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Statistical geometry of caging effects in random thin-rod structures

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Abstract

A derivation is given for the caging density of a static, random thin-rod structure at which uncorrelated contacts on a rod on average form a cage which arrests sidewise translations. Some implications of this result for colloidal sediments, random packings and rod glasses are discussed.

Keywords: Colloidal rods; Sedimentation of colloids; Random packing; Caging effects; Rod glasses; Rigid fibers

1. Introduction

Sedimentation of colloidal particles has been studied extensively for both uncharged [1] and charged [2] spheres. Also elongated colloids have been investigated such as silica ellipsoids [3], silica rods [4] and boehmite rods [5]. Particles settle under the influence of gravity or a centrifugal force and pack into a deposit (with usually a random-like microstructure) at the bottom of the vessel. When deposition is rapid in comparison with typical diffusion times, the colloids will be quenched into a random packing. When in addition the colloids are hard particles without attractions or double-layer repulsions, their random packing density (rpd) will be close to the rpd for *macroscopic* objects. This is borne out by colloidal hard-sphere deposits with volume fraction ϕ close to the rpd of $\phi \approx 0.64$ for macroscopic spheres [6].

This analogy between colloidal sediments and macroscopic packings is very general and also applies to non-spherical particles. Significant features of (isotropic) sediments of colloidal rods are the low density in comparison to spheres, and the monotonic

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decrease in density with increasing particle aspect ratio [7]. The rpd of macroscopic rods exhibits precisely the same features [7,8].

These findings confirm that random packing is a geometrical problem, involving particle shape (aspect ratio) rather than absolute size. There is no general solution for this problem in the form of a relation between the rpd and the particle shape. For the limiting case of thin rods, however, a simple model explains the experimentally observed dependence of the rpd on the aspect ratio [7]. This model (see also Section 3) neglects any correlation between mechanical contacts on particles, which for thin rods seems to be a reasonable approximation [7].

Here we explore another consequence of this random contact approximation: the quantification of the notion of a "cage of neighbors" which blocks rod translations in an isotropic collection of rods. One motivation for this analysis of caging effects is to improve our understanding of the density of a random packing or sediment of (colloidal) thin rods.

Caging effects have been invoked earlier to visualize hindered self-diffusion in a concentrated suspension as the motion of a test sphere from one mobile cage of neighbors to another [9]. In the dynamics of colloidal rods a cage has been pictured as a tube of fluctuating neighbors which temporarily restricts sidewise translations and end-over-end rotations [10]. Our notion of a cage somewhat resembles this description, with the difference that we consider a *static* collection of *non*-Brownian rods in the following thought experiment.

Thin rigid rods are placed one by one with fixed, randomly distributed orientations and positions in a three-dimensional continuum, subjected only to the constraint that they cannot penetrate each other. At a certain density ϕ we remove the restrictions that keep the rods fixed. At low ϕ the rod collection lacks any mechanical stability and collapses under influence of gravity. With increasing density the probability that the rods will arrest each other rises even up to the point where the rod collection is unable to densify at all. Here we focus on the density ϕ_t at which at least *sidewise* rod motions are caged.

In Section 2 we present the statistical geometry required to calculate ϕ_t. The main steps are: (i) the realization that the caging of a static rod is equivalent to the two-dimensional caging of a disc; (ii) the evaluation of the average number of uncorrelated contacts which trap a disc; (iii) the conversion of this average to the volume fraction ϕ_t. In Section 3 we discuss the results and some implications for the random rod packing.

2. The translation cage and caging density

Consider a random collection of identical thin rigid rods. A test rod T experiences n contacts with neighbor rods. We define a translation cage (t-cage) as a configuration of these contacts which block all translations of T, except the translation parallel to its long axis. (This lengthwise motion is never completely blocked for thin rods, even at high densities. In this section "translations" always denote the sidewise motions

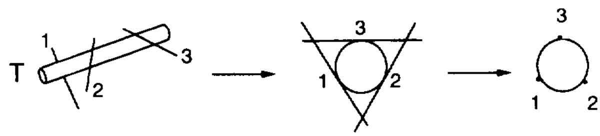

Fig. 1.

