.

PARABOLIC APPROXIMATION

In order to demonstrate the effect of a negative χ parameter we implement a variation of the parabolic approximation [3], valid in the strong stretching limit of the grafted chains. In this limit, the mean-field potential felt by a single chain $\mu_N(x)$ is a quadratic function of the distance x from the nearest surface [14]. Taking into account the symmetry around the mid-plane one can write

$$\beta\mu_N(x) = \begin{cases} A - Bx^2 & 0 \leqslant x \leqslant w/2 \\ A - B(w-x)^2 & w/2 \leqslant x \leqslant w, \end{cases} \tag{1}$$

where $B = 3\pi^2/8N^2a^2$, $A(w)$ is an integration constant to be determined later, and $\beta = 1/k_B T$. This potential has to be equal to the sum of the different interactions of the grafted chain with its environment. The latter can be obtained from the excess free energy associated with the free chains $V_P = (1/a^3)\int dx\, v_P(x)$, where

$$\beta v_P = \frac{a^2}{24\phi_P(x)}|\phi_P'(x)|^2 + \frac{\phi_P(x)}{P}[\ln\phi_P - 1] + \chi\phi_N(x)\phi_P(x). \tag{2}$$

The first term is the elastic energy of the free polymer chains, the second term is their translational entropy, and the last term is the enthalpic interaction between the grafted and free chains.

Taking into account the incompressibility constraint the mean-field potential can be obtained from the variation of the interaction energy $\mu_N(x) = -\delta V_P/\delta\phi_N$, which yields

$$\beta\mu_N(x) = -\frac{a^2}{24[1-\phi_N(x)]}\left[\frac{1}{1-\phi_N(x)}|\phi_N'(x)|^2 + 2\phi_N''(x)\right] - \frac{1}{P}\ln[1-\phi_N(x)] - 2\chi\phi_N(x). \tag{3}$$

Please note that due to the incompressibility of the polymer melt the last term has the same form as an effective excluded volume contribution with $v_{\mathrm{eff}} \simeq 2|\chi|a^3$. The above equation combined with Eq. (1) defines a differential equation for $\phi_N(x)$ in the interval $0 \leqslant x \leqslant w$, to be solved numerically. Since there is one free parameter, $A(w)$, three constraints are required. These are provided by mass conservation, $N\sigma a = \int dx\, \phi_N(x)$, and by two boundary conditions $\phi_N' = 0$ at $x = 0$ and $\phi_N' = 0$ at $x = w/2$. The former reflects our choice of a neutral surface that is equally indifferent to the two polymer species, while the latter reflects the symmetry of the problem. The free energy of interaction per unit area can then be calculated from

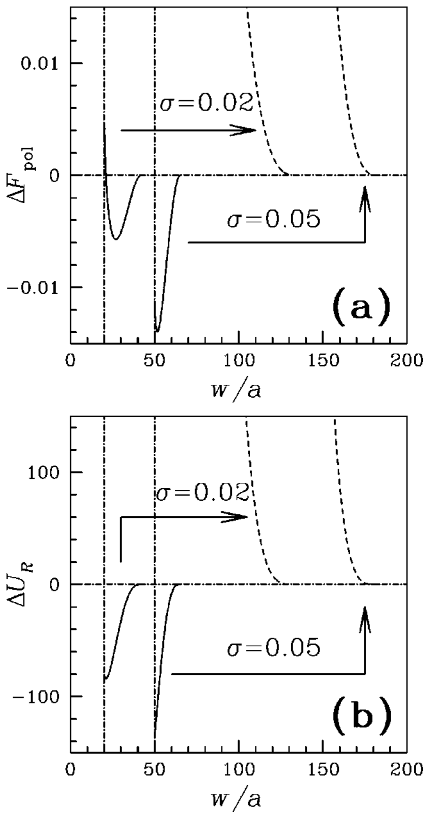

FIG. 2. (a) Excess free energy of interaction per unit area ΔF_{pol} between two flat surfaces (in units of k_BT/a^2) and (b) interaction energy of two grafted colloids ΔU_R (in units of k_BT) as function of the reduced intersurface distance w/a. The two solid curves correspond to $\chi = 0$ with grafting densities $\sigma = 0.02$ and $\sigma = 0.05$. The two dashed curves correspond to the same grafting densities with a negative enthalpic interaction $\chi = -0.15$. The polymerization indices are $N = P = 500$. The radii of the colloids in (b) is $R = 400a$. For clarity, the distances of closest approach ($w = 2N\sigma a$) are indicated by vertical lines at $w = 20a$ and $w = 50a$.

