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Brownian diffusion in concentrated suspensions of interacting particles

By J. M. RALLISON

Department of Applied Mathematics and Theoretical Physics, University of Cambridge, Silver Street, Cambridge CB3 9EW, UK

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In this paper we set out to calculate the self-diffusivity of a Brownian particle in a concentrated suspension. The problem is treated by regarding the neighbours of a test particle as forming a 'cage'. For short time $t < t_c$, say, the particle is partially constrained by the cage and an equation is proposed to describe the coupled dynamics of particle and cage. The equation is shown to be asymptotically exact in some cases and acceptably accurate for other simple systems by comparing with Monte Carlo simulations. For times $t > t_c$, the particle diffuses sufficiently far to escape its original cage (and finds itself in a new one). A quantitative estimate for t_c is proposed and verified for a system of rod-like particles by numerical simulation. By combining these two ingredients an estimate of the long-time ($t \gg t_c$) self-diffusivity of a particle is made. For rod-like particles t_c is the reptation time, and the result here is compared with the theory of Doi & Edwards (1978*a*, *b*), and with experiment. For a system of spheres comparison is made with the tracer light-scattering experiments of Kops-Werkhoven & Fijnaut (1982). In both cases good agreement is found when the particle concentration is sufficiently high.

1. Introduction

We consider in this paper the self-diffusion of a Brownian particle in a neutrally buoyant suspension of identical particles having sufficiently high concentration for interaction between particles to be important. By *self-diffusion* we mean the random walk of a marked particle as it moves in a quiescent suspension under the influence of both the random Brownian impacts from solvent molecules and collisions with other suspended particles. (Note that at non-zero concentration this differs from the *down-gradient diffusion* generated by a particle concentration gradient; see e.g. the discussion in Rallison & Hinch 1986.) In general the mean-square displacement of the marked particle (which starts at the origin, say) is not a linear function of time. Initially the growth is linear, but after the particle has diffused a distance comparable with its diameter there is a relative 'vacuum' of other particles behind it (i.e. closer to the origin), but an increased density of particle centres ahead (further from the origin), and this imbalance tends to hinder further progress by the test particle (see also Batchelor 1983). After many collisions with neighbours, however, the average test-particle motion is diffusive (though with a lower diffusivity than in an infinitely dilute system).

Since the particles are immersed in a viscous fluid, each affects the motion of its neighbours hydrodynamically. In a dilute system even comparatively distant particles can hinder the self-diffusion of a test particle with a consequent (small) extra reduction in the diffusivity (see e.g. Rallison & Hinch 1986). In a concentrated

system, however, the largest hydrodynamic forces are of lubrication type and act to prevent overlap of particle pairs. In the calculations presented in this paper, hydrodynamic interactions are ignored, but potential forces between particles which prohibit overlap are included. This provides a considerable theoretical simplification. Our expectation is that because the most important interaction effects are still included in the analysis, this will prove to be a good approximation for (sufficiently) concentrated suspensions.

The bulk of theoretical work on suspension properties has been concerned with dilute systems in which the particles are assumed not to affect each other at all, or in which only small groups (pairs, triples, etc.) of particles simultaneously interact. These theories can provide only the first few terms of a power series in the small volume concentration of particles ϕ. A notable exception is the work of Doi & Edwards (1978*a*, *b*) concerning the rotational diffusion of rods in a semidilute concentration regime, for which the volume concentration is low but the distance between adjacent rods is small compared with their length. Doi & Edwards demonstrate that the rotational diffusivity of a test rod is reduced substantially by its overlapping neighbours, in fact by a factor $\hat{\phi}^{-2}$ where $\hat{\phi}$ is an 'effective concentration' of rods ($\hat{\phi} = nl^3$, l being a rod length, and n the number density of rod centres).

