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Physica A 274 (1999) 516–524

PHYSICA A

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Sphere caging by a random fibre network

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Received 28 April 1999; received in revised form 23 June 1999

Abstract

We analyse the remarkable efficiency of a random distribution of rigid thin rods (with diameter σ) to 'cage' a test sphere (with diameter $D \gg \sigma$) by purely geometric hindrance due to rod–sphere contacts. The average number of random contacts which traps a sphere in three dimensions corresponds to a volume fraction $\phi_c = 7(D/\sigma)^2$ of very long rods or fibres. Some implications for confinements and dynamics of (colloidal) particles in fibre structures are discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Fibre networks; Confined colloids; Fibrous porous media; Statistical geometry

1. Introduction

The Brownian motion of a tracer particle in a static porous medium is, among other possible causes, always hindered by the exclusion of the tracer from the hard obstacles forming the medium. This geometrical hindrance is a modest effect for point diffusion, i.e. the thermal motion of particles which are much smaller than typical pore dimensions. For larger tracer particles, however, the geometrical hindrance may dominate the dynamics, even up to the extent that the tracer is completely immobilized by the surrounding static obstacles. We will refer to the latter situation as the caging of a tracer at a certain caging volume fraction ϕ_c of obstacles. Caging effects have been

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PII: S0378-4371(99)00282-4

invoked earlier, for example, to visualize hindered self-diffusion in colloidal suspensions [1]. Instead of Brownian host particles in a liquid, we consider fixed obstacles without any hydrodynamics, which makes the caging effect a purely geometrical problem.

In this study the static obstacle is a randomly oriented, rigid thin rod (a 'fibre'). Even a very thin fibre is a large obstacle for a tracer sphere. Thin rods are therefore very effective 'cage formers' at low rod volume fractions. At the same time the caging of a sphere by random thin rods is relatively easy to analyse, because the rod–sphere contacts which form the cage are only weakly correlated for sufficiently thin rods. A practical motivation for us is also the fact that a static collection of random fibres models a variety of fibrous structures, such as paper, gels of colloidal rods (boehmite, imogolite) [2], fibres in random rod packings [3,4] and fibrous biostructures [5]. A random fibre network may also be seen as a special case of a polymer solution in which the polymers are stiff and highly entangled.

In Sections 2 and 3 we present the statistical geometry required to calculate the caging density ϕ_c. The main steps are the evaluation of the average number of blocking points (contacts) which traps a sphere (Section 3) and the conversion of this number to a rod volume fraction ϕ_c (Section 2) making use of the excluded volume of a rod–sphere pair. The available pore space for the sphere and its mean free path is also described. Some consequences of our caging model for real fibre systems (and practical filtration of small particles) are discussed in Section 4.

2. Thin-rod contacts with a sphere

We evaluate the number of intersections (or contacts) between static, randomly oriented rods and a single test sphere. This is essentially an excluded volume problem. The orientationally averaged excluded volume of two randomly oriented spherocylinders with respective diameters σ, D and lengths ℓ, L is given by Onsager [6]:

$$V_{ex} = (\pi/6)(\sigma + D)^3 + (\pi/4)(\sigma + D)^2(\ell + L) + (\pi/4)(\sigma + D)\ell L . \tag{1}$$

If one spherocylinder is a sphere ($\ell = 0$) and the other spherocylinder is a thin rod with a diameter $D \ll \sigma$, the excluded volume reduces to:

$$V_{ex} = (\pi/4)\sigma^2 L + (\pi/6)\sigma^3 \quad \text{for } \frac{\sigma}{D} \gg 1 . \tag{2}$$

Note that the excluded volume in Eq. (2) is a spherocylinder formed by translation of the sphere with diameter σ over the length L of the thin rod (see Fig. 1). When the sphere centre is located inside the excluded volume, the thin rod intersects the sphere. The number N_s of such intersections experienced by a test sphere is therefore:

$$\begin{aligned} N_s &= \rho V_{ex} \\ &= \rho(\pi/4)\sigma^2 L(1 + (\tfrac{2}{3})\sigma/L) , \end{aligned} \tag{3}$$

where ρ is the average rod number density. Eq. (3) neglects all contact correlations: the intersections (or contacts) of rods with the sphere are taken to be statistically