$$F_{\mathrm{pol}}(w) = \frac{1}{a^3}\int_0^w dx\{v_P(x) - \mu_N(x)\phi_N(x)\} + 2k_BT\frac{\sigma}{a^2}NA(w). \tag{4}$$

The above expression results from a transformation from single chain trajectories to an average volume fraction $\phi_N(x)$. The first term is the standard free energy of an order parameter in a local field $\mu_N(x)$, while the last contribution is a reminiscence of the single chain partition function [3].

The effect of a negative χ parameter is demonstrated in Fig. 2(a), where the excess free energy of interaction $\Delta F_{\mathrm{pol}}(w) = F_{\mathrm{pol}}(w) - F_{\mathrm{pol}}(\infty)$ is plotted as function of the intersurface separation w. When the two polymer species are chemically the same (namely, $\chi = 0$) an attractive minimum appears at short distances. This attractive minimum disappears in the presence of attractive enthalpic interactions between the two species ($\chi = -0.15$ in the figure [15]). This behavior is quite general, and below we provide criteria for the transition between attractive and repulsive behavior.

The interaction energy of two colloids can now be estimated using the Derjaguin approximation [16]

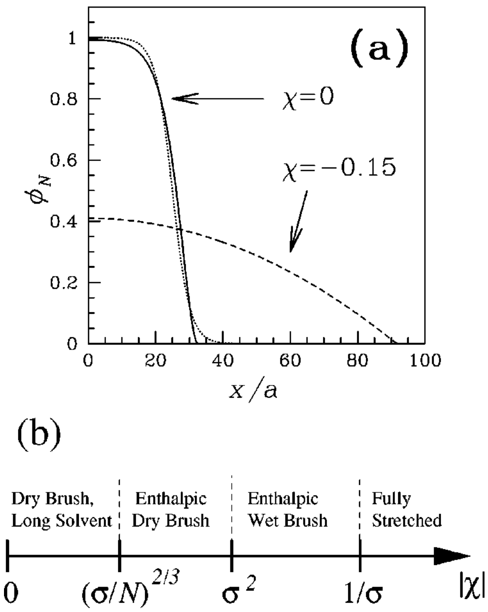

FIG. 3. (a) Volume fraction profiles ϕ_N for $\chi=0$ (solid curve) and $\chi=-0.15$ (dashed curve) as function of the distance from the surface x/a. The physical parameters are $\sigma=0.05$ and $N=P=500$. The dotted line corresponds to the hyperbolic profile with $\lambda=5.15$. (b) Sequence of brush states as function of the negative Flory parameter χ. See text for more details.

$$\Delta U_R(w)=\pi R\int_w^{\infty}dw'\,\Delta F_{\rm pol}(w'). \tag{5}$$

Typical interparticle interaction energies are plotted in Fig. 2(b) for colloids of radii $R=400a$. Clearly, the interparticle attraction disappears when enthalpic interactions are included.

DISCUSSION

Since the nature of the intersurface interactions depends strongly on the shape of the two brushes when they begin to overlap, it is instructive to consider a single brush in contact with a polymer melt [2,4–7]. In Fig. 3(a) two volume fraction profiles of the grafted chains are plotted corresponding to $\chi=0$ and $\chi=-0.15$. Since at high grafting densities the free polymers are too large to penetrate deep into the grafted layer, the grafted layer forms a so-called dry brush whose width $h\simeq N\sigma a$ is determined by packing constraints.

