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Steric interaction of an incoming particle with grafted rods: Exact solutions and unusual force profiles

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We examine the problem of a grafted rod or rods compressed by a sphere, concentrating on the steric force exerted by the rods on the sphere. We show that this problem can be solved exactly to yield simple and nontrivial expressions for the repulsive force. In particular, there are several different regimes and in some of these the force exhibits surprising maxima and minima as a function of compression. This has applications to systems of stiff grafted polymers, particularly biopolymers. One experimental realization of our system might be a rod-coil diblock copolymer with the coil grafted to a solid surface.

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The interaction of grafted polymers with hard bodies is of fundamental importance in a number of fields, most notably in colloidal stabilization [1] and cellular biology. Almost all the focus has been on very flexible polymers, and our understanding of these kinds of polymers grafted to surfaces is now very good [2,3]. There have been several attempts to model what happens when single or many grafted polymer chains are compressed by hard bodies [4–14]. This models the situation for polymerically stabilized colloids as well as several biological scenarios such as the interaction between membrane proteins and foreign bodies. These studies have turned up some novel behavior, but have been subject to two major constraints. First, they have concerned, almost entirely, very flexible chains. They are thus not applicable to many biopolymers, which are relatively rigid. Second, they often involve approximations, sometimes of a rather uncontrolled kind. In this Rapid Communication we try and fill this gap by examining the case of a rigid rodlike polymer tethered to a surface and compressed by an incoming sphere. This system has two relatively different features. First, it can be solved exactly to yield mathematically simple solutions. Second, the force curves are nontrivial, and this apparently simple system can exhibit several regimes, often with maxima and minima in the force as a function of compression.

Our geometry is shown in Fig. 1. A rodlike molecule of length L is tethered by one end to a surface. The tether is such that the rod is free to rotate anywhere above the surface with no energy penalty. The rod is then compressed by a sphere of radius R, with surface-to-surface distance between the sphere and the tether surface equal to H. The distance H is the independent variable in our problem, and the force between the sphere and the rod is the dependent variable. It is convenient to begin by setting $R=1$, so all lengths are measured in terms of the sphere radius. We consider first the symmetrical case where the center of the sphere is directly above the tether point ($d=0$ in Fig. 1). The general expectation would be that as H is slowly decreased below L, the sphere experiences a gradually increasing force, due to the reduction in entropy of the rod upon confinement. We will show that this is often not the case. In some regimes the force actually decreases as H decreases and in others in can show both a minimum and a maximum as a function of H.

We begin with a slightly simpler problem, in which the force does behave in an intuitive way. In this we replace the sphere of radius $R=1$ by a disk of radius $R=1$, again centered above the tether point. In this scenario there are three compression regimes:

(i) $H>L$; the rod never touches the disk.
(ii) $L^2-1<H^2<L$; the rod can touch the disk, but cannot reach the edge of the disk.
(iii) $H^2<L^2-1$; the rod can only touch the disk at its edge.

It is clear that regime (iii) can only occur if $L>1$. We can evaluate the configurational partition function for the system in all three compression ranges. If we use a spherical polar coordinate system with the normal to the tether surface as the z axis and θ the angle made by the rod with that axis, the partition function is

$$Z=\int_0^{2\pi} d\phi \int_{\theta_m}^{\pi/2} d\theta \sin\theta = 2\pi\cos\theta_m , \qquad (1)$$

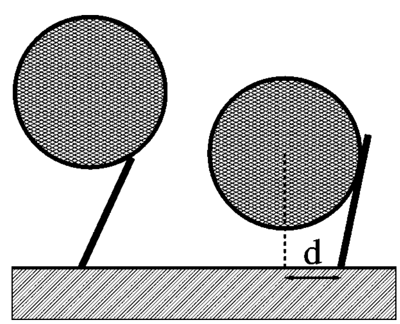

FIG. 1. Geometry for compression by a sphere. At left is the case where the rod is touching, but not tangent to the sphere. At right is the case where the compression is stronger and the rod is tangent.

