

Cohesion and aggregation of flexible hard rods with an attractive interaction

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Long flexible rods are considered; these are hard cylindrical particles with a contour length less than their persistence length. We show that an attractive interaction between the rods, with a range of the order of the diameter of the hard core, causes dilute phases of the rods to collapse to a dense phase with a volume fraction of order 0.1. The temperature of this collapse is insensitive to the persistence length; it is significantly lower than that for perfectly rigid rods even for very large persistence lengths. [S1063-651X(97)16305-X]

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I. INTRODUCTION

Rodlike polymers [1], such as DNA, have been observed to form aggregates of many molecules [2]. This aggregation or coagulation is associated with a sudden increase in compressibility as the number of free particles drops [2,3]. Here we study the cohesion of a pair of polymer molecules which have a small amount of flexibility, too much to be neglected but much less than that required to form a coil. The results of this study are then applied to estimate when the polymer molecules aggregate. We suggest that the formation of dense aggregates is quite general for rodlike molecules. The polymers are sufficiently rigid to be still rodlike [4], and we refer to them as flexible rods. They interact via a hard-core and a short-ranged attractive interaction. By short ranged we mean an interaction which has a range of the order of the diameter of the hard core of the rod [5]. Such short-ranged interactions are inherently highly anisotropic.

Although the effect of attractive interactions on the behavior of spherical particles has been extensively studied [6], the effect on nonspherical particles is much less well understood. Even in the case of perfectly rigid rods there have been only a few studies [5,7]. For flexible rods, as far as the author is aware, the only studies which address the interplay between flexibility [1] and attractive interactions [5,8] are those of Helfrich and Harbich on tubular vesicles [9], and of Odijk [10]. This is surprising in view of the fact that the polymers which are of interest are rarely much shorter than their persistence length.

Any short-ranged interaction, such as van der Waals interactions between polymer molecules, will scale with the length of the particles and will be very anisotropic. This degree of anisotropy makes treating the attractive interactions as either isotropic or a slowly varying function of angle, such as a low-order Legendre polynomial, wholly inappropriate. The results of Khokhlov and Semenov [7], Samborski and Evans [11], and those for Kihara potentials [12,13], are for models very different from the rods we consider here.

We first study rods which are perfectly rigid, and then rods which have a persistence length which is of the same order as their length. Dilute solutions of both these types of

rods phase separate into an extremely dilute solution and a solution with a volume fraction of order unity, but considerably stronger attractive interactions are required to produce this phase separation if the rods are flexible. Our main conclusions are that flexibility stabilizes the rods against aggregation, and its contribution to this stability is of the same order as that due to the orientational degree of freedom, for any reasonable values of the length and persistence length of a rodlike polymer. However, even flexible rods are much more prone to aggregation than spherical particles [14], i.e., they aggregate at much lower values of the Hamaker constant than are required for spheres. The dense phase formed on aggregation is shown to be at volume fractions of order 0.1: at these densities long rodlike molecules possess at least nematic ordering (and may be columnar or even solid).

II. ROD-ROD INTERACTIONS AND BOUND PAIRS

Van der Schoot and Odijk [5] studied perfectly rigid rods with an attractive interaction $E(R,L)$. This attraction is of the form

$$E(R, \gamma) \sim \begin{cases} -\frac{A}{|\sin \gamma(\Omega, \Omega')|} f\left(\frac{R}{D}\right), & \gamma \geq D/L \\ -\frac{A}{D/L} f\left(\frac{R}{D}\right), & \gamma \leq D/L, \end{cases} \quad (1)$$

which is the qualitative form for rods interacting via van der Waals [8] forces. Any other short-ranged interaction will also have an $E(R, \gamma)$ of a similar form [10]. The function f is a decaying function of R/D , such that $f(0)=1$ and $f(x) \rightarrow 0$ as $x \rightarrow \infty$. A is the Hamaker constant and is positive. The rods have diameter D and length L , and R is the distance of closest approach between the center lines of the two rods [5]. The orientations of the two rods are Ω and Ω'_g and γ is the angle between the center lines of the rods. Equation (1) for the potential is valid for rods whose centers of mass are within a small fraction of L apart. If the rods are parallel the energy is, as we would expect, proportional to L/D . This scaling with L/D produces a very deep well for long rods which are parallel or near parallel to each other. Equation (1) is only the attractive part of the interaction; if $R < D$, then the hard cores of the rods overlap and the energy is ∞ .