The free polymers only penetrate a narrow layer of width λ, which is determined by the balance between the energy required to squeeze some free chains into the dense brush and the elastic response of the polymer chains to local variations in the density. These can be estimated by assuming a hyperbolic tangent profile for the volume fraction of the grafted chains $\phi_N(x)=(1-\tanh[(x-h)/\lambda])/2$. The elastic contribution to the free energy per unit area is then [10]

$$\beta F_{\rm el}\simeq\frac{1}{12a\lambda}. \tag{6}$$

To first approximation the stretching energy can be estimated by calculating the energy difference between a sharp boxlike brush density and the smooth one [6,10]:

$$\beta F_{\rm pen}\simeq\frac{\pi^4}{32}\frac{\sigma\lambda^2}{Na^4}. \tag{7}$$

Minimizing the total free energy $F_{\rm tot}=F_{\rm el}+F_{\rm pen}$ with respect to λ yields

$$\lambda\simeq\left(\frac{4}{3\pi^4}\right)^{1/3}\left(\frac{N}{\sigma}\right)^{1/3}a. \tag{8}$$

For the parameters of Fig. 3(a) one obtains $\lambda\simeq5.15a$. The corresponding hyperbolic profile is indicated in the figure by a dotted line. The good agreement with the numerical profile demonstrates that indeed $F_{\rm el}$ and $F_{\rm pen}$ are the dominant terms in the free energy.

The effect of enthalpic interactions with a negative χ parameter on the structure of the brush is somewhat analogous to replacing a θ solvent with a good solvent, where mixing of solvent molecules with the grafted polymer chains is encouraged [4]. The enthalpic contribution to the free energy of a dry brush can be easily estimated by

$$\beta F_\chi\simeq\frac{\chi}{a^3}\int dx\,\phi_N(x)\phi_P(x)\simeq\frac{\chi\lambda}{4a^3}. \tag{9}$$

When $|\chi|$ is large enough F_χ exceeds $F_{\rm el}$ and the penetration length λ results now from the competition between F_χ and $F_{\rm pen}$. Thus, for $|\chi|\gtrsim(\pi^8/48)^{1/3}(\sigma/N)^{2/3}$ the brush enters the *enthalpic dry brush* regime [see diagram in Fig. 3(b)], where the size of the brush is still $h\simeq N\sigma a$ but the penetration length follows a different scaling law,

$$\lambda\simeq\frac{4}{\pi^4}\frac{N|\chi|}{\sigma}a. \tag{10}$$

As the enthalpic interactions become stronger, the penetration length λ increases until $\lambda\simeq h$. This happens for

$$|\chi|\simeq\frac{\pi^4}{4}\sigma^2. \tag{11}$$

At this point the free chains penetrate all the way through the brush, while the grafted chains further stretch into the polymer melt. The brush is now in the *enthalpic wet brush* regime [see Fig. 3(b)].

In this regime the enthalpic term dominates the potential $\mu_N(x)$ [Eq. (2)] and the density profile is parabolic, $\phi_N(x)=B(h^2-x^2)/2|\chi|$, while $h=(8/\pi^2)^{1/3}(|\chi|\sigma)^{1/3}Na$. Indeed, for the parameters of Fig. 3(a) with $\chi=-0.15$ one obtains $h\simeq91a$.

When $|\chi|$ is further increased beyond $|\chi|=\pi^2/8\sigma$, the grafted chains reach their maximal possible length $h_{\rm max}=Na$ and we enter the *fully stretched brush* regime [Fig. 3(b)]. The parabolic approximation can be modified in order to take into account the finite extensibility of the chains [17] but this is beyond the scope of the current work.

van der WAALS INTERACTIONS

The repulsion between the grafted layers should be now compared with the van der Waals interactions. These interactions result from sharp variations in the dielectric properties across an interface separating two materials. When two surfaces of material (1) are separated at a distance l by media (2) the nonretarded van der Waals interaction energy can be written as [15]

$$F_{\mathrm{vdW}} = -\frac{A_{121}}{12\pi l^2}. \tag{12}$$

The Hamaker constant A_{121} depends on the static dielectric constants of the two media and their refractive indices. When the surfaces as well as the intervening media are polymers the contrast is usually not very strong and the Hamaker constants are typically of order 10^{-21}J (recall that $1k_BT \simeq 4 \times 10^{-21}$ J).

When two dry brushes interact with each other the contrast at the brush/melt interfaces should be considered in addition to the brush/surface interfaces. The former gives a stronger contribution, since the separation between the two brushes $l = w - 2N\sigma$ is smaller than the bare intersurface separation. In contrast, when two wet brushes interact with each other the brush/melt interface is no longer well defined because of the parabolic concentration profile, which decreases rather moderately to zero [see Fig. 3(a)]. Furthermore, since the free melt chains are present inside the brush, the contrast is much smaller. This leaves only the van der Waals attraction between the bare surfaces, which is too weak at the distance imposed by the swelling of the brush.