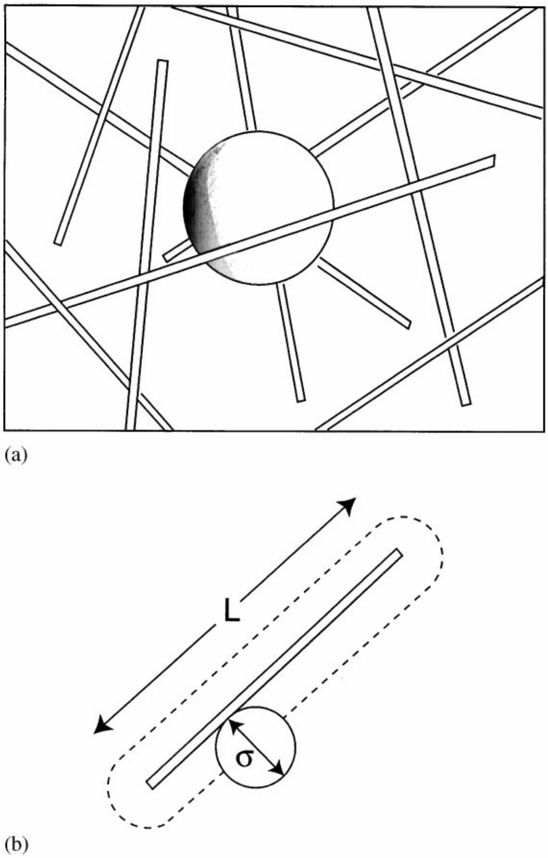

Fig. 1. (a) Schematic of a test sphere (diameter σ) in a structure of random thin rods. (b) Excluded volume V_{ex} (2) of the sphere and one rod. Note that V_{ex} is independent of the rod orientation.

independent. Such random contacts will probably only occur for very thin, high-aspect ratio rods. Two limiting cases are the number of intersections or contacts for very long rods

$$N_s = \rho(\pi/4)\sigma^2 L \quad \text{for } \frac{L}{\sigma} \gg 1 \tag{4}$$

and the number of contacts for very short rods:

$$N_s = \rho(\pi/6)\sigma^3 \quad \text{for } \frac{L}{\sigma} \ll 1 \, . \tag{5}$$

The latter limit is only reached for small rods which are point particles with respect to the large test sphere. For thin rods, without end effects, the solid volume fraction is

$$\phi = \rho(\pi/4)D^2 L \quad \text{for } \frac{L}{D} \gg 1 \tag{6}$$

which modifies Eq. (3) to

$$N_s = \phi\left(\frac{\sigma}{D}\right)^2 (1 + (2/3)\sigma/L),$$
$$= \phi\left(\frac{\sigma}{D}\right)^2 \quad \text{for } \frac{L}{\sigma} \gg 1 . \tag{7}$$

Obviously, an increase in average contact number N_s reduces the mobility of the sphere. Before we deal with a completely caged sphere (Section 3) we describe the reduced mobility of an uncaged sphere in terms of a mean free path traversed by a ballistic sphere until it hits a fibre. This path is calculated as follows. After travelling a distance ℓ, the sphere has swept a spherocylinder with length ℓ and diameter σ. The average number of rods, N, which intersects this spherocylinder is the rod number density ρ times the orientationally averaged exclude volume for this cylinder and a thin rod (see Eq. (1)):

$$N = \rho[(\pi/6)\sigma^3 + (\pi/4)\sigma^2(\ell + L) + (\pi/4)\sigma\ell L] . \tag{8}$$

The mean free path is

$$\bar{\lambda} = \ell/N . \tag{9}$$

For a small displacement, the free path length depends on ℓ. For the long-distance limit where ℓ is larger than both the sphere diameter σ and the rod length L, Eqs. (8) and (9) lead to:

$$\bar{\lambda} = \ell/\rho(\pi/4)[\sigma^2\ell + \sigma\ell L]$$
$$\approx 1/\rho(\pi/4)\sigma L \quad \text{for } \frac{L}{\sigma} \gg 1 . \tag{10}$$

In terms of the thin-rod volume fraction ϕ in Eq. (6) we obtain

$$\frac{\bar{\lambda}}{\sigma} = \frac{1}{\phi}\left(\frac{D}{\sigma}\right)^2 = \frac{1}{N_s} \quad \text{for } \frac{L}{\sigma} \gg 1 \tag{11}$$

with N_s given by Eq. (7). Eq. (10) is verified by simulations on ballistic sphere transport in Ref. [7].