Although potential (1) is a continuous function of R , we will characterize it by a length $R_c + D$, which will be be-

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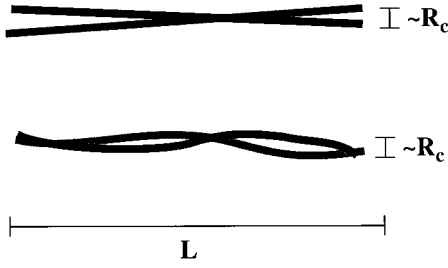


FIG. 1. Bound pairs of rigid (top) and flexible (bottom) rods.

tween $\sim 1.5D$ and $\sim 4D$. R_c is thus the difference between the range of the attractive potential and the range of the hard repulsive interaction. For a given $f(x)$ there is no unique way to estimate R_c , but a simple way is to view R_c as a cutoff. Then $R_c + D$ is the distance at which the potential energy is, say, 0.2 of its value at D . For example, if $f(R/D) = (D/R)^4$ [5], then $R_c \approx 0.50$.

We consider the free energy change when one rod ‘‘captures’’ another, i.e., when a pair of rods are restricted so that they are near the minimum of the potential of Eq. (1). This is done because the interaction energy of a pair of rods is near zero unless they are parallel or nearly parallel; the interaction between crossed rods is a factor of D/L less than that between parallel rods; see Eq. (1). See Fig. 1 for schematic illustrations of bound pairs of rigid and flexible rods. When this free energy change is positive, we expect very few pairs to be found closely bound in the potential minimum, and we expect that the fluid is stable. However, when it is negative we expect not only bound pairs but triplets and larger clusters to form. Note that the formation of a bound pair of rodlike polymers is very similar to the adsorption of a one rodlike polymer molecule onto a line [15].

III. PERFECTLY RIGID RODS

As the length to diameter ratio of a perfectly rigid rod tends to infinity, any attractive interaction which scales as the length of the rod will cause a fluid of rods to collapse [5]; i.e., a dilute solution will spontaneously phase separate into an extremely dilute solution, and a solution with a volume fraction of order 0.1. Very long rods, due simply to their repulsive cores, must possess at least nematic ordering at these volume fractions. Thus we see immediately that these rods do not form a liquid. We know that short rods with L of the same order as D do form a liquid, so for some intermediate value of L/D the liquid phase will disappear above a transition to a phase with nematic ordering.

We proceed to estimate the free energy difference ΔF between a pair of rods bound in the potential minimum, and a pair of noninteracting rods. For two rods to be in the potential minimum their center lines should remain within $R_c + D$ throughout their whole lengths. Then their energy ΔU will scale as L/D ,

$$\Delta U \sim -A \frac{L}{D}. \quad (2)$$

The R_c dependence comes from the volume inside of which the rods’ center lines are within R_c . If the center lines of two

perfectly rigid rods are to remain within R_c throughout their whole lengths, then the angle γ between them must be $\leq R_c/L$ (see Fig. 1), and their centers of mass must be less than R_c apart. The first of these two restrictions changes the orientational entropy of the rods by $\sim \ln(R_c/L)^2$, and the second changes their translational entropy by $\sim \ln(cR_c^3)$ [16]. The concentration $c = N/V$ for N rods in a volume V . Thus the difference in entropy ΔS between a pair of bound rigid rods and a free pair is

$$\Delta S \sim 2 \ln(R_c/L) + \ln(cR_c^3). \quad (3)$$

Combining with Eq. (2),

$$\Delta F = \Delta U - T\Delta S \sim -A \frac{L}{D} - T[2 \ln(R_c/L) + \ln(cR_c^3)]. \quad (4)$$

