The Random Contact Equation and Its Implications for Colloid Rods in Packings, Suspensions, and Anisotropic Powders

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The Random Contact Equation and Its Implications for (Colloidal) Rods in Packings, Suspensions, and Anisotropic Powders

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The experimentally observed asymptotic scaling $\phi(L/D)$ = constant, for the random packing volume fraction (ϕ) of rods with high aspect ratio (L/D), is shown to be the consequence of *uncorrelated* rod−rod contacts, the constant being equal to $\langle c \rangle = 5.4 \pm 0.2$ contacts per rod. The weak dependence of $\langle c \rangle$ on the particle shape accounts for the drastic decrease in random packing density going from spheres to thin rods. Moreover, $\langle c \rangle \approx 5.4$ is large enough for isotropic rod packings to be metastable "rod-glasses" with respect to a fully ordered nematic phase. In addition to rod packings, literature results on colloidal sediments, rheology, and percolation of random rods are (re)interpreted to conclude that uncorrelated pair contacts suffice to explain densities of a variety of (mechanical) thin-rod systems.

1. Introduction

In nature and technology a wide variety of random-like structures can be found which are composed of elongated particles. Examples are packings of rice grains or plant seeds, cellulose,[1] fibrous porous media and anisotropic powders,[2,3] random fibers in composite materials,[4−6] and sediments or gels of colloidal rods.[7−9] An unexplained general feature of such systems is that packing densities are low when the particle aspect ratios are high. For example, sediment densities of rod-like colloids are considerably lower than the random packing density for spheres (Figure 1). The present study was initiated to interpret this observation. A literature search offered few starting points. The density of random rod or fiber packings has, with the exception of the work of Milevski[10,11] and Nardin et al.,[12] received very little attention. Studies on powders[13−15] and random materials[16−18] mainly deal with spherical particles.

Perhaps this preference for spheres is based on the premise that nonspherical particles have more (size and orientation) parameters which will complicate the analysis
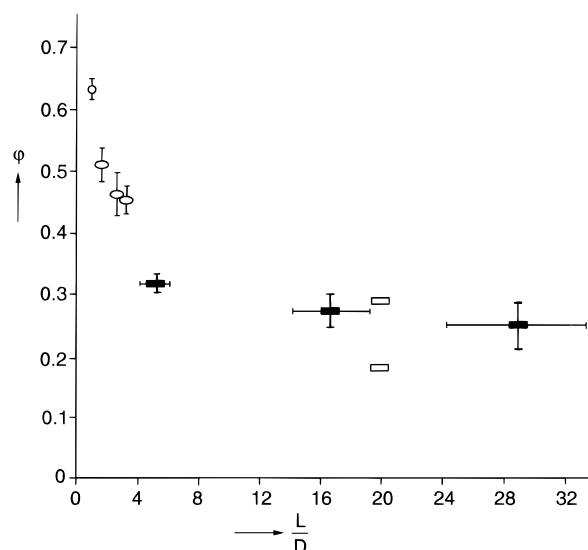

Figure 1. Sediment volume fractions (ϕ) versus aspect ratio (L/D) of various inorganic colloids: (circle) silica spheres,[24] (ovals) hematite (FeOOH) spindels,[9] (open rectangles) boehmite (AlOOH) rods,[25] and (filled rectangles) silica rods.[7] The uncertainty in the data is mainly due to some size (and shape) polydispersity, and alignment of rods.[7]

of particle stackings in comparison with spheres, as stated for example in ref 13. Here we take the opposite view: structures of thin rods with a high aspect ratio are relatively simple and matters are actually more complicated for compact particle shapes. The assumption is that for sufficiently thin rods mechanical contacts are effectively uncorrelated: the random thin-rod array is essentially a collection of independent pairs of rods. For spheres stackings, for example, higher order contact correlations are important, making such a simple model invalid.

The purpose of this article is to explain the random contact model and to investigate its consequences for the density of various rod systems. Section 2 discusses the basic feature of the model, namely that if contacts are uncorrelated, their number per particle varies *linearly* with the particle concentration. The volume fraction (ϕ) of random (colloidal and macroscopic) rod packings as a function of the rod aspect ratio, L/D, is discussed in section 3. The scaling $\phi(L/D)$ = constant, first noted by Nardin et al.,[12] is shown to be the result of random contacts. The

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rescaled packing densities $\phi(L/D)$ are compared with Onsager's results[19,20] for the isotropic−nematic phase transition for colloidal rods in section 4. In sections 5 and 6 implications of the random contact model are discussed for fiber composites and rods in a percolating structure or gel. Section 7 summarizes the main conclusions and contains some speculations about the origin of random contacts and their consequences for other particles such as disks.