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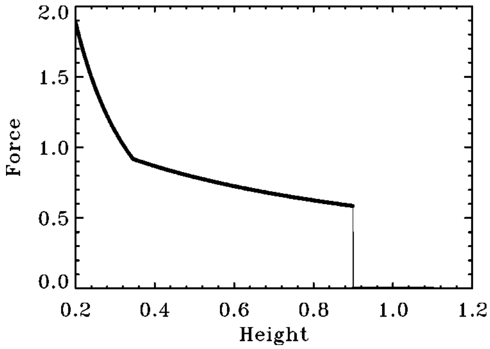

FIG. 2. Force vs height curve for the case $L=0.9, d=0$. The force is in units of kT/R and all lengths are in units of R. In this case the force is a monotonically increasing function of compression. It undergoes a sudden jump at contact and a sudden change in slope at the crossover between the tangent and nontangent regimes.

where θ_m is the minimum possible angle made by the rod with the normal. We can find $\cos\theta_m$ in all three regimes as: (i) $\cos\theta_m=1$; (ii) $\cos\theta_m=H/L$; (iii) $\cos\theta_m=H/\sqrt{H^2+1}$.

This allows us to find the Helmholtz free energy $F=-kT\ln Z$ in each case and hence the repulsive force $f=-(\partial F/\partial H)$. The forces in all the cases can be evaluated as

$$f_1=0,$$

$$f_2=kT\frac{1}{H}, \tag{2}$$

$$f_3=kT\frac{1}{H(1+H^2)}.$$

Upon compression the force behaves in an expected way, it increases monotonically with increasing compression, but is noncontinuous at the disc edge.

We now carry out the same procedure for the sphere problem. One important point is that there are again three compression regimes (Fig. 1):

(1) $H>L$, the rod and sphere never touch.

(2) $\sqrt{L^2+1}-1<H<L$, the rod and the sphere can touch but the rod ends at the sphere, i.e., it is not tangential to the sphere.

(3) $H<\sqrt{L^2+1}-1$, the rod can touch the sphere, and when it does it is tangential to it.

From the geometry we can readily evaluate $\cos\theta_m$ in each case. We find: (1) $\cos\theta_m=1$; (2) $\cos\theta_m=[L^2+H^2+2H/2L(1+H)]$; (3) $\cos\theta_m=\sqrt{H^2+2H}/1+H$. The forces are then

$$f_1=0,$$

$$f_2=kT\frac{2+2H+H^2-L^2}{(1+H)(L^2+H^2+2H)}, \tag{3}$$

$$f_3=kT[H(H+2)(1+H)]^{-1}.$$

The force in regime (1) is as expected: if the sphere and rod cannot touch there can be no steric force. The force in regime (3) where the rod is tangential is also much as one would expect: it increases monotonically with compression and is $\frac{1}{2}kTH^{-1}$ for $H\ll R$. The unusual behavior comes from regime (2). One surprise is that the function f_2 describing the force in regime (2) exhibits a maximum at $H=-1+\sqrt{(2+\sqrt{5})L^2-2-\sqrt{5}}$. This maximum implies that in some cases the compression of the rod exhibits a force which initially decreases as the rod becomes more compressed. To examine this further we note that f_2 is the valid force only in the regime $\sqrt{L^2+1}-1<H<L$. This gives us the conditions that the maximum occurs in the physical region $L_1<L<L_2$, where $L_1=\frac{1}{2}\sqrt{2+2\sqrt{5}}\approx1.272$ and $L_2=(3+\sqrt{5})(1+\sqrt{5})^{-1}\approx1.618$. If these conditions are satisfied, the force will exhibit a maximum as a function of compression.

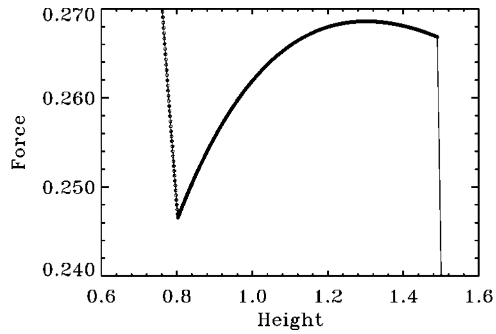

FIG. 3. Force vs height curve for the case $L=1.5, d=0$. The units are the same as Fig. 2. Note that the force now has a maximum and a minimum.

There are three scenarios for the force versus compression curve, and these are controlled by L. The first (Fig. 2) is for $L<L_1$, i.e., for rods which are smaller than or close to the sphere radius. In this case the compression is as one would expect. As H is gradually decreased there is a sudden jump from $f=0$ to $f=kTL^{-1}(1+L)^{-1}$ at $H=L$. The force then increases monotonically with compression. There is a jump in the slope of the force at $H=\sqrt{L^2+1}-1$, where the rod changes from nontangential to tangential, but the force itself is always a monotonic function of compression.