Our temperature units are such that Boltzmann’s constant is unity. As the length L of the rods increases, the Hamaker constant A needed to produce a negative free energy change for binding tends to 0 as $T/(L/D)$. So, at the temperature at which binding starts to occur, the energy of configurations of the rods in which they are not nearly parallel is near zero; it is of the order of A , and our approximation of considering only an equilibrium between tightly bound states and noninteracting states is valid. This behavior was observed by van der Schoot and Odijk [5] in their study of the second virial coefficient of this model. The entropy cost (3) of forming a bound pair is much greater than unity, and so the free energy is a rapidly varying function of temperature near the point where Eq. (4) = 0. Therefore, as the temperature is lowered, the changeover from almost all molecules being free to almost all of them being bound in pairs, occurs over a small range of temperature.

If a pair of rods overlaps for some length, $D \ll L' < L$, ΔF is simply Eq. (4), but with L' substituted for L . It is then easy to see that at the temperature at which ΔF of Eq. (4) becomes negative the ΔF ’s for all $L' < L$ are positive. Our crude analysis of the free energy of a pair of rods thus suggests that the minimum of the free energy switches from being with the pair hardly interacting at all to being with the pair lying alongside each other for essentially their whole lengths, at the temperature for which Eq. (4) = 0.

IV. FLEXIBLE RODS

We now examine flexible rods, and estimate the additional entropy loss when they form bound pairs. The physical picture is the same as for rigid rods: a pair of rods gains a large amount of energy by lying parallel, but in doing so suffers a large reduction in entropy. As both parts of the free energy are large, we again expect a quite sudden collapse from a dilute phase to a much denser ordered phase. A flexible rodlike colloidal particle is modeled by a homogeneous cylindrical elastic filament [1,17]. The filament follows a continuous curve in space; see Fig. 1. This curve is described by a unit tangent vector $\mathbf{t}(s)$ to the curve at each point on the curve s . At nonzero temperature the filament fluctuates, causing correlations between tangent vectors at different points on the curve to decay as the separation of the points increases [17],

$$\langle \mathbf{t}(s) \cdot \mathbf{t}(s + \delta s) \rangle = \langle \cos \theta(\delta s) \rangle = \exp(-\delta s/P), \quad (5)$$

for two points on the curve separated by a distance δs along the filament. The angular brackets indicate an ensemble average. θ is the angle between the two tangent vectors and P is the persistence length [1,18] of a filament. The persistence length (which is a function of temperature) measures the flexibility of the rod. The angle between the tangent vectors of two points separated by a persistence length is, on average, around 1 rad. A perfectly rigid rod has an infinite persistence length.

The attractive interaction of Eq. (1) is only appropriate for a perfectly rigid rod; γ is not well defined if the rods are not completely straight. However, if a flexible rod is broken up into segments much shorter than P , then we can define an interaction between flexible rods which is a sum of the interactions between these segments. γ is defined as being the angle between the two polymer curves at the centers of mass of the segments, allowing Eq. (1) to be used for the segment-segment interaction. There is an ambiguity as the length of the segments has to be chosen, but the effect of this ambiguity in making our potential model slightly ill defined is far too small to affect our qualitative discussion. We continue to consider the energy as being A times the length the pair of polymers are within $R_c + D$ of each other.

As with perfectly rigid rods, we consider the configurations of a pair of rods in which they are interacting via the attractive interaction. In order for the rods to interact via the attractive potential throughout their whole lengths L , their center lines must remain within R_c for their whole length. For a given configuration of one of the pair of rods, the second rod is restricted to a cylindrical volume of diameter R_c surrounding the first rod. The confinement of flexible rods into tubes is well understood [9,19]. The entropy cost ΔS is extensive in the length of the rod L , and scales as $L/R_c^{2/3}P^{1/3}$ [19]. The length $R_c^{2/3}P^{1/3}$ is the deflection length [18,19] for a rod constrained to lie in the potential well of width R_c . If $\delta s \ll P$, we may expand both the cos and exp functions of Eq. (5), giving

$$\sqrt{\langle \theta^2(\delta s) \rangle} = \left(\frac{2\delta s}{P} \right)^{1/2}, \quad \delta s \ll P. \quad (6)$$