2. The Random Contact Model

2.1. Arbitrary Particles. Consider an assembly of (on average) randomly oriented particles with a test particle T and a neighbor N, their centers joined by a vector $\vec{r}$. In free space, N could adopt any orientation, but now particle T forbids a fraction, $f_{ex}(\vec{r})$, of the possible orientations. This excluded fraction is also the probability that N, with its center fixed at $\vec{r}$, will contact T when given a random orientation. Suppose there is a number density, $\rho(\vec{r})$, of such randomly distributed particles. Then the contact probability is density dependent, and the average number of contacts per particle, $\langle c \rangle$, is

$$\langle c \rangle = \frac{1}{2} \int f_{ex}(\rho, \vec{r}) \rho(\vec{r}) \, d\vec{r} \qquad (1)$$

where the factor $^1/_2$ avoids double counting of contacts. In a simple mean-field approximation $\rho(\vec{r})$ is replaced by the average number density ρ, and $f_{ex}(\rho, \vec{r})$ by $f_{ex}(\vec{r})$. The latter assumption implies that two particles form a contact with a probability which is on average independent of other contact formations. Hence

$$\langle c \rangle \approx \frac{1}{2} \bar{\rho} \int f_{ex}(\vec{r}) \, d\vec{r} \qquad (2)$$

The integral in (2) can be identified as the orientational average *excluded* volume, v_{ex}, for a *pair* of randomly oriented particles.[19,20] So the number density of the particle array is

$$\bar{\rho} = 2\langle c \rangle / v_{ex} \qquad (3)$$

This is a mechanical equation of state (the "random contact equation") for a system of fixed random particles with uncorrelated mechanical contacts. The significance of eq 3 is that in such a system, for a given $\langle c \rangle$, the particle concentration is uniquely determined by v_{ex} and hence by the particle shape. The number of contacts per particle may, in turn, be fixed by physical requirements. For example $\langle c \rangle$ could have a particular value required to achieve mechanical stability in a dense random packing, or it could be the minimal value needed to construct a percolating structure. One can also imagine gels and sediments of (colloidal) particles with $\langle c \rangle$ somewhere between the percolation threshold and the dense-packing value. The various particle systems will be discussed in section 3 and thereafter.

2.2. Rigid (Thin) Rods. The orientational average excluded volume of a pair of random rods, modeled by cylinders of length L with two hemispherical caps of diameter D, is given by[19,20]

$$v_{ex} = (\pi/2)L^2 D + 2\pi D^2 L + (4/3)\pi D^3 \qquad (4)$$

The volume fraction, ϕ, of the spherocylinders with volume v_p is:

$$\phi = \bar{\rho} v_p \qquad v_p = (\pi/6)D^3 + (\pi/4)D^2 L \qquad (5)$$

Thus for spherocylinders eq 3 leads to

$$\phi \frac{L}{D}\left[4\frac{D}{L} + \frac{3(L/D)}{3(L/D) + 2}\right] = \langle c \rangle \qquad (6)$$

which for high aspect ratios reduces to

$$\phi \frac{L}{D} \sim \langle c \rangle \qquad \frac{L}{D} \gg 1 \qquad (7)$$

with $\sim$ denoting a limiting relation valid at high aspect ratios. For cylinders without end caps one finds the same asymptotic relation, because for thin rods ($L/D \gg 1$) the detailed shape of the rod ends is irrelevant. For the limiting case of spheres ($L/D \rightarrow 0$), eq 6 gives the unphysical result $\phi = \langle c \rangle/4$. For a random sphere packing $\langle c \rangle$ is about 6,[21-23] which would correspond to $\phi = 1.5$. Contacts between hard, impenetrable spheres are highly correlated, so the random contact model is not valid. We shall see in section 3, however, that for *thin* hard rods the model is appropriate.

3. Experiments on Random Rod Packings

Figure 1 shows some packing densities for sediments of colloidal particles, prepared in our laboratory, with decreasing aspect ratios: silica spheres,[24] hematite spindels,[9] boehmite rods,[25] and silica rods.[7] The trend is that packing densities decrease quite drastically with increasing aspect ratios, as one would expect from eq 6. However, the data hardly allow a quantitative conclusion. In particular aspect ratios are not high enough to verify eq 7. Collecting more data for Figure 1 is not an easy task. Colloids with well-defined shape and (extreme) aspect ratios are difficult to synthesize. Moreover, surface forces (Van der Waals attractions) may influence packing densities.

Therefore we "simulated" colloidal sediments by preparing packings of macroscopic, rigid rods with well-defined aspect ratios (Figure 2). The rods are smooth nonsticking objects made of wood, plastic, and copper wire. Packing experiments went as follows. The total volume of rods for a certain experiment (usually in the range 1−10 L) was determined from the total weight of the rods and their mass density. Rods were sprinkled in small portions in a rigid vessel with a diameter of at least 5 times the rod length. Then the vessel was shaken erratically by hand for a few seconds and the final packing volume was determined. The whole procedure was repeated 10 times for each rod species to obtain the average volume fractions of Figure 3.

