Comment on "Attraction between Nanoparticles Induced by End-Grafted Homopolymers in Good Solvent"

Roan recently demonstrated that brush-coated spheres can attract each other, contrary to the long-held opinion that grafted polymers only produce repulsive interactions. He concluded this based on self-consistent field theory (SCFT) predictions that showed $F(D) < F(\infty)$, where $F(D)$ represents the free energy of two particles separated by a distance D. The original calculation [1] was somewhat unphysical because it allowed the grafting distribution to adjust as the spheres approached, but the attraction still remained when Roan corrected this oversight [2]. Nevertheless, both calculations contradict the fact that, under good-solvent conditions, the free energy of two interacting particles can *never* be less than that of two isolated particles.

To prove that $F(D) \geq F(\infty)$, we refer to the Landau-Ginzburg free energy functional,

$$F_{\rm LG}[\phi_1, \phi_2; D] = E[\phi_1, \phi_2; D] - TS_1[\phi_1] - TS_2[\phi_2], \quad (1)$$

which provides the free energy for specified brush profiles. Here $\phi_i(\mathbf{r}_i)$ represents the brush profile on the ith particle, where $\mathbf{r}_i$ is a coordinate relative to its center. In the model used by Roan, the internal energy takes the simple form,

$$E[\phi_1, \phi_2; D] = \frac{v k_B T}{2} \int [\phi_1(\mathbf{r}_1) + \phi_2(\mathbf{r}_1 - D\hat{\mathbf{n}})]^2 d\mathbf{r}_1, \quad (2)$$

where $v > 0$ for a good solvent and $\hat{\mathbf{n}}$ is the unit vector pointing from the center of particle 1 to that of particle 2. Within the mean-field approximation, the entropy $S_i[\phi_i]$ of the ith brush depends solely on its own profile ϕ_i and can be calculated in a straightforward manner using SCFT [3].

In terms of the Landau-Ginzburg functional, the free energy of the two particles is

$$F(D) = F_{\rm LG}[\phi_1^*, \phi_2^*; D], \quad (3)$$

where ϕ_1^* and ϕ_2^* are the profiles that minimize $F_{\rm LG}[\phi_1, \phi_2; D]$ subject to the constraint that neither profile enters the volume occupied by either particle. Naturally, ϕ_1^* and ϕ_2^* must also be acceptable profiles for infinite separation, although not necessarily the ones that minimize the Landau-Ginzburg functional, and thus

$$F(\infty) \leq F_{\rm LG}[\phi_1^*, \phi_2^*; \infty]. \quad (4)$$

Increasing the separation to infinity (without changing the profiles) cannot possibly raise the internal energy, or in other words, $E[\phi_1^*, \phi_2^*; \infty] \leq E[\phi_1^*, \phi_2^*; D]$. This follows immediately from the inequality, $[\phi_1^*(\mathbf{r}_1) + \phi_2^*(\mathbf{r}_1 - D\hat{\mathbf{n}})]^2 \geq [\phi_1^*(\mathbf{r}_1)]^2 + [\phi_2^*(\mathbf{r}_1 - D\hat{\mathbf{n}})]^2$, assuming that $v \geq 0$. Since the entropy of the brushes remains constant when the profiles are held fixed, we have

$$F_{\rm LG}[\phi_1^*, \phi_2^*; \infty] \leq F_{\rm LG}[\phi_1^*, \phi_2^*; D]. \quad (5)$$

Combining the inequalities in Eqs. (4) and (5), we obtain

$$F(\infty) \leq F_{\rm LG}[\phi_1^*, \phi_2^*; D] = F(D). \quad (6)$$

This proof is, in fact, reasonably general. It only relies on the mean-field approximation and an interaction energy that corresponds to good solvent (i.e., $v \geq 0$), both of which Roan has assumed in his calculations. Beyond that, the two particles need not be identical or even spherical in shape. The proof applies equally to the original calculation [1], where the grafting points were permitted to slide freely over the surface of the particle, as it does to the subsequent calculations [2,4], where a uniform grafting density was enforced. Although the inequality, $F(D) \geq F(\infty)$, implies that the interaction between the brush-coated particles must be repulsive when they first come into contact (contrary to Refs. [1,2,4]), it is still possible, in principle, for the slope of $F(D)$ to reverse at closer separations without violating the inequality. Hence attractions are not entirely ruled out; they just cannot happen in the way that Roan predicts.

There is good evidence that the erroneous attraction is solely a result of numerical inaccuracy. In Ref. [2], Roan divides his free energy into three contributions, $F = F_v + F_s + F_0$, and finds that the second term is consistently very small. This is in fact a good test that the calculation has been performed correctly, because F_s should equal zero according to the equality,

$$\int G_+(\mathbf{r}, N) d\mathbf{r} = \int G_+(\mathbf{r}', 0) \bar{G}(\mathbf{r}', N) d\mathbf{r}' = 1. \quad (7)$$

This identity is easily proved by expressing the partial partition functions as $G_+(\mathbf{r}, N) = \int G_+(\mathbf{r}', 0) q(\mathbf{r}, \mathbf{r}', N) d\mathbf{r}'$ and $\bar{G}(\mathbf{r}, N) = \int q(\mathbf{r}, \mathbf{r}', N) d\mathbf{r}'$, in terms of the usual propagator, $q(\mathbf{r}, \mathbf{r}', s)$, that satisfies the diffusion equation with the initial condition, $q(\mathbf{r}, \mathbf{r}', 0) = \delta(\mathbf{r} - \mathbf{r}')$.

M. W. Matsen
Department of Physics
University of Reading
Whiteknights
Reading, RG6 6AF, United Kingdom

Received 11 February 2005; published 1 August 2005
DOI: 10.1103/PhysRevLett.95.069801
PACS numbers: 61.41.+e, 61.46.+w, 82.70.Dd

[1] J.-R. Roan, Phys. Rev. Lett. **86**, 001027 (2001).
[2] J.-R. Roan, Phys. Rev. Lett. **87**, 059902(E) (2001).
[3] The SCFT calculation of $F_{\rm LG}[\phi_1, \phi_2; D]$ is much the same as that of $F(D)$, except each brush has its own separate field, $w_i(\mathbf{r}_i)$, which must be adjusted so as to achieve the specified profile, $\phi_i(\mathbf{r}_i)$.
[4] J.-R. Roan and T. Kawakatsu, J. Chem. Phys. **116**, 7295 (2002); J.-R. Roan, Int. J. Mod. Phys. B **17**, 2791 (2003).