The second case (Fig. 3), $L_1<L<L_2$, is nontrivial. Again as H is decreased below L there is a jump in the force. However, in this case the force rises to a maximum and then decreases to a minimum before increasing again.

The third case (Fig. 4), $L>L_2$, is again surprising, because as H decreases below L the force also decreases. It then reaches a minimum at $H=\sqrt{L^2+1}-1$ and then increases.

This calculation is for the case where the grafting point is directly below the center of the sphere. There are three different scenarios, two of them at least, not intuitively obvious from a cursory examination of the problem. More generally, there will a distance $d\neq0$ between the grafting site and the perpendicular from the sphere to the surface. For $d\neq0$ the geometry looks more complicated and a solution by means of a straightforward extension of the $d=0$ case looks difficult. However, the problem is in fact easy, since it is only the solid angle excluded by the sphere that matters. This depends only on the distance from the grafting point to the center of the sphere. which is $H'=\sqrt{(H+1)^2+d^2}-1$. To obtain the correct partition function we thus replace H by H'. This allows us to calculate the force in three regimes:

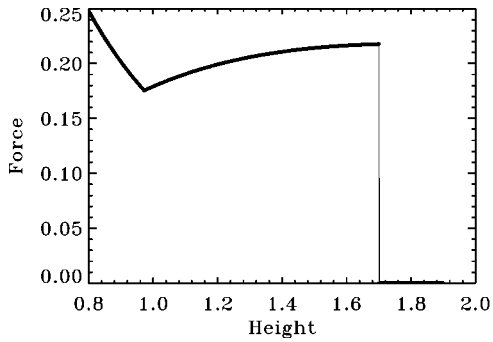

FIG. 4. Force vs height curve for the case $L=1.7,d=0$. The units are the same as Fig. 2. After the initial jump at contact the force decreases as the compression increases.

(1) $H>\sqrt{(1+L)^2-d^2}-1$; (2) $\sqrt{1+L^2-d^2}-1<H<\sqrt{(1+L)^2-d^2}-1$; (3) $H<\sqrt{1+L^2-d^2}-1$.

The vertical forces in these regimes are

$$f_1=0,$$

$$f_2=kT\frac{(1+H)(d^2+2+2H+H^2-L^2)}{(d^2+1+2H+H^2)(L^2+d^2+2H+H^2)}, \quad (4)$$

$$f_3=kT\frac{1+H}{(d^2+1+2H+H^2)(d^2+2H+H^2)}.$$

The general case $d\neq 0$ retains much of the same behavior seen in the case $d=0$. For $d>\sqrt{2L+L^2}$ there is always zero force, i.e., the rod never touches the sphere. Also, if $d>L$ then regime (3) never occurs. However, there are some differences, particularly when we take the limit $H\to 0$, i.e., we bring the sphere into contact with the grafting surface. For $d=0$ we find a force which diverges as $\frac{1}{2}H^{-1}$. In the case $L<d<\sqrt{(L+1)^2-1}$ the force at contact is finite,

$$f_{2\ contact}=kT\frac{d^2+2-L^2}{(d^2+1)(L^2+d^2)}. \quad (5)$$

Even in the case $d<L$ the force is still finite,

$$f_{3\ contact}=kTd^{-2}(d^2+1)^{-1}. \quad (6)$$

The reason for this lack of divergence when $d\neq 0$ is clear. When $d=0$ the rod has no freedom to move when $H=0$. However, when $d\neq 0$ the rod can have significant freedom to rotate even when the sphere is touching the grafting surface.

One other significant difference between $d=0$ and $d\neq 0$ is the presence of a horizontal force on the sphere. This force can be calculated by taking $kT\partial \ln Z/\partial d$. It turns out that this force is always equal to $d/(H+1)$ times the vertical force, i.e., the force vector always lies on a line connecting the grafting site and the center of the sphere.