Rods with small aspect ratios (say below $L/D \approx 30$) flow more or less like a liquid, so packings assume the shape of the vessel. Here the determination of the packing volume is fairly easy. With an increasing aspect ratio, however, rods have an increasing tendency to form solid-like stiff structures. For example, deposition of copper rods with an aspect ratio of about 77 (Figure 2B) produces a fairly rigid plug which retains its shape outside a vessel. In such a case the packing volume was determined by measuring the dimensions of the plug. It should be

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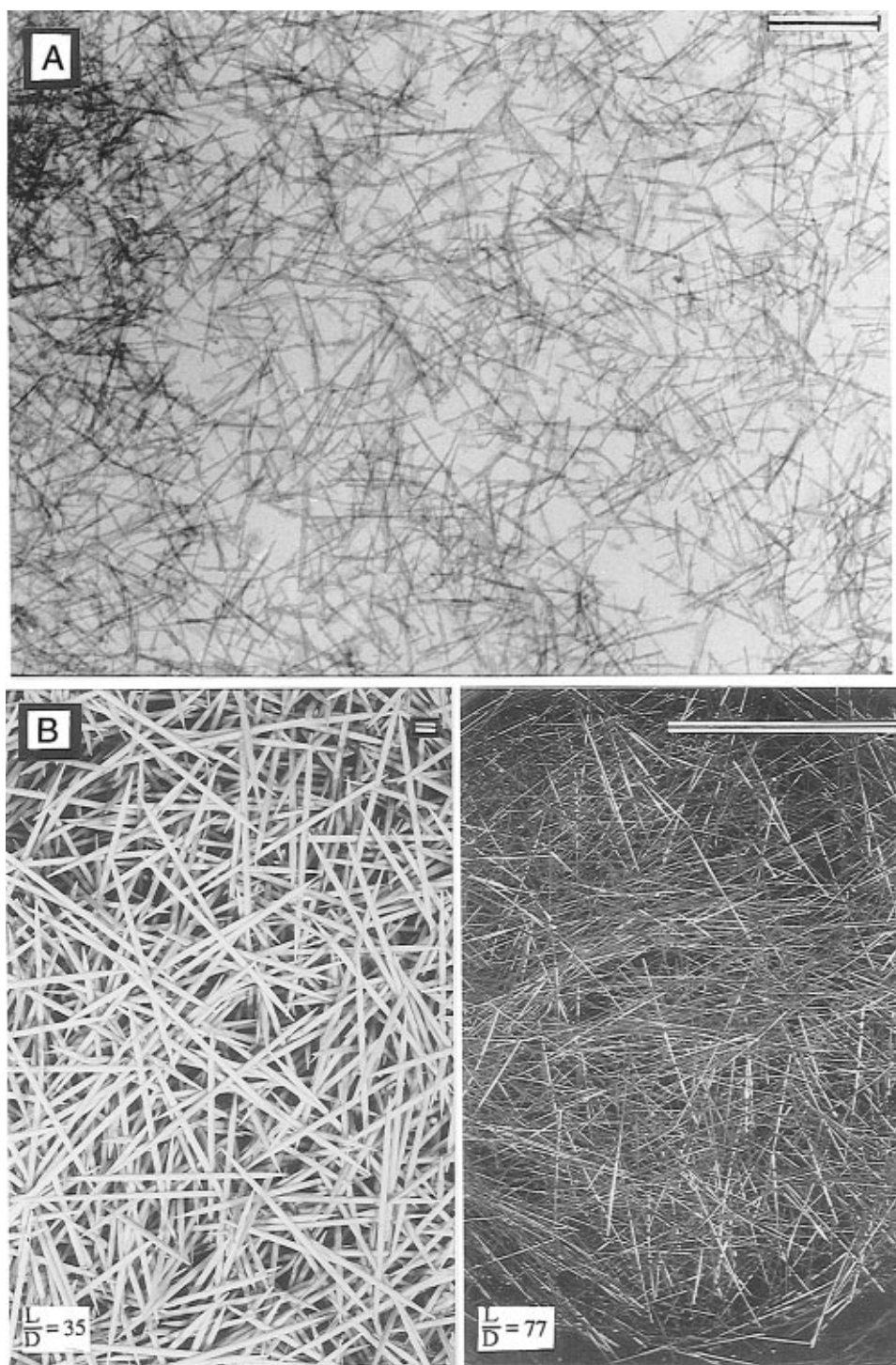(25) Philipse, A. P.; Pathmamanoharan, C., unpublished results.