3. Sphere caging

Each of the N_s contacts of the thin rigid rods in Eq. (7) with the test sphere is considered as a blocking point for the sphere. Since these contacts are taken to be uncorrelated we ask for the average number $\langle N \rangle$ of randomly placed, static contacts which cage the sphere, i.e. which prohibit all translational motions of the sphere. Suppose contacts are placed one by one at random positions on the sphere surface until they form a cage. Let N_c be the number of contacts in this cage and $P(N_c = k)$ the probability that N_c has a particular value k. One can also place a given number of

n random contacts on the sphere surface and evaluate the probability p_n that these n contacts form a cage. The probabilities are related as [8]

$$1 - p_n = P(N_c > n) = \sum_{k=n+1}^{\infty} P(N_c = k)\,. \tag{12}$$

The average number of contacts in a cage follows from

$$\begin{aligned}\langle N\rangle &= \sum_{k=0}^{\infty} kP(N = k)\\ &= \sum_{n=0}^{\infty}\sum_{k=n+1}^{\infty} kP(N_c = k) = \sum_{n=0}^{\infty}(1 - p_n)\,.\end{aligned} \tag{13}$$

The caging probability p_n, and thus the average size $\langle N\rangle$ of a cage, depends on the dimensionality of the problem. To illustrate the caging concept we first consider the one-dimensional case which can be easily solved. Suppose a sphere can only move in one dimension, for example because it is confined in a straight cylinder. A plane perpendicular to the cylinder axis divides the sphere into two hemispheres. At least $N_{\min} = 2$ contacts are required to immobilize the sphere, with each contact blocking a hemisphere. If n contacts are all located on the same hemisphere they do not form a cage, because the sphere can escape. The probability for this situation is

$$1 - p_n = \left(\frac{1}{2}\right)^{n-1} \quad \text{for } n \geqslant 2\,. \tag{14}$$

It is clear that

$$1 - p_n = 1 \quad \text{for } n \leqslant 1\,. \tag{15}$$

Hence the average number of caging contacts in Eq. (13) is

$$\langle N\rangle = 2 + \sum_{n=2}^{\infty}\left(\frac{1}{2}\right)^{n-1} = 3\,. \tag{16}$$

For a sphere which can only move in a plane, the caging problem is the same as for a disc which is immobilized by contacts on its circumference. Here one needs at least a triangular configuration of $N_{\min} = 3$ contacts to form a cage. The average cage size for a sphere in 2-D in Eq. (13) turns out to be $\langle N\rangle = 5$, a result which is derived elsewhere [8]. The network of random fibres in this study (and usually in practice) is a 3-D structure so we have to address sphere caging in three dimensions. We use the following numerical procedure to evaluate $\langle N\rangle$. The minimal number of contacts to cage a sphere in three dimensions is a tetraeder of four contacts, so we start with four points placed at random on the sphere surface. Each point is the origin of a force $\boldsymbol{F}$ directed to the sphere centre. The sphere is caged when the moduli of the forces can be chosen such that $\Sigma\boldsymbol{F} = 0$. For $n \geqslant 5$ it suffices to show that there is at least one combination of four points (or equivalently forces) that fix the sphere. For each n,

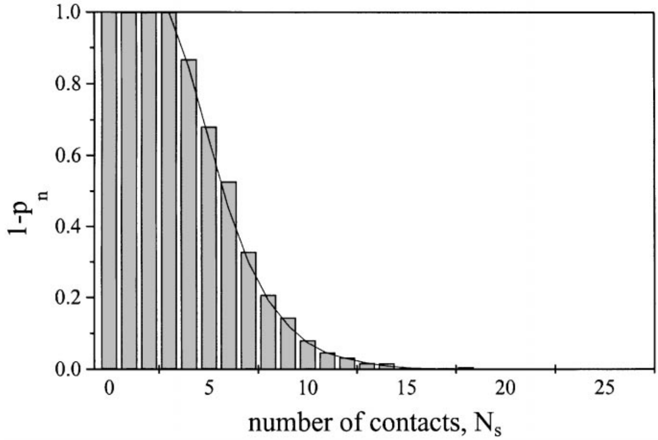

Fig. 2. Probability $1 - p_n$ that a sphere is uncaged (i.e. free to translate) as function of the number of random contacts N_s, simulated for a three-dimensional sphere.