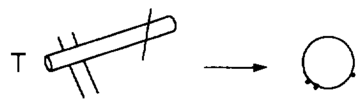

Fig. 2.

forbidden by the t-cage.) A t-cage requires at least $n = 3$ contacts with neighbors which can be represented by their main axis only (See Fig. 1). Length and orientation of the neighbors are irrelevant and also displacement of contacts parallel to the main axis of T does not influence caging properties. Thus the neighbor rods can be projected on a plane perpendicular to the direction of T and reduced to the points of contact. It follows that the three-dimensional t-cage for a thin rod is equivalent to a trap for a two-dimensional disc, formed by contact points on its circumference. Clearly $n = 3$ is not a sufficient condition to trap the disc, that is, for a t-cage to be present. For example, the configuration shown in Fig. 2 allows translation of the rod (c.q. the disc). The caging probability obviously increases with increasing n. We will now evaluate the average number of contacts on a caged rod.

The key assumption is that contacts are uncorrelated [7]. Suppose they are placed one by one at random positions on the circumference of the disc, until a t-cage is formed. Let γ_t be the number of contacts in this t-cage and $P(\gamma_t = k)$ the probability that γ_t has a particular value k. Alternatively, one can also place a given number of n contacts randomly on the disc edge and ask for the probability p_n that these n contacts will form a t-cage. The probabilities are related as

$$1 - p_n = P(\gamma_t > n) \tag{1}$$

$$= \sum_{k=n+1}^{\infty} P(\gamma_t = k)\,. \tag{2}$$

We are interested in the expectation value $\langle\gamma_t\rangle$. It can be expressed in terms of the p_n:

$$\langle\gamma_t\rangle = \sum_{k=0}^{\infty} kP(\gamma_t = k) = \sum_{n=0}^{\infty} \sum_{k=n+1}^{\infty} P(\gamma_t = k) = \sum_{n=0}^{\infty} (1 - p_n)\,. \tag{3}$$

The caging probability p_n is found as follows. The radii to the contacts divide the disc into sectors. Let ψ be the largest sector angle. A t-cage is present if and only if

$\psi < \pi$. Thus

$$1 - p_n = \int_{\pi}^{2\pi} P_n(\psi) \frac{d\psi}{2\pi}, \tag{4}$$

in which $P_n(\psi)/2\pi$ is the normalized probability density for ψ. This density satisfies the following recursion relation:

$$P_n(\psi) = \frac{2\pi - \psi}{2\pi} P_{n-1}(\psi) + 2 \int_{\psi}^{2\pi} P_{n-1}(\theta) \frac{d\theta}{2\pi} \quad \text{for } \psi \geqslant \pi. \tag{5}$$

This can be seen as follows. Consider a disc with a configuration of n contacts and a largest sector angle ψ. This configuration is formed by adding the last contact to a precursor with $n - 1$ contacts. There are two possibilities: (i) the precursor already contains the sector angle ψ and the last contact is placed with a probability $(2\pi - \psi)/2\pi$ in another sector; (ii) the largest precursor sector has an angle $\theta > \psi$, and the last contact divides it into two sectors with angles ψ and $\theta - \psi$. This division can be done in two ways which accounts for the factor 2 in front of the integral in Eq. (5). (Note that if $\psi < \pi$ there is a third possibility: the precursor already contains the sector with angle ψ, but also one larger sector which is divided by the last contact into two sectors each smaller than ψ. Thus Eq. (5) does not hold for $\psi < \pi$.) The solution of Eq. (5) with the appropriate initial conditions

$$P_2(\psi) = \begin{cases} 0 & \text{if } \psi < \pi, \\ 2 & \text{if } \psi > \pi \end{cases} \tag{6}$$

is given by

$$P_n(\psi) = n(n-1) \left(\frac{2\pi - \psi}{2\pi} \right)^{n-2} \quad \text{for } n \geqslant 2, \ \psi \geqslant \pi. \tag{7}$$

Substitution of Eq. (7) in (4) yields

$$1 - p_n = n(\tfrac{1}{2})^{n-1} \quad \text{for } n \geqslant 2, \tag{8}$$

and it is obvious that

$$1 - p_n = 1 \quad \text{for } n \leqslant 1. \tag{9}$$

Using

$$\sum_{n=0}^{\infty} n x^{n-1} = \frac{d}{dx} \left(\sum_{n=0}^{\infty} x^n \right) = \frac{d}{dx} \left(\frac{1}{1-x} \right) = \frac{1}{(1-x)^2},$$

we finally find for the average number of contacts $\langle \gamma_t \rangle$ in Eq. (3):

$$\langle \gamma_t \rangle = 2 + \sum_{n=2}^{\infty} n \left(\tfrac{1}{2} \right)^{n-1} = 5. \tag{10}$$