Figure 2. (A) Impression of a two-dimensional random distribution of silica rods on an electron microscope grid.[7] The bar is 200 nm. (B) "Simulation" of a three-dimensional sediment of random rods with a random packing of wooden rods (left) and copper wire (right). The bars represent 2 cm. The pictures illustrate the analogy between the microstructure of colloidal (A) and macroscopic (B) rod packings.

emphasized that the transition of liquid to solid-like behavior is not due to stickiness, surface roughness, or friction. The transition is solely due to a change in aspect ratio. The origin of this curious phenomenon is not yet clear.

The determination of packing density as described above is reproducible within 5−10%. The time for *erractic* shaking is not very critical. We observed that tapping systematically against a vessel yielded a modest density increase because of "nematic" ordering of rods near the wall. Vibration induced by placing a vessel for several minutes on a vortex mixer generally produced some densification, also because of rod alignment at the walls.

We also checked that using larger vessels did not change the results significantly, so wall effects are not important.

The final results are shown in Figures 3 and 4. Near $L/D = 1$ the density is close to the random sphere packing value of $\phi = 0.64$. At higher aspect ratios, volume fractions decrease considerably, just as for the colloids. (Note that the data for colloids in Figure 1 are not too different from those of their macroscopic counterparts). For comparison we checked the extensive literature on fiber packings ("fibrous media"), reviewed in refs 2 and 3. However, aspect ratios are seldom specified and it is not always clear whether particles are rigid or not. Two interesting exceptions are results from Milevski[11] and Nardin et al.,[12]
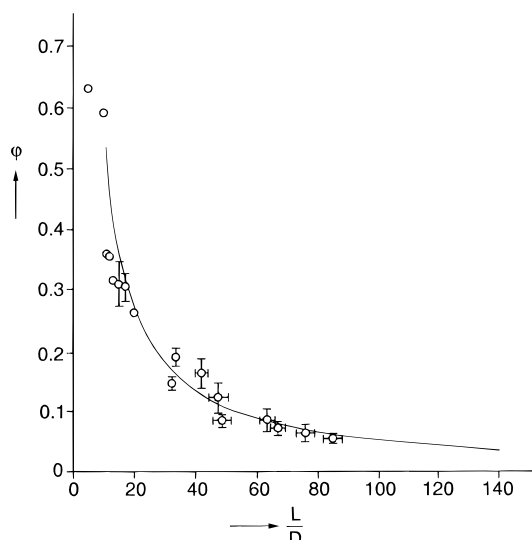
Figure 3. Volume fractions (ϕ) of packings as in Figure 2B decrease strongly with increasing aspect ratio (L/D). (The drawn line is the hyperbolic fit $\phi(L/D) = 5.4$ from Figure 4). For $L/D < 35$ smooth, nonsticking plastic tubes and wooden rods (Figure 2A) were used. For larger L/D pieces were cut from a copper wire (diameter 0.19 mm), which form stackings of the type shown in Figure 2B.
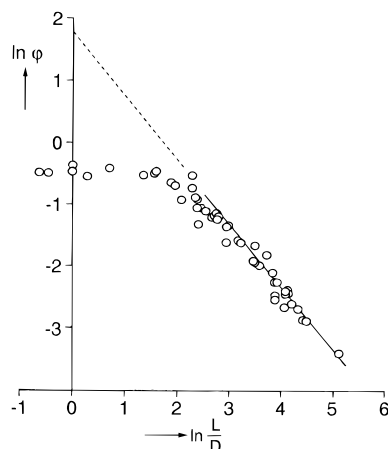
Figure 4. This double logarithmic plot includes data from Figure 3 and results obtained by Milevski[11] and Nardin et al.[12] for packing of rods of steel, fiber glass, various plastics, and wood. For thin rods ($L/D \geq 15$), $\phi(L/D)$ is virtually constant. The fit corresponds to $\phi(L/D) = 5.4(\pm 0.2)$. Within the random contact model (see the text), this equals the number of contacts per rod. Particle dimensions in this figure are in the range of several microns to several centimeters, which indicates that properties of random rod packings are scale independent. The data for $\ln(L/D) < 0$ are for disks;[12] see also section 7.

showing the same pronounced decrease in packing density with increasing aspect ratio as in our data. The three independent data sets in Figure 4, which cover a wide range of rod sizes and materials, yield the following insights.

First, rods have a unique random close packing density which only depends on the aspect ratio. (This was first stated explicitly by Nardin et al.[12]). It is therefore unjustified to attribute low rod packing densities *a priori* to interparticle friction, attraction, or surface irregularities.[14,16,26,27] Of course, such accidental factors may prevent rods from reaching their maximal density, just as sticky spheres will not arrange as densely as in the Bernal packing.[21]

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Secondly, for sufficiently thin rods ($L/D > 15$) the product $\phi(L/D)$ is virtually constant, as can be seen in the bilogarithmic plot in Figure 4. According to the model underlying eq 3, the scaling simply expresses that contacts on a thin rod are uncorrelated and that the number of these contacts, $\langle c \rangle$, is virtually the same for all rod packings. A fit of our data for $L/D > 15$ to $\phi(L/D)^\alpha = \langle c \rangle$ yields $\alpha = 0.98(\pm 0.04)$ and $\langle c \rangle = 5.0(\pm 0.4)$, which is in excellent agreement with the data of Milevski[11] and Nardin et al.[12] Including their data in the fit (shown in Figure 4) yields $\langle c \rangle = 5.4(\pm 0.2)$. Apparently about five to six contacts fix a rod in a packing in a mechanically stable position.