Table 1
Contact number for sphere caging in d dimensions

Dimension d	Minimum N_{min}	Average $\langle N \rangle$
1	2	3
2	3	5
3	4	7

10 000 sets of randomly placed contacts are generated. The numerical analysis (see Fig. 2) yields for the average cage size:

$$\langle N \rangle = \sum_{n=0}^{\infty} (1 - p_n) = 7.0 . \tag{17}$$

4. Results and discussion

Table 1 summarizes the results for the caging of a sphere. The minimal and average amount of (fibre) contacts (in Table 1) needed to cage a sphere in $d = 1, 2, 3$ dimensions are generated by

$$N_{\mathrm{min}} = d + 1, \qquad \langle N \rangle = 2d + 1 . \tag{18}$$

This result for $\langle N \rangle$ has only been verified analytically for $d = 1$ (Eq. (16)) and $d = 2$ (in Ref. [8]). We note here that the method followed for $d = 1, 2$ (i.e the direct counting of caging configurations) is difficult to extend to higher dimensions. Work is in progress, however, to give a general proof of $\langle N \rangle = 2d + 1$ using a geometrical analysis which will be discussed elsewhere [9].

The average number of contacts in Eq. (7) equals $N_s = \langle N \rangle = 7$ at the fibre volume fraction ϕ_c. Our final result for the caging density is therefore:

$$\phi_c = \frac{7(D/\sigma)^2}{1+(2/3)\sigma/L}$$

$$= 7\left(\frac{D}{\sigma}\right)^2 \quad \text{for } \frac{L}{\sigma} \gg 1 . \tag{19}$$

This result confirms our expectation that thin rigid fibres or rods are very efficient to cage or trap a test sphere. The reason for this efficiency is that even for rods of vanishing thickness, the excluded volume experienced by the test sphere, and therefore the contact probability, is large. (Not that the rod caging volume fraction ϕ_c goes to zero when the rod thickness $D \to 0$.) At rod densities $\phi \geqslant \phi_c$ the majority of test spheres will be unable to translate, which makes the static rod network at the same time a reflection boundary for free spheres outside the network. In the language of separation techniques the network is an efficient fibrous porous medium [10] in a filtration process. (Perhaps blood clothing is also a case in point, where structures of fibrin fibres efficiently capture blood platelets.)

Eq. (19) possibly suggests that the rod aspect ratio L/D is not a relevant parameter for the present caging problem. However, in a dense structure of randomly oriented thin rods, the rod volume fraction may be fixed by the rod aspect ratio. For the random dense rod packing, for example, it has been found [3,4,11]:

$$\phi\frac{L}{D} \approx 5.4 \pm 0.2, \quad \frac{L}{D} \gg 1 . \tag{20}$$

Suppose a sphere with diameter $\sigma = \sigma_c$ will be caged in this packing. In view of Eqs. (19) and (20):

$$\frac{\sigma_c}{D} \approx 1.1\sqrt{L/D}\,, \tag{21}$$

which gives an indication for the sphere size which will be unable to enter a random rod packing.

The decrease in caging density for larger values of σ/D is illustrated in Fig. 3. This figure shows the probability (from Fig. 2) that $n = N_s$ contacts with rods (see Eq. (3)) will trap the sphere. The figure illustrates the rapid increase of the caging probability for a large sphere above a threshold volume fraction corresponding to an average of $N_s = 4$ rod sphere contacts; the minimal number needed to form a cage which traps the sphere. At the caging density ϕ_c in Fig. 3 obtained from Eq. (19), the average number of contacts equals the average number $\langle N \rangle = 7$ for a cage. At this density about 20% of spheres in the fibre network still has some mobility; only for $N_s > 10$ virtually all spheres are trapped.