The angle $\sqrt{\langle \theta^2(\delta s) \rangle}$ is the rate at which the curve followed by the polymer is moving away from an axis along the vector $\mathbf{t}(s)$, as δs increases. Therefore, we simply integrate $\sqrt{\langle \theta^2(\delta s) \rangle}$ from 0 to r to give the distance d between the curve and this axis at a distance of r along the polymer,

$$d = \left(\frac{2^3}{3} \right)^{1/2} \frac{r^{3/2}}{P^{1/2}}. \quad (7)$$

When $d = R_c$, $r \sim R_c^{2/3}P^{1/3}$ is the length of the longest segment of the polymer which can fit into the potential well without being perturbed: the deflection length. Over contour lengths less than the deflection length, the polymer configurations are little affected by the confinement, but on longer length scales the number of configurations of the polymer chain are dramatically reduced by the need to remain within R_c of the other polymer.

The entropy reduction due to the suppression of undulations of the polymer is assumed to be of the order of unity per deflection length. This assumption is confirmed by the results of more systematic calculations; see Ref. [18]. Adding the entropy change for a rigid rod, Eq. (3) [18,19],

$$\Delta S \sim 2 \ln(R_c/L) + \ln(cR_c^3) - \frac{L}{R_c^{2/3}P^{1/3}}. \quad (8)$$

The last term in Eq. (8) is due to the stretching of an elastic filament, so that all undulations which deviate more than R_c from a fixed axis are smoothed out. This additional term scales as L , at constant P , and so will dominate for sufficiently large L . Thus ΔS for flexible rods increases linearly with L , for large L , while for perfectly rigid rods it increases only logarithmically. The energy gained by these rods ΔU is the same as for perfectly rigid rods, Eq. (2). Of course, this is not strictly true, but the energy will still scale linearly with L ; the only change is in the numerical prefactor, which we are ignoring. Thus the free energy change ΔF is

$$\Delta F \sim -A \frac{L}{D} + T \left(\frac{L}{R_c^{2/3}P^{1/3}} - 2 \ln(R_c/L) - \ln(cR_c^3) \right). \quad (9)$$

Replacing L by L' in Eq. (9) gives the free energy change for two rods which follow each other for a fraction L'/L of their lengths. As for rigid rods, at the temperature for which Eq. (9)=0, the free energy of a pair of rods bound for part of their lengths is positive. So, again, partial binding of the rods is not favored.

V. DISCUSSION

In order to study the length and flexibility dependence of aggregation, we equate the free energy difference between bound and free pairs of rods to zero. This gives us an equation which we solve for $(A/T)_0$: the reduced Hamaker constant at which the free energy of formation of a bound pair is zero. $(A/T)_0$ is then our estimate of the Hamaker constant above which the polymer aggregates. For rigid rods we have [5]

$$\left(\frac{A}{T} \right)_0 \sim \frac{-2 \ln(R_c/L) - \ln(cR_c^3)}{L/D}, \quad (10)$$

and for flexible rods

$$\left(\frac{A}{T} \right)_0 \sim \frac{-2 \ln(R_c/L) - \ln(cR_c^3) + L/(R_c^{2/3}P^{1/3})}{L/D}. \quad (11)$$

Note the very slow $P^{-1/3}$ decrease of $(A/T)_0$ with increasing P . No realistic value of P/D is sufficiently large to render the flexibility term in Eq. (11) negligible. For a rod of length $L/D = 50$, say, even if $P/D \gg 50$, a free rod will bend by much more than $R_c = 0.5D$, and so constraining a rod not to bend by more than $0.5D$ costs considerable entropy. However, our theory suggests that for flexible rods, with $L/P \approx 1$, the flexibility term is never dominant. $(A/T)_0$ may double when flexibility is accounted for, but it does not seem to increase by an order of magnitude.