In the literature, incidently, there is some confusion about the relation(s) between packing densities and particle shape. Bigg[28] concludes erroneously from Milevski's data[10,11] that for thin rods the density decreases *exponentially* with the aspect ratio. In reality the decrease is much slower. German[14] suggests for Milevski's data[10,11] the correlation

$$1/\phi = (1.98 + 0.038(L/D)^2)^{1/2} \qquad (8)$$

At high L/D, however, this equals $\phi(L/D) \cong 5.13$, i.e. the random contact scaling. Attempts have also been made to predict packing densities of nonspherical particles from the *sphericity* parameter[13,9]

$$\psi = 4.87 v_p^{2/3}/s \qquad (9)$$

which characterizes the shape of a particle with volume v_p and surface area s. For a sphere, $\psi = 1$, and for all other shapes, $\psi < 1$. For thin rods,

$$\psi = 1.32(D/L)^{1/3} \qquad \frac{L}{D} \gg 1 \qquad (10)$$

By comparing this result with (our analysis of) Figures 3 and 4, it is clear that at least for thin rods the sphericity parameter has no predictive value, because ϕ scales in a different manner with the aspect ratio. The correct relation $\phi(L/D) = $ constant for thin rods was noted for the first time by Nardin et al.[12] These authors try to explain the relation with an equivalence between random stackings of rods and spheres. This equivalence, however, does not invoke the relevant parameters for the density, namely excluded volumes and mechanical contacts. It is these parameters which, as explained in section 2, account for packing density.

Returning to Figure 4, we note that below $L/D \approx 15$ the bilogarithmic density curve would follow the dotted line if particle contacts would remain only weakly correlated. Instead the curve nods to a horizontal, expressing the increasing influence of multicontact correlations in packings of compact objects. A theoretical model for the density curve in Figure 4 below $L/D \approx 15$ is lacking. However, we know at least that for spheres the contact number in a dense random arrangement is about 6.[21-23] This suggests that $\langle c \rangle$ varies little over the whole aspect ratio range in Figure 4. This invariance suffices to explain the low packing density of thin rods. A sphere of diameter D finds its contacting neighbors in an excluded volume of order D^3. For a rod of length L, mechanical stability is provided by about the same number of neighbors, with their centers in a much larger excluded volume of order DL^2. Hence, in accordance with eq 3, the number density of rod centers, and thus the packing fraction, is low. The absolute value of $\langle c \rangle \approx 5.4$ has an interesting consequence

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when a comparison is made (section 4) with a thermodynamic system.

4. Isotropic Rod Glasses

In a thermodynamic treatment of colloidal thin rods, the same rescaled density $\phi(L/D)$ appears as for mechanical packings. Onsager and others[19,20,29] have calculated that an isotropic hard-rod suspension will become instable with respect to nematic crystal formation at a rescaled density

$$\phi_i \frac{L}{D} \sim 3.29 \qquad \frac{L}{D} \gg 1 \qquad (11)$$

whereas only a nematic phase is stable above

$$\phi_n \frac{L}{D} \sim 4.19 \qquad \frac{L}{D} \gg 1 \qquad (12)$$

For the random close rod packings in section 2 we found

$$\phi_{rcp} \frac{L}{D} \approx 5.4(\pm 0.2) \qquad \frac{L}{D} \gtrsim 15 \qquad (13)$$

which is significantly larger than the (numerically determined[20]) densities in eqs 11 and 12. Thus a colloidal random close rod packing will crystallize spontaneously to a more dense nematic phase. This relaxation is, of course, absent for the macroscopic rods in Figure 2B, which are permanently arrested in an isotropic "glassy" state. Such rod glasses are reminiscent of the Bernal sphere glass.[30] A colloidal hard-sphere fluid starts to crystallize at $\phi \cong 0.49$, whereas above $\phi \cong 0.55$ only an ordered colloidal crystal is stable.[30] These densities are below the random packing concentration ($\phi = 0.64$), just as for thin rods. We can conclude that the Bernal glass ($\phi = 0.64$) is not unique: Figure 4 represents a whole *family* of metastable glasses.