To convert $\langle \gamma_t \rangle$ into a rod volume fraction ϕ_t we again apply the random contact approximation. Suppose $f(\boldsymbol{r}, \rho)$ is the probability, averaged over all rod orientations, that two rods contact each other for a given center-to-center vector $\boldsymbol{r}$. The average number of contacts experienced by a rod is then [7]

$$\langle \gamma \rangle = \int f(\boldsymbol{r}, \rho) \rho(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} \, . \tag{11}$$

(In [7], the quantity $\langle c \rangle$ is used, being the ratio of the total number of contacts and rods. This should not be confused with $\langle \gamma \rangle$, as occasionally happens in [7]. In fact $\langle \gamma \rangle = 2\langle c \rangle$, because every contact is felt by two particles.) For a random distribution of rod centers, the number density $\rho(\boldsymbol{r})$ can be replaced by its average value ρ. For uncorrelated contacts the probability $f(\boldsymbol{r}, \rho)$ equals its value $f(\boldsymbol{r})$ for independent pairs of rods. Hence

$$\langle \gamma \rangle \approx \rho \int f(\boldsymbol{r}) \, \mathrm{d}\boldsymbol{r} \tag{12}$$

$$= \rho V_{\mathrm{ex}} \, , \tag{13}$$

where we have identified the integral in Eq. (12) as the orientationally averaged excluded volume V_{ex}. For thin rods with length L and diameter D it turns out that [11,12] $V_{\mathrm{ex}} \sim \frac{1}{2}\pi D L^2$ and $\phi \sim \frac{1}{4}\pi D^2 L \rho$, thus Eq. (13) becomes

$$\phi \frac{L}{D} \sim \frac{1}{2} \langle \gamma \rangle \quad \text{for } \frac{L}{D} \gg 1 \, , \tag{14}$$

in which $\sim$ denotes an asymptotic equality valid at high aspect ratio. The caging density ϕ_t at which the average number of contacts experienced by a rod in Eq. (14) equals the average "size" of a t-cage in Eq. (10) is therefore

$$\phi_t \frac{L}{D} \sim 2.5 \quad \text{for } \frac{L}{D} \gg 1 \, . \tag{15}$$

3. Discussion

In the Introduction we mentioned the thought experiment in which static (non-Brownian) rods are placed one by one at random positions and random orientations. As the volume fraction increases, the average number of contacts per rod, $\langle \gamma \rangle$, increases (Eq. 14), as well as the probability $p(\phi)$ that the $\langle \gamma \rangle$ contacts form a t-cage. Interpolating Eq. (8) and using Eq. (14) we find

$$1 - p(\phi) \sim 4\phi \frac{L}{D} 2^{-2\phi L/D} \quad \text{for } \phi \frac{L}{D} \geqslant 1 \, , \tag{16}$$

which is plotted in Fig. 3. The figure illustrates in the first place the low densities at which for high aspect ratios caging effects (and random packing) occur. For example, for $L/D = 50$, the caging probability starts to rise at $\phi = 2\%$, the t-caging density of Eq. (15) is reached at $\phi_t = 5\%$, and the system gets jammed in a random packing at

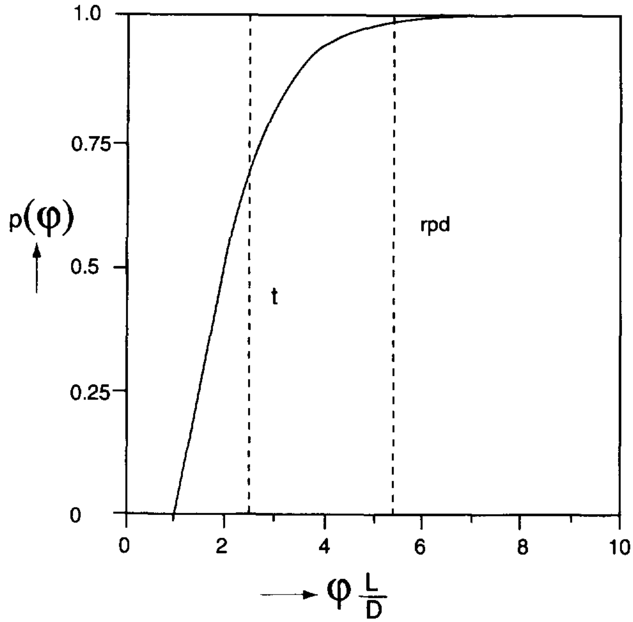

Fig. 3. As the volume fraction ϕ of a random collection of fixed rods increases, the average number of contacts $\langle\gamma\rangle$ (Eq. (14)) on a rod increases and hence the probability that this number forms a translation cage, $p(\phi)$, in Eq. (16) as defined in Section 2. A caged rod has on an average five contacts, and t denotes the "caging density" at which $\langle\gamma\rangle = 5$. Also the experimental random packing density (rpd) is indicated [7,8].