The pore space in the fibre network in which an untrapped particle can move, can be characterized in various manners. One can probe 'cylindrical pores' by translating spheres over a certain distance until they hit a fibre. The average length of such a

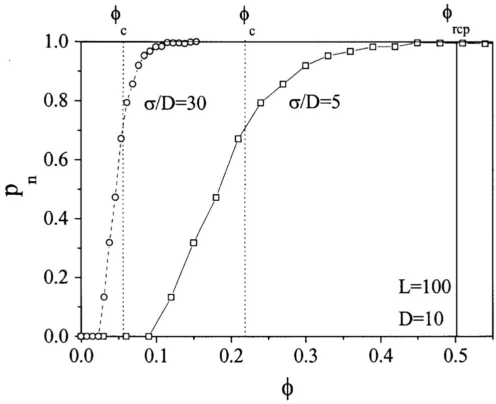

Fig. 3. Sphere-caging probability versus rod volume fraction ϕ for rod–sphere diameter ratio's $\sigma/D=5$ and 30. The dashed vertical line is the caging density ϕ_c defined in Eq. (19). The drawn line indicates the random close packing density ϕ_{rcp} [3] for rods with aspect ratio $L/D=10$.

pore is the mean free path in Eqs. (9)–(11). Another way of probing the pore space is by inflating smallest test spheres until they touch one fibre [7]. Ogston [11,12] has studied the resulting distribution of 'spherical pores'. The mean free inflation diameter in a network of long straight fibres is according to Ogston [11,12]:

$$\bar{\sigma}=\frac{D}{2}\sqrt{\frac{\pi}{\phi}}\,. \tag{22}$$

This result, confirmed by simulations [7], obviously differs from the mean free path in Eq. (11), and actually should be compared to the average diameter, $\bar{\sigma}$, of a sphere which has *one* intersection with a fibre. Substitution of $N_s=1$ in Eq. (7) yields

$$\bar{\sigma}=\frac{D}{2}\sqrt{\frac{4}{\phi}}\,. \tag{23}$$

This diameter is slightly larger than Ogston's result (22), because we allow intersections of the sphere by a fibre whereas Ogston [11,12] assumes that the fibre is at least a distance $\sigma/2$ removed from the sphere centre.

The origin of the scaling $\bar{\sigma}\sim\phi^{-1/2}$ in Ogston's more elaborate approach [12] is not quite clear. We find here that the scaling is simply a consequence of the rod–sphere excluded volume. Our analysis also emphasizes that Eq. (22) underestimates the size of a sphere which will be trapped by randomly oriented fibres, because one contact cannot cage a sphere.

For a static isotropic thin-rod collection the assumption of random contacts has been made [3,4] in analogy with Onsager's second virial approximation [6] for thermal rods. One argument is that the surface fraction of contact area vanishes for $L/D\to\infty$, so contact areas reduce to point contacts. Whether such point contacts are indeed uncorrelated however, has not been rigorously proven yet. It should be noted that the experimentally observed [3,4,11] invariance in Eq. (20) strongly suggests that contact correlations for thin rods are weak, otherwise higher-order ϕ terms would be noticeble in experiments [3,4]. For such thin rods, intersections with a sphere as in Fig. 1A would be weakly correlated as well.

5. Conclusions

The density of random, rigid thin rods which cage a sphere in three dimensions can be obtained from the rod–sphere excluded volume, in combination with a numerical analysis of the contact distribution on the sphere. One prediction is that the caging density of fibres is proportional to the square of the fibre diameter. The essential assumption of random sphere-fibre contacts in our approach is probably only strictly justified in the limit of infinite rod aspect ratio. The model, nevertheless, illustrates the possibility of quantifying the trapping ('freezing') of spheres by a rigid fibre network. As such it may be a reference for studies on more complicated fibrous media found in, for example, suspensions of colloidal rods [7,13] or structures of bipolymers [14] and microtubules [15].

Acknowledgements

This work is part of the research Program of the Foundation for Fundamental Research on Matter (FOM) with financial support from the Netherlands Organization for Scientific Research (NOW). Dr. G.J. Vroege is thanked for helpful comments. Mrs. M. Lanen-Vos and Mrs. M. Uit de Bulten-Weerensteyn were very helpful in the preparation of the manuscript.

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