Members of this family may have very different crystallization kinetics. In the colloidal Bernal packing,[30] spheres are structurally arrested and crystal growth is absent. Sufficiently thin rods, however, always keep some freedom of motion parallel to their long axis. (This phenomenon is well-known from the theory of dynamics of rod-like macromolecules.[31,32]) By a sequence of such lengthwise Brownian motions, rods can diffuse into ordered regions. Any attraction (or friction) between contacting rods will slow down the lengthwise motions. In this respect attractions decrease the relaxation rate of the random rod packing. The impact of attractions, however, is complicated because they also imply torques between the rods which favor a nematic alignment.[33]

For macroscopic rods, incidently, the lengthwise motion can also be used to insert an extra rod in a packing of constant volume, thereby raising the density. This does not contradict the notion of a *unique* close packing density which only depends on the aspect ratio. Both sphere and rod packings are close in the sense that compression by gravity or a piston cannot densify the system without particle degradation or deformation. It is this macroscopic compressibility which vanishes at a density given by eq 13.

5. Fiber Composites and Rheology

The results from sections 2 and 3 imply a fundamental restriction on the density of *randomly* distributed aniso-

tropic powders such as reinforcing rigid fibers in a polymer matrix. If the density is significantly above the random close packing value of $\phi(L/D) = 5.4(\pm0.2)$, it is very likely that particles are to some extent aligned to form bundles, or perhaps they are fractured. (Note that breaking particles lowers the aspect ratio and therefore increases the random packing density.) This alignment may be due to Brownian motion (section 4). For large fibers such as whiskers,[6,34] however, any ordering of particles is more likely due to mechanical vibrations or shear forces.

The presence of fiber bundles, incidently, is reported to limit the fracture strength of composites.[34] It is noteworthy that such a limitation may be solely due to a too high fiber concentration. In that case optimization of processing steps, such as mixing of fibers and resin, will not be very effective. Instead the rescaled density $\phi(L/D)$ should be lowered. The product $\phi(L/D)$ is also a determining factor for the rheology of thin-rod systems.

A theory for the effect of interactions on the shear viscosity of (Brownian) rods has been developed for dilute suspensions.[35] For high concentrations of rods or fibers, semiempirical relations have to be used such as the Maron−Pierce equation[5]

$$\eta_r = (1 - \phi/\phi_{max})^{-2} \qquad (14)$$

or the Krieger−Dougerty equation[36]

$$\eta_r = \left(1 - \frac{\phi}{\phi_{max}}\right)^{-[\eta]\phi_{max}} \qquad (15)$$

which relates the relative suspension viscosity, η_r, to the intrinsic viscosity, $[\eta]$, and the rod volume fraction, ϕ. The intrinsic viscosity increases with the aspect ratio, as predicted by, for example, Kuhn and Kuhn.[37] Recently this prediction was verified for inorganic colloids in a study on the low-shear viscosity of rigid silica rods.[38] Here we are interested in the volume fraction ϕ_{max} at which, according to eq 14, the viscosity diverges because the highly entangled rigid rods can no longer respond to the applied shear. Particle alignment, or course, may occur before ϕ_{max} is reached. However, if the system remains isotropic, ϕ_{max} is expected to shift to low values for high rod aspect ratios, if the random contact model (eq 7) applies.

Bergström[34] indeed found a considerable decrease from $\phi_{max} = 0.61$ for suspensions of compact Al_2O_3 particles to $\phi_{max} = 0.28$ for anisotropic powders (silicon−carbide whiskers with average aspect ratio $L/D = 9.5$). Kitano et al.[5] studied more systematically the rheology of a variety of fibers in a polymer matrix. The particles are fairly polydisperse and it is difficult to assess from their report whether systems are always isotropic. Using eq 14 to determine ϕ_{max}, the authors found the following linear fit for its dependence on the *average* aspect ratio:[5]

$$\phi_{max} = 0.54 - 0.0125 \frac{L}{D} \qquad (16)$$

A similar linear correlation was mentioned by Tsao and Danforth[6] in a study on silicon−carbide whiskers. Equation 16 has, however, no physical justification and is also incorrect for high aspect ratios, where ϕ_{max} is predicted to become negative instead of approaching zero. Table 1 lists values of $\phi_{max}(L/D)$, taken from the results of Kitano.[5] The qualitative trend is that at sufficiently high L/D the density approaches a constant value of about $\phi_{max}(L/D) \approx$

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Table 1.   Volume Fractions ϕ_{max} for Divergence of Viscosity of Fibers in a Polymer Matrix[5]

L/D^a	$\phi_{max}(L/D)^b$	L/D^a	$\phi_{max}(L/D)^b$
6	2.6	18	5.7
8	3.5	23	6
9^c	2.7	27	4.9

^{a} Average aspect ratios. ^{b} ϕ_{max} estimated by extrapolation.[5] ^{c} From ref 29.