At the heart of Doi & Edwards' calculation is the idea for a concentrated system of a 'cage' of neighbours for a test particle which inhibit its diffusive motion. The same idea has been proposed in related contexts by de Gennes (1971), Pusey (1975) and others. The idea is intuitively appealing and suggests the possibility of analysing the diffusive motion in two stages:

(*a*) for short times $t < t_c$ a particle is confined within a cage, and its behaviour must be calculated by analysing the cooperative motion of the cage together with the particle itself;

(*b*) at time t_c the particle escapes from the original cage having diffused a distance d_c in the x-direction, say, and finds itself under a new set of partial constraints within which a new random walk can start again. Thus for times $t \gg t_c$ the test particle will have escaped from many cages, taken many independent random steps of size d_c, and so its long-time motion will be diffusive in character, with diffusivity of order d_c^2/t_c. Indeed, if successive cages are uncorrelated with one another, this long-time x-diffusivity is $d_c^2/2t_c$.

For calculational purposes there are two difficulties with this picture of the diffusion process. First, the definition of the escape time t_c is unclear. Equivalently, so far as the determination of the long-time diffusivity is concerned, the extent of the correlation between successive cages needs to be specified. A second and more subtle difficulty is that in considering the average motion of a marked particle it is not clear which other particles constitute the cage. In particular in a dilute suspension the identities of the current neighbours of a test particle are continually changing. In a sufficiently concentrated suspension, however, the neighbours of a test particle are locked together for a time long compared with that taken for an isolated particle to diffuse across an interparticle separation, and in consequence the particles forming the cage must move with the marked particle and (most of) their identities are fixed for $0 < t < t_c$.

Two concentrated suspensions are discussed in detail in this paper, and we may identify the physical meanings of d_c and t_c at the outset. Consider first a suspension of Brownian spheres of radius a (§5). If the suspension is dilute, the expected times

spent by two particles in collision (say within a distance of order a of each other) is of order a^2/D_0 where D_0 is the diffusivity of a sphere in isolation. In that case the 'cage' terminology is unhelpful since only small groups of spheres simultaneously collide and most of the 'bars' of the cage are missing. On the other hand, at concentrations comparable with that required for random close-packing of the spheres, the time for which a pair of particles are in close proximity is long compared with a^2/D_0 (indeed infinitely long at that concentration for which the self-diffusivity vanishes) and all directions of motion are blocked to a test sphere. A useful (albeit still imprecise) definition of t_c which in principle embraces both the dilute and concentrated cases is the expected time for which a particle remains within an $O(a)$ distance of a neighbour. By definition, for this system the cage size d_c is of order a. It is apparent that the self-diffusivity cannot become established (in a light-scattering experiment, say) for correlation times shorter than t_c. It should be noted that t_c here is *not* the time taken for a test particle to diffuse freely across a nearest-neighbour distance (as suggested by Pusey 1975 and Batchelor 1983); as shown in Rallison & Hinch (1986) this is not the case for dilute systems, and in §5 we show that it is also incorrect for concentrated suspensions of spheres.

The second system of interest is a semidilute suspension of slender Brownian rods of length l (§4). Here the longitudinal motion of a test rod is comparatively free, but lateral motion is strongly impeded. In this case the collision time for a pair of rods t_c is of order l^2/D_0 (i.e. the time taken for a rod to diffuse freely along its length) and does not depend strongly on the concentration of rods. At issue, however, is how far the rod can diffuse laterally in time t_c, i.e. the cage size d_c. It is tempting to identify d_c as the geometric lengthscale given by the nearest-neighbour distance between particles (as do Doi & Edwards 1978) for semidilute rods. This amounts, in effect, to an assumption that the neighbouring particles form an impenetrable barrier to progress by the test particle and cannot be pushed out of the way. We critically re-examine this in §4 and show that in general it is false for systems of rod-like particles.

To determine the long-time self-diffusivity then, we must first solve a difficult many-body problem appropriate for times $t < t_c$ during which a particle is interacting with the cage. This forms the subject of §3. On the basis of this 'constrained' solution it is possible to deduce when the particle first expects to evade its immediate neighbours so that t_c, d_c and hence the long-time diffusivity D may be inferred. The theory is applied to artificial and real systems of rods in §4, and to concentrated suspensions of spheres in §5. In some cases we are able to compare results with experiment, elsewhere only numerical data from Monte Carlo (or 'Brownian dynamics') simulations are available. These simulations have been the source of some confusion and criticism (Fixman 1985*a*, *b*) and in consequence we start in §2 with a discussion of the proper simulation of interacting Brownian particles. The main conclusions of the paper are summarized in §6.