The most notable feature of the force curves is that they are often nonmonotonic, and it is natural to ask why this occurs. The partition function, Z, measures the orientational freedom of the rod: the larger Z is, the more freedom the rod has. The force depends on how Z changes with H. Clearly Z always decreases with H so the force is positive. However, f can increase or decrease depending on the local geometry of the compressing surface. It is easy to show that for weak compressions by any surface of revolution that $f=-kT\theta'_m\theta_m$, and that the slope of the force curve is then $f'=-kT(\theta'^2_m+\theta''_m\theta_m)$, where the prime means d/dH. Clearly if θ''_m is sufficiently negative the force can actually decrease with decreasing H. This can be made more concrete by considering weak compression by power-law surfaces of revolution, $z=A|x|^\alpha$, where A and α are positive constants. Calculation shows that at contact $f'<0$ for $\alpha\leqslant 2$ and for $\alpha>4$. However, for $2<\alpha<4$, $f'>0$. The slope of the force thus depends rather subtly on the compressing surface and for $2<\alpha<4$ we expect nonmonotonic force curves.

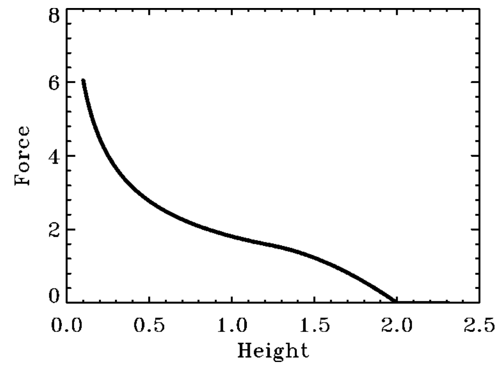

FIG. 5. Force curve for a brush of rods with $L=2$. The force is in units of $kT\rho/R$, and all lengths are measured in units of R.

Thus far we have shown that the case of a single rod can be solved exactly and has nontrivial behavior. Although this is an interesting problem in itself, a natural question to ask is what occurs if we have many rods grafted to a plane, with ρ rods per unit area [15]. We can solve this problem exactly, and obtain very simple expressions for the force in the limit where the rods do not interact with each other, i.e., in the limit where the rod diameter, $d_{rod}\to 0$. We integrate the force from rods between an in plane radius r and $r+dr$. If $H>\sqrt{1+L^2}-1$ then the only force that contributes is f_2 and we need to integrate $2\pi\rho d f_2$ from $r=0$ to $r=\sqrt{(1+L)^2-(1+H)^2}$. This leads to a simple force law,

$$f_A=2\pi\rho kT(1+H)\ln\left[\frac{2L(H+1)}{L^2+H^2+2H}\right], \quad H>\sqrt{1+L^2}-1. \quad (7)$$

If $H<\sqrt{1+L^2}-1$ then the region of integration needs to be divided in two. An inner circle of radius $\sqrt{L^2-H^2-2H}$ where f_3 contributes, and an outer annulus to radius $r=\sqrt{(1+L)^2-(1+H)^2}$, where f_2 contributes. The total force in this region is again fairly simple,

$$F_b=2\pi\rho kT(1+H)\ln\left[\frac{1+H}{\sqrt{H(H+2)}}\right], \quad H<\sqrt{1+L^2}-1. \quad (8)$$

The behavior of this multirod system is simpler than the single rod system and there is only one type of force curve, shown in Fig. 5. Several things are to be noted. First, the force is always a monotonically increasing function of compression. The initial force at $H=L$ is 0, and for small compressions is $2\pi\rho kT(L-H)/L$. Thus, a brush of rods has no sudden jump in force at contact. Moreover, the initial increase in force is larger for shorter brushes. For compressions below $H=\sqrt{1+L^2}-1$ the force curve is universal in that it depends only on H and not on the length of the rods. For very strong compressions, $H\rightarrow 0$, the force diverges as $-\ln H$.

In this paper we have shown that a simple and exactly solvable model of grafted rods interacting with a sphere exhibits somewhat surprising and nontrivial behavior. Much of the novelty comes from the interaction of a single rod with a sphere, which produces several different scenarios and generally exhibits a nonmonotonic force curve. The many-rod case shows monotonic behavior and yields simple expressions for the force as a function of compression. There are several possible extensions of the approach used here. One would be to use rods which are hinged but where the hinge pays an energy penalty for bending away from the surface normal. It is likely this problem can be solved exactly, but at the expense of more complicated expressions for the force. The second extension would be to include rod-rod interactions. It is unlikely that an exact solution to this could be found, although a virial expansion may provide some approximate expressions. Here we have calculated only the steric forces. Naturally there are other forces such as dispersion forces and electrostatic forces which need to be included in a real experimental system. We have also concentrated on the case of an external particle with a given position. There is another class of problems where the force is the independent variable and the compression is measured. In these kind of problems sudden jumps in the height can occur as a result of our nonmonotonic force profiles.

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