5−6. This indicates that

$$\eta_r \approx \left(1 - \frac{\phi}{\langle c \rangle}\frac{L}{D}\right)^{-2} \tag{17}$$

With $\langle c \rangle \approx 5-6$, there is a more appropriate estimate of the divergence of the viscosity. Equation 17 also suggests that viscosities should be plotted versus $\phi(L/D)$ instead of ϕ. Note that in Table 1 $\phi_{max}(L/D)$ becomes *smaller* at low aspect ratios, just as for the random packing densities in Figure 3. This trend, due to the finite aspect ratio, is also predicted by eq 6.

6. Percolating Rods and Rod Gels

Besides the dense rod assemblies in the previous sections, it is also worthwhile to consider *dilute* rod systems in terms of the random contact model. For example, when rods are randomly distributed in a polymer matrix, a percolation path will be formed at some (low) critical threshold density, ϕ_t. If this threshold corresponds to a fixed number of uncorrelated contacts, the scaling $\phi_t(L/D)$ = constant can be expected, in accordance with eq 7.

Bigg[28] studied rod percolation experimentally by measuring the electrical conductivity of an insulating matrix containing stainless steel fibers. The composite changes from an insulator to a conductor over a very narrow range of fiber concentration. Biggs principal conclusion is that the metal fibers should have a high aspect ratio to obtain low threshold densities. This is indeed the trend we would expect from eq 7. However, as Biggs also indicates,[28] the fibers are very flexible and the composite samples are two-dimensional. This does not allow a quantitative comparison with eq 7 for rigid rods in a 3-D stacking.

Boissonade et al.[39] performed a Monte Carlo simulation of a system of random rods on a 3-D simple cubic lattice. They wanted to test a prediction of the form $\phi_t(L/D)^2$ = constant, for high aspect ratios. The authors found, instead, that their simulation results approach the relation $\phi_t(L/D)$ = constant (Figure 5), adding the comment that larger aspect ratios $L/D > 15$ would be required to ascertain this relation.[39] Balberg et al.[40] investigated the onset of percolation of three-dimensional, continuous systems of spherocylinders over a wider range of aspect ratios. Figure 5 shows some of their results for randomly oriented particles which indeed confirm the asymptotic scaling, with $\langle c \rangle$ on the order of 1:

$$\phi_t\frac{L}{D} = O(1) \qquad \frac{L}{D} \gg 1 \tag{18}$$

Balberg et al.[40] discuss percolation in terms of *excluded* volumes instead of particle volumes. This is the correct approach, but to explain eq 18 the additional assumption of random contacts seems to be required.

Other examples of dilute rod assemblies can be found for rods or fibers in a colloidal suspension. They easily form aggregates or even space filling "physical" particle
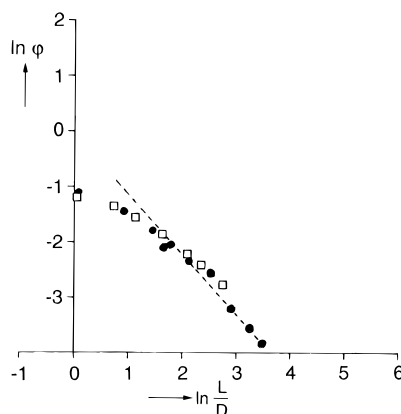
(39) Boissonade, J., Barreau, F., Carmona, F. *J. Phys. A.: Math. Gen.* **1983**, *16*, 2777.
(40) Balberg, I., Binenbaum, N.; Wagner, N. *Phys. Rev. Lett.* **1984**, *52*, 1465.

Figure 5. Simulation results (□) of Boissonade et al.[30] for the percolation threshold density (ϕ_t) for random rods on a cubic lattice and results (●) from Balberg et al.[32] for a continuum of random spherocylinders. The data seem to approach a value of $\phi_t(L/D)$ on the order of 1 (dotted line) at high aspect ratio.

gels as a result of (moderate) attractions between the particles.[8,41] The consequence of eq 7 is, as for percolating structures, that densities will be low for long thin particles. The percolation density of eq 18 is an indication for the minimal gel density for random rods. This is qualitatively confirmed by gels or imogolite fibers.[8] These fairly rigid alumino silicate tubes have a diameter of 2 nm and an average aspect ratio on the order of 400.[8] Space filling, transparent gels may be formed at volume densities as low as $\phi \approx 10^{-3}$, which is also the order of magnitude found from eq 18.