2. Monte Carlo simulations of interacting Brownian particles

The motion of an individual particle in a concentrated quiescent suspension is influenced by three forces. First, the random Brownian impact of solent molecules (with successive impacts occurring on a very short timescale); secondly, the viscous resistance imposed by the solvent; and thirdly the result of collisions with other suspended particles.

The random motion of a particle is often modelled by a Langevin equation so if x is its position at time t, m its mass and ζ the viscous resistance exerted by solvent molecules (neglecting hydrodynamic interactions)

$$m\ddot{x}+\zeta\dot{x}+F=f(t), \tag{1}$$

where f is the rapidly fluctuating Brownian force, and $F(x)$ the slowly varying net force exerted by neighbouring particles (see e.g. Hinch 1975). Now the correlation time for the fluctuations is so short compared with all other timescales in the problem that we may write

$$\langle f(t)f(t')\rangle = \mathscr{F}\delta(t-t')$$

where $\langle\cdot\rangle$ denotes an ensemble average, and by the fluctuation–dissipation theorem the magnitude of the fluctuation is given as

$$\mathscr{F} = 2kT\zeta.$$

It is well known that (1) gives rise to a diffusive process at long times. For the purpose of a Monte Carlo simulation on a timescale long compared with the inertial relaxation time m/ζ, equation (1) may be replaced by the time-stepping procedure

$$x(t+\Delta t) = x(t)-\frac{F\Delta t}{\zeta}+h(t), \tag{2}$$

where $h(t)$ is a random variable with zero mean and variance given as

$$\langle h^2\rangle = 2D_0\,\Delta t.$$

The diffusivity D_0 is given by the Stokes–Einstein relation as kT/ζ. The advantage of (2) is that a very much longer time-step can be used than is required for the Langevin equation (1), since the short-lived inertial features do not have to be resolved.

For 'hard' particles F is very sharply peaked, but varies, we assume, on a lengthscale long compared with a single Brownian displacement. Equation (2) therefore still represents a valid computational procedure which will model the hard force provided the step size Δt is sufficiently small for the degree of interpenetration of particles determined by F to be small (in fact of order $(\zeta\Delta t)^{\frac{1}{2}}$) compared with their size. It means however that the probability density for x is poorly resolved in regions of order $(\zeta\Delta t)^{\frac{1}{2}}$ from the particle surface. Other procedures that deal with the interactions may be equally accurate but perhaps easier to generate computationally, e.g. particle overlap may be prohibited by assuming that particles provide a fixed reflective surface from which a test particle 'bounces' elastically (Doi, Yamamoto & Kano 1984); or a wholly unreflective surface from which there is no bounce at all; alternatively the potential may be 'softened' slightly so that a small overlap is permitted, but the particles are subsequently pushed apart (present work). Yet a further possibility is that all random steps which infringe the no-overlap requirement are ignored completely.

Fixman (1985*a*, *b*) has criticized the simulation of Doi *et al.* (1984), and by implication also the simulations in this paper, on the grounds that too large a time-step was used in comparison with his own work. There is no doubt that for a full phase-space analysis a small step would be needed, but, as noted above, provided (*a*) no particles pass through one another in a single step, and (*b*) many random steps are taken during the time evolution, the diffusivity should be accurately determined. A partial check on the validity of the results can be made by varying Δt: in the

Brownian dynamics simulations described later in this paper no statistically significant change in the results was detectable on halving Δt. We should also mention in this context the assumption in the theoretical analysis of Harris (1965) that particles collide 'elastically'. The term is potentially misleading in that it suggests an inertial 'billiard-ball' collision, whereas on the diffusion timescale inertia is insignificant. We have noted above however that all methods of dealing with the interactive force term F in (2) are equivalent in the limit $\Delta t \to 0$, and thus the system described by Harris does model the self-diffusion process.

On the other hand Frankel & McGuire (1983), whose work is sometimes quoted in this context, make the assumption that particles move freely between collisions in the same way as in the kinetic theory of gases, and thus – although their conclusions support those here in certain respects – the underlying dynamics are fundamentally different and comparisons must be treated with suspicion.