There will be c^2 pair interactions, c^3 triplet interactions, etc. Not only bound pairs of rods but also bound triplets and larger aggregates [20] are possible in a fluid. In particular, the energy of a triplet is $-3AL$, but the entropy cost in forming a triplet will not be much more than twice that of forming a pair. Thus we expect triplets and larger aggregates to form and the compressibility to diverge at a lower A/T than given by Eqs. (10) or (11). If the system is allowed to go to equilibrium, then presumably a dense bulk phase will appear: the aggregates found in Ref. [2] are almost certainly not true equilibrium structures. However, within our qualitative theory $(A/T)_0$ is an adequate estimate of the ratio of the Hamaker constant to the temperature at which aggregation sets in; an estimate of the third virial coefficient [5] only changes $(A/T)_0$ by a factor of order unity. Given that in the aggregates the rods are $\sim R_c + D$ apart, if these aggregates grow to macroscopic size, as presumably they will, then the fluid will collapse until the density is high enough that the packing fraction is of order $(R_c/D + 1)^{-2}$. The collapse will be halted by entropic and excluded volume repulsions at these densities. The entropic repulsions occur because as the volume fraction increases the space available for the rods to undulate in decreases. The volume per rod in an aggregate is $\sim (R_c + D)^2 L$, which gives the volume fraction inside an aggregate as $(R_c/D + 1)^{-2} \approx O(0.1)$. This dense phase must be at least a highly ordered nematic but it may be a columnar phase [21,22]. Thus, it is clear that long rods with an attraction with a range of order D do not form a liquid phase, i.e., there is no coexistence between two isotropic phases.

The large jump in volume fraction from D/L or less to 0.1 is a direct consequence of the fact that the polymer molecules have the lowest free energy in one of two states: free, in which they behave similarly to a dilute gas of hard rods, and bound, in which they form a much denser nematic or columnar phase. The binding of a pair of polymer molecules is very similar to adsorption [8,15]. Our free energies (4) and (9) are appropriate for adsorption of rigid and flexible rods, respectively, onto a line. The jump between zero and complete adsorption we have found may be contrasted with the continuous adsorption found for flexible polymers, those

with $L \gg P$ [15]. The difference between the rodlike and the flexible polymers is that rodlike polymers cannot form loops, i.e., configurations in which the path followed by the polymer enters and leaves the potential well of the other polymer more than once are highly unfavorable. This is obviously true for perfectly rigid rods which cannot bend at all, but also for $L \lesssim P$, once two polymer molecules have parted the entropy cost in bending them back to join again is much greater than unity.

Finally, we consider the relevance of our findings for experiment. First, for long rigid or flexible rods we see a characteristic, dramatic collapse of a dilute phase to a much denser phase. This is not found for spherical molecules. We predict that the collapse to either a dense bulk phase or a large aggregate of many molecules side by side, is generic to rods and should be observable in any dilute solution of very long molecules, in which the attractive interactions are increased above a threshold. In the case of the DNA studied by Wissenburg *et al.* [2], if we assume a persistence length $P \approx 50$ nm [23] for the DNA, then $L/D \approx P/D \approx 25$. With these values, the contributions of the flexibility and orientational terms to $(A/T)_0$ are of the same order; we therefore cannot treat the DNA as being perfectly rigid. Without the numerical coefficients of the terms in Eq. (11), and at least a semiquantitative knowledge of the interactions, the theory has little predictive ability. However, if experiments such as those of Ref. [2] could be repeated for several L/D ratios, the presence of contributions to ΔS due to flexibility could be determined, and the scaling of the last term of Eq. (8) confirmed (or refuted).

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$V^{N/2} R_c^{3N/2} / [(N/2)! 2^{N/2}]$. The difference in the logarithms of these two partition functions gives the free energy change. If only a fraction of the N particles are bound in dimers there is an additional combinatorial term which we neglect.

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