For such gels we can apply eq 7 to estimate the attraction energy ΔH_p for a rod when it makes $\langle c \rangle$ attractive contacts with neighboring rods via

$$\Delta H_p = \langle c \rangle \Delta H_c = \phi\frac{L}{D}\Delta H_c \tag{19}$$

where ΔH_c is the average attraction energy per contact. Suppose rods stick together by Van der Waals attractions only. For two *crossed* cylinders at a small surface-to-surface distance, σ, the attraction energy is then[42]

$$\Delta H_c \approx -\frac{A}{12}\frac{D}{\sigma} \qquad \sigma < D \tag{20}$$

where A is the Hamaker constant. This is the *minimal* attraction: for other rod configurations the energy is larger. The attraction (in units of thermal energy, kT) is therefore at least

$$\frac{\Delta H_p}{kT} \approx -\frac{A}{12kT}\frac{\langle c \rangle D}{\sigma} = -\frac{A}{12kT}\phi\frac{L}{\sigma} \tag{21}$$

For contacting rods, σ is the distance of closest approach determined by, for example, organic surface layers or surface roughness. The combination $\langle c \rangle D/\sigma$ is obviously larger than unity. Lyklema[42] lists many Hamaker constants for various combinations of materials and solvents, most of them in the range $A = 1-70$ kT at room temperature. So the attraction energy per rod in eq 21 may be quite substantial.

7. Conclusions and Speculations

The main conclusions from the previous sections are the following. (1) The rescaled density $\phi_{rcp}(L/D) \approx 5.4$ of

(41) Philipse, A. P. *Colloids Surf. A* **1993**, *80*, 203.
(42) Lyklema, J. *Fundamentals of Colloid and Interface Science*; Academic Press: London, 1991; Vol. I.

(macroscopic) random thin-rod packings can be understood as the result of about 5.4 uncorrelated rod contacts per rod. This contact number seems to vary little for random packings of particles—at least for the particle shapes in this study—which explains the low packing density of thin rods or fibers in comparison to that of spheres. (2) The random contact model also accounts qualitatively for the trend in sediment densities of colloidal particles. The notion of colloidal sphere glasses can be extended to (thin) rods: dense random packings are in both cases metastable with respect to an ordered crystalline phase. A rough estimate can be given of the attraction energy per rod in an isotropic gel. (3) The density $\phi_{max}(L/D)$, at which the viscosity of *isotropic* thin-fiber suspensions diverges, seems to differ little from $\phi_{rcp}(L/D) \approx 5.4$, which explains the observation that the suspensions cease to flow at much lower volume fractions than for spheres. Experiments and simulations on percolating rods also suggests the "random contact" scaling $\phi(L/D) \sim \langle c \rangle$, but with a smaller average contact number on the order of 1.

The experimental results discussed in this study support the idea that independent pair contacts are a key property of *thin*-rod arrangements. For compact particles (spheres), as noted earlier, contact correlations cannot be neglected. What is special about thin rods? An analogy can be drawn with Onsager's thermodynamic treatment of isotropic thin rods in which the virial series for the osmotic pressure is truncated at the second virial term.[19,20,29] That is, pair *interactions* are taken to be independent. In a mechanical rod arrangement this may be translated into independent pair *contacts*. To understand this independence we should perhaps focus (in the mechanical case) on excluded surfaces instead of excluded volumes, which after all increase with the aspect ratio. (We want something which vanishes when $L/D \to \infty$.) A contact excludes a certain surface area of a rod for other contacts. This excluded particle area depends on rod orientations, but its average will be on the order of the cross sectional area D^2 of a rod. The surface area of a thin rod is proportional to DL, so the excluded surface fraction scales with $\langle c \rangle D^2/DL = \langle c \rangle D/L$. (Note that the solid volume fraction ϕ scales in the same manner.) For spheres this fraction is fairly large, but for rods it vanishes in the limit $L/D \to \infty$. This limit corresponds to an "ideal surface coverage" of noninteracting point contacts.

What about other particle shapes? In Figure 4 at $\ln(L/D) < 0$ some packing densities are shown for random disks[12] of height L and diameter D. They seem to extend the horizontal log–log plot near $L/D = 1$ (spheres). However, for sufficiently thin disks the log–log plot will decrease linearly, as for rods, if contacts are uncorrelated. For a pair of randomly oriented disks the excluded volume is[19,43]

$$V_{ex} = \pi^2 D^3/8 \tag{22}$$

which gives on substitution in eq 3

$$\phi \frac{D}{L} \sim \frac{4}{\pi} \langle c \rangle \qquad \frac{L}{D} \ll 1 \tag{23}$$

which should be compared to the result for thin rods in eq 7. If indeed $\langle c \rangle$ is an invariant for random packings, then the total density versus aspect ratio curve would have a peak at the random sphere packing density and two fairly symmetrical branches which approach zero at extreme aspect ratios in a similar manner. It is, admittedly, questionable whether true random packing with uncorrelated contacts is possible for disks. The analogy with thermodynamic platelets gives little hope in this respect because third and higher order virial terms always contribute.[44] Whether this leads to serious deviations from eq 23 is an open question.

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(43) Stroobants, A.; Lekkerkerker, H. N. W. *J. Phys. Chem.* **1984**, *88*, 3669.
(44) This was pointed out by a referee.