3. Diffusion in strongly constrained systems

This section examines the diffusion of a particle for times $t < t_c$ during which it is unable to escape the constraints provided by its neighbours. The aim is to find its mean-square displacement as a function of time. The simplest system with inviolable constraints involves a one-dimensional random walk and we consider two versions of such a system below.

3.1. *Diffusion of particles around a ring*

Consider a set of N impenetrable particles which are constrained to move on a ring as shown in figure 1 and which interact only by collision. The linear distance traversed round the ring by a single test particle from its initial position is denoted by x_0. (If the particle performs several complete circuits then x_0 will exceed the total circumference L of the ring.) Suppose further that the particles are identical and Brownian, that each in isolation would have diffusivity D_0, that at zero time the particles are distributed uniformly around the ring, and for the sake of simplicity that hydrodynamic interactions between particles may be neglected. Then for times sufficiently short that no interactions have taken place, the distribution of x_0 is Gaussian and $\langle x_0^2 \rangle = 2D_0 t$. The corresponding expression for general times t is complicated (see below), but for long times a simple result may be derived.

As $t \to \infty$ we expect that $\langle x_0^2 \rangle \to \infty$ and hence, since the particles are impenetrable, that the r.m.s. displacement of every particle is asymptotically the same. It follows that the statistics for x_0 are the same as those for every x_i, and so asymptotically also for the centre of number

$$\xi = \sum_{i=0}^{N-1} \frac{x_i}{N}.$$

Now in the absence of collisions, ξ is the sum of N independent random variables each of which is Gaussian with mean zero and variance $2D_0 t$. It follows that ξ would itself be Gaussian with zero mean and variance $\langle \xi^2 \rangle = 2D_0 t/N$. At first sight it appears that the presence of collisions will affect this conclusion, but if particle interactions are such that when particles i and $i+1$ collide their centre of mass motion is not changed, then ξ is unaffected by collisions, and the result still applies, independently of the details of the interactive force mechanism. Then, as $t \to \infty$

$$\langle x_0^2 \rangle \sim \langle \xi^2 \rangle \sim \frac{2D_0 t}{N} \tag{3}$$

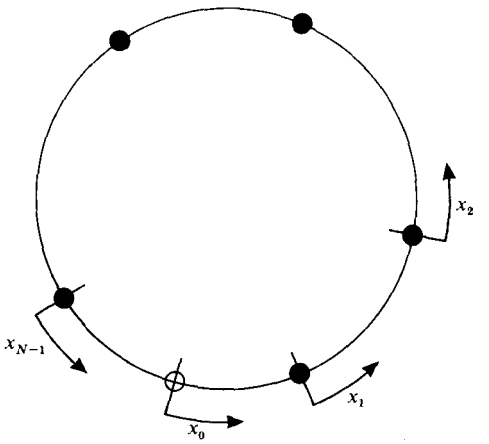

FIGURE 1. Definition sketch for the diffusion of N impenetrable particles around a ring with circumference L.

and hence for long times x_0 is governed by a diffusion process with effective diffusivity $D = D_0/N$.

To complete the analysis of this problem it remains to determine the rapidity of the change from the zero-time diffusivity D_0 to the asymptotic value D_0/N. This is explained in the next section.

3.2. *Diffusion of particles along an infinite line*

We consider next the diffusion of impenetrable particles, each having size a, along an infinite line. Suppose that at time $t = 0$ the particles are distributed by a Poisson process uniformly along the line with number density n and that the particle concentration is small in the sense that $na \ll 1$. Again let x_0 be the deviation of a test particle from its original position. We seek to determine the distribution of x_0 as $t \to \infty$.

This problem has been considered from a probabilistic point of view by Harris (1965). The crucial observation that he makes is that whenever two particles collide each particle may be regarded as taking on from that point onward the random walk of the other; i.e. if the particles were unlabelled, any time evolution of their configuration would appear identical with that of the same particles if the particles were transparent to one another (see figure 2). It follows that the statistics of x_0 at some time t can be obtained by counting the number of other particle trajectories that x_0 crosses, which may itself be determined via the maximum statistic for a Brownian random walk (see e.g. Karlin & Taylor 1975).

The conclusion from Harris' (1965) calculation is that as $t \to \infty$ the distribution of x_0 is Gaussian with mean zero and mean-square displacement

$$\langle x_0^2 \rangle \sim \frac{1}{n}\left(\frac{4D_0 t}{\pi}\right)^{\frac{1}{2}}. \tag{4}$$

It follows that for long times the particle moves infinitely far from its starting position, but that its motion is never purely diffusive in character since $\mathrm{d}\langle x_0^2 \rangle/\mathrm{d}t \neq$ constant. Further for large times the net distance traversed is much smaller than for an unimpeded particle.

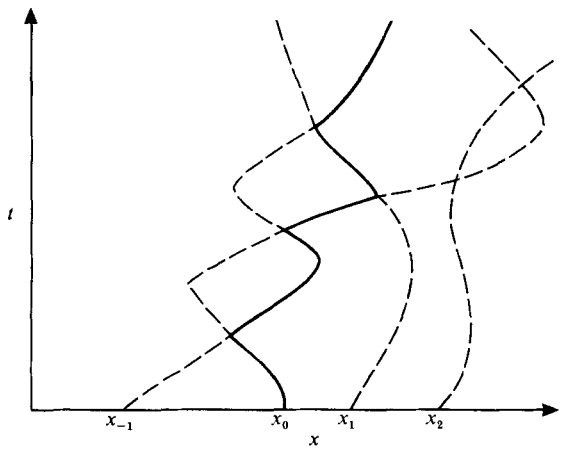

FIGURE 2. Sketch of trajectories for diffusing impenetrable particles moving along an infinite line. ---, trajectories without collisions; ——, actual trajectory of test particle.

3.3. *A physical interpretation and hypothesis*

A physical interpretation which unifies the results (3) and (4) may be made as follows. If we suppose that at time t a certain number $N(t)$ of particles have interacted directly or indirectly with the labelled particle (x_0) then the result (3) suggests writing

$$\frac{\mathrm{d}}{\mathrm{d}t}\langle x_0^2\rangle = \frac{2D_0}{N(t)},$$

and comparison with (4) gives

$$N(t) \sim (2\pi)^{\frac{1}{2}} n (2D_0 t)^{\frac{1}{2}} \quad \text{as } t \to \infty.$$

Now $(2D_0 t)^{\frac{1}{2}}$ is the r.m.s. distance that an unimpeded particle would have travelled, and $n(2D_0 t)^{\frac{1}{2}}$ is the mean number of particles in that region. This estimate for $N(t)$ is intuitively in accord with Harris' analysis above in suggesting that the particles that form instantaneously a diffusing group around a test particle are those that must necessarily move with it and that lie in a zone whose size increases with the *unimpeded* test particle displacement. (More precisely, in fact, with a maximum statistic for the unimpeded random walk. Unfortunately, the maximum, though a better estimate of the size of influence, is much harder to calculate, and at the level of conjectural approximation here it is much easier to use the r.m.s. which at least scales with the maximum.)

So far we have done no more than to rewrite the results above, but the new interpretation suggests a technique for analysing more complex systems of interacting identical Brownian particles. For suppose that when a test particle is displaced through a distance x_0, an expected number $\mathcal{N}(x_0)$ of particles (including the test particle itself) are themselves caused to be displaced. Then we conjecture that in the diffusing system

$$\langle x_0^2\rangle(t) = \int_0^t \frac{2D_0\,\mathrm{d}t'}{\mathcal{N}[(4\pi D_0 t')^{\frac{1}{2}}]}. \tag{5}$$

Equivalently, if an effective diffusivity $D(t)$ at time t is defined so that

$$\langle x_0^2\rangle(t) = 2Dt,$$

then
$$\frac{D(t)}{D_0} = \frac{1}{t}\int_0^t \frac{\mathrm{d}t'}{\mathscr{N}[(4\pi D_0 t')^{\frac{1}{2}}]} = \frac{1}{2\pi D_0 t}\int_0^{(4\pi D_0 t)^{\frac{1}{2}}} \frac{\xi\,\mathrm{d}\xi}{\mathscr{N}(\xi)}. \tag{6}$$

For example for Harris' (1965) system, $\mathscr{N}(0) = 1$ (the test particle) and

$$\mathscr{N}(x_0) = 1 + nx_0,$$

so that
$$\langle x_0^2\rangle(t) = \frac{1}{n}\left(\frac{4D_0 t}{\pi}\right)^{\frac{1}{2}}\left[1 - \frac{1}{n(4\pi D_0 t)^{\frac{1}{2}}}\log\left(1 + n(4\pi D_0 t)^{\frac{1}{2}}\right)\right]. \tag{7}$$

By construction this result is asymptotically correct at times $t \to 0$ and $t \to \infty$ for then

$$\langle x_0^2\rangle \sim \begin{cases} 2D_0 t & t \to 0, \\ \dfrac{1}{n}\left(\dfrac{4D_0 t}{\pi}\right)^{\frac{1}{2}} & t \to \infty. \end{cases}$$

For intermediate times no analytic result is available, and we compare (7) with a numerical simulation in §3.4. Agreement is good. In particular, the timescale on which the diffusivity changes from one asymptote to the other is correctly predicted as $1/D_0 n^2$ – which might have been anticipated on dimensional grounds.

It should be emphasized that we are unable to supply any formal proof of (5) except for one-dimensional systems and then only asymptotically for short and long times. Our claim is that it correctly represents the physics of the problem, and that for intermediate times it is an over-simplified approximation which nevertheless produces good agreement with numerical simulations.

For two- and three-dimensional systems no exact results like Harris's are available, essentially because the basic idea that colliding particles are identical no longer applies, but in §§3.4 and 4.2 we resort to numerical experiments to test the correctness of (5). In every case it proves to be a good approximation over the whole range of t with errors apparently decreasing as $t \to \infty$.

The usefulness of (5) for complex systems is that it separates the two stochastic elements in the calculation: the statistical geometry enters the calculation only through $\mathscr{N}$; and once $\mathscr{N}$ is known the Brownian motion within the geometry may be determined.

3.4. *Numerical simulation for the diffusion of particles around a ring*

Returning to the system of §3.1 shown in figure 1 we have

$$\mathscr{N}(x_0) = \begin{cases} 1 + \dfrac{N-1}{L}x_0 & x_0 \leqslant L, \\ N & x_0 \geqslant L, \end{cases}$$

and hence writing $\tau \equiv D_0 t/L^2$ as a non-dimensional time (6) predicts

$$\frac{D(t)}{D_0} = \begin{cases} \dfrac{1}{N-1}\dfrac{1}{(\pi\tau)^{\frac{1}{2}}}\left[1 - \dfrac{1}{N-1}\dfrac{1}{(4\pi\tau)^{\frac{1}{2}}}\log\left(1 + (N-1)(4\pi\tau)^{\frac{1}{2}}\right)\right] & \tau \leqslant \dfrac{1}{4\pi}, \\ \dfrac{1}{2\pi\tau}\left[\dfrac{1}{N-1}\left(1 - \dfrac{\log N}{N-1}\right) - \dfrac{1}{2N}\right] + \dfrac{1}{N} & \tau \geqslant \dfrac{1}{4\pi}. \end{cases} \tag{8}$$

There are thus two important timescales: the time $L^2/D_0 N^2$ at which a test particle first feels the influence of its neighbours, and the longer time L^2/D_0 when it sees the finiteness of the ring, and hence of the total number of its neighbours.

Numerical solution

A numerical solution of this problem (similar in character to one proposed by Pusey 1974) was generated as follows. A number N of particles were placed at random on a line of length $L = 50$. The ends of the line were identified by use of periodic boundaries. The particles were considered to have unit width ($a = 1$) so that any two particles closer than 1 unit overlapped. A repulsive force (of the form $a/(a+d)$ with d the distance of closest approach) was then switched on to push the particles apart.

At each time step the particles were each subject to a random displacement (of $\pm\frac{1}{2}$) to represent the Brownian impulse in accord with (2). It would be possible to vary randomly the magnitude as well as the direction of $h(t)$, but this is unnecessary for producing good random-walk statistics. Furthermore since for a given value of $\langle h^2 \rangle$ the random function with smallest maximum has constant magnitude this choice permits the largest value of Δt consistent with the requirement that no particle can 'jump over' another in a single time-step. Pairs of particles that were then found to overlap were pushed apart again by the repulsive force mechanism. The first few time steps were required to fully randomize the particle positions (bearing in mind that the method described for generating the initial configuration favours close pairs of particles). After this initial shaking, the positions of the particles were monitored as a function of time and their r.m.s. displacement

$$\left[\frac{1}{N}\sum_{i=0}^{N-1}(x_i(t)-x_i(0))^2\right]^{\frac{1}{2}}$$

was calculated. By averaging over a (large) number of time evolutions, a numerical prediction for $\langle x_0^2 \rangle (t)$ was obtained.

The results for values of $N = 6$, 10, 20 were all qualitatively similar, and since the theory requires $na \ll 1$, we make comparisons with theory for the case $N = 6$, i.e. $na \approx 0.1$. In figure 3 is shown the average of 20 simulations, together with the result given by (8). The discrepancy between the two is no more than 7 % over the full range of t, and this is less than the statistical error in the numerical result.

The theory is surely not *exactly* correct: the predicted weak lack of smoothness in the curve when $\tau = 1/4\pi$ seems an unsatisfactory feature. Nevertheless the agreement is gratifying and lends confidence to the use of (5) for all t. Perhaps the most surprising feature is that the asymptotic value $D = D_0/N$ is attained when $\tau \approx 0.1$, i.e. when an unimpeded particle would have diffused only one third of the way around the ring. This is presumably because the more extensive random walks of the ensemble, which are less probable when particles interact, are curtailed by interactions sooner than less extensive walks.

4. Diffusion in suspensions of rods

The principal aim of this section is a critical reappraisal of the Doi–Edwards (1978*a*, *b*, hereinafter referred to as DE) theory for the rotational diffusivity D^{r} of a slender rod in a semidilute suspension. The *semidilute* regime is defined (Batchelor 1971) by the requirements that the volume concentration of rods is small, but that the rods overlap significantly. Thus if each rod has length l, and the number density of rod centres is n, the latter requirement gives $\hat{\phi} = nl^3 \gg 1$, and the former that $\hat{\phi} \ll r^2$, where r is a large aspect ratio for the rod. In fact, as pointed out by DE, a

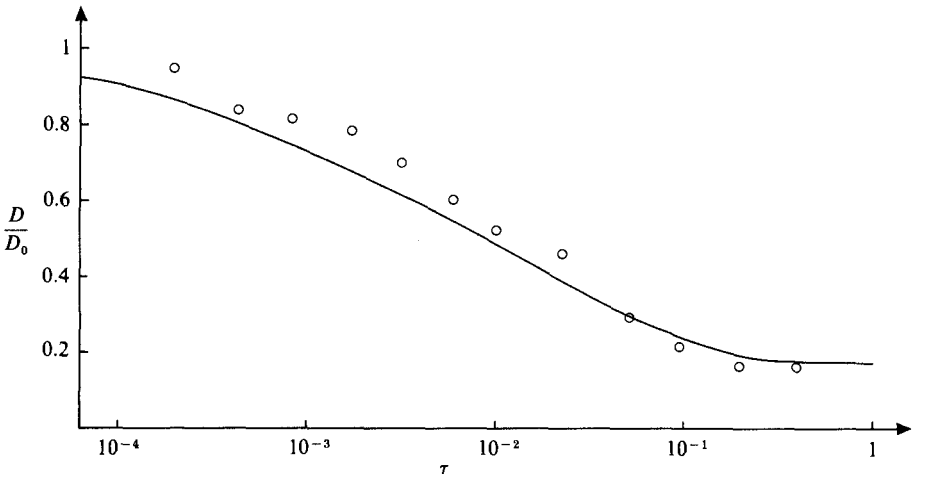

FIGURE 3. Diffusion of $N = 6$ particles round a ring: effective diffusivity plotted as a function of dimensionless time $\tau = D_0 t/L^2$. ——, theory, equation (8); ○, results from an average of 20 Monte Carlo simulations.

stronger constraint is required in order that a nematic transition not occur in which the rods are preferentially aligned rather than having random orientations. This condition can be written (Flory 1956) $\hat{\