CONCLUSIONS

In this paper we have suggested a simple mechanism for stabilizing grafted colloids in a polymer melt. We have shown that a negative χ parameter for the interaction between the grafted polymer chains and the mobile melt chains will induce swelling of the brush and consequently strong interbrush repulsion. This mechanism can have various implications for creating novel polymer-based materials.

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[1] S. Alexander, J. Phys. (France) **38**, 983 (1977).
[2] P. G. de Gennes, Macromolecules **13**, 1069 (1980).
[3] A. N. Semenov, Zh. Éksp. Teor. Fiz. **88**, 1242 (1985) [Sov. Phys. JETP **61**, 733 (1985)]; S. T. Milner, T. A. Witten, and M. E. Cates, Macromolecules **21**, 2610 (1988); E. B. Zhulina, O. V. Borisov, and V. A. Priamitsyn, J. Colloid Interface Sci. **137**, 495 (1990).
[4] H. R. Brown, K. Char, and V. R. Deline, Macromolecules **23**, 3383 (1988).
[5] T. Witten, L. Leibler, and P. Pincus, Macromolecules **23**, 824 (1990).
[6] L. Leibler, A. Ajdari, A. Mourran, G. Coulon, and D. Chatenay, in *OUMS Conference on Ordering in Macromolecular Systems , 1994*, edited by A. Teramoto, M. Kobayashi, and T. Norisuje (Springer-Verlag, Berlin, 1994), p. 301.
[7] M. Aubouy, G. H. Fredickson, P. Pincus, and E. Raphaël, Macromolecules **28**, 2979 (1995); K. S. Shull, *ibid.* **29**, 2659 (1996); C. Ligoure, *ibid.* **29**, 5459 (1996); C. Gay, *ibid.* **30**, 5939 (1997).
[8] A. Budkowski, U. Steiner, J. Klein, and L. J. Fletters, Europhys. Lett. **20**, 499 (1992); R. Yerushalmi-Rozen, J. Klein, and L. J. Fletters, Science **263**, 793 (1994); L. T. Lee, B. J. Factor, F. Rondelez, and M. S. Kent, Faraday Discuss. **139**, 98 (1994).
[9] A. Gast and L. Leibler, Macromolecules **19**, 686 (1986); C. M. Wijmans, E. B. Zhulina, and G. J. Fleer, *ibid.* **27**, 3238 (1994); R. Hasegawa, Y. Aoki, and M. Doi, *ibid.* **29**, 6656 (1996); P. G. Ferreira, A. Ajdari, and L. Leibler, *ibid.* **31**, 3994 (1998).
[10] A. N. Semenov, Macromolecules **25**, 4967 (1992).
[11] For reviews, see M. W. Matsen and M. Schick, Curr. Opin. Colloid Interface Sci. **1**, 329 (1996); F. S. Bates and G. H. Fredrickson, Phys. Today **52** (2), 32 (1999).
[12] E. L. Thomas, Polymer Preprints **40**, 973 (1999).
[13] I. Borukhov and L. Leibler (unpublished).
[14] The parabolic potential can be understood using an analog from classical mechanics where the contour of a grafted chain is mapped onto the trajectory of a pointlike particle in an external potential [3]. The length of the chain is mapped onto the time it takes the particle to reach the surface. The constraint that different chain ends are at different distances from the surface while all chains are of the same length *N*, means that the time it takes for the particle to reach the surface is independent of the starting point. This is a basic feature of an harmonic potential, hence Eq. (1).
[15] We choose a value typical of blends of PMMA and poly(vinylidene fluoride) (PVDF). See, e.g., W. H. Jo and I. H. Kwon, Macromolecules **24**, 3368 (1991); J. C. Canalda, Th. Hoffman, and J. Martinez-Salazar, Polymer **36**, 981 (1995).
[16] J. N. Israelachvili, in *Intermolecular and Surface Forces*, 2nd ed. (Academic Press, London, 1980).
[17] D. F. K. Shim and M. E. Cates, J. Phys. (France) **50**, 3535 (1989).