about $\phi_{\text{rpd}} \approx 11\%$. This random packing density (rpd) follows from

$$\phi_{\text{rpd}}\frac{L}{D} \cong 5.4\ (\pm 0.2) \quad \text{for } \frac{L}{D} \geqslant 15\,, \tag{17}$$

which is the result from packing experiments on thin rods, discussed in detail elsewhere [7,8]. Fig. 3 shows that at the packing density the caging probability in Eq. (16) virtually equals unity, indicating that in a random rod packing sidewise rod translations are strongly hindered. What about rod rotations?

The t-cage constructed by three contacts, as sketched in Section 2, still allows rotation of the rod. As the number of contacts increases, the possibilities for (end-over-end) rotation decrease. Above a certain contact number, the rod experiences a "tube-cage", allowing only lengthwise rod motions. (This reminds of caging effects in polymer dynamics [10]). The average value of the number of contacts in a tube-cage is yet unknown. (It will certainly be larger than the number $\langle\gamma_t\rangle = 5$ in a t-cage). It would be interesting to find out whether the tube-caging density corresponds to the rpd. One argument for this correspondence is that if rods can only perform lengthwise motions, the random rod collection cannot densify, because these motions are randomly oriented. So the rod centers cannot move collectively, which could account for the incompressibility of a random dense packing.

So far we have only considered macroscopic rods which do not exhibit Brownian motion. The statistical geometry in Section 2 does not depend on particle size. Thus, as far as the microstructure of colloidal rod sediments resembles stackings of random, macroscopic hard rods, it is meaningful to compare colloid densities with Eqs. (15)–(17), and curves such as in Fig. 3. However, for colloidal rods other factors than those dealt with in Section 2, such as double-layer repulsions or van der Waals attractions may influence the density. Further, structures may also become anisotropic because rods gradually diffuse into regions with orientational order. This instance of the isotropic–nematic phase transition for rigid rods indeed occurs in concentrated colloidal rod dispersions [14]. (The presence of t-cages would not prevent this transition because rods at least have the possibility to reorient gradually by a sequence of lengthwise diffusive motions). According to Onsager and others [11–13] the isotropic thin-rod fluid is stable below ϕ_I, whereas above ϕ_N only the nematic phase is thermodynamically stable:

$$\phi_I \frac{L}{D} \sim 3.29; \quad \phi_N \frac{L}{D} \sim 4.19 \qquad \text{for } \frac{L}{D} \gg 1 . \tag{18}$$

These densities are higher than the caging density ϕ_t in Eq. (15), but below the experimental random packing concentration in Eq. (16). So isotropic rods in a t-cage of average size would not experience a thermodynamic driving force, whereas randomly packed rods are metastable with respect to a liquid-crystalline nematic phase. In that sense the packed rods, as noted earlier [7], can be seen as a glass, analogous to randomly packed spheres which are "Bernal glasses" with respect to a colloidal-sphere crystal [6].

4. Conclusions

We have analyzed the statistical geometry of uncorrelated rod–rod contacts in a static, random thin-rod structure of the type which may be encountered in colloidal rod sediments or (macroscopic) random rod packings. Our main conclusion is that on an average 5 uncorrelated contacts are required to form a t-cage, which blocks all translations of a test rod *perpendicular* to its long axis. The corresponding caging density ϕ_t at which the average number of contacts per rod equals five, is about half the random packing concentration. At the packing concentration, which is metastable with respect to a nematic crystal, virtually all rods are in a t-cage.

Finally, we note that the random contact approximation in our model is probably only correct in the limit of infinite aspect ratio. The model, nevertheless, illustrates the possibility of quantifying the cooperative entanglement (caging) of rods. This may be of interest for future studies of the glass transition or the phenomenon of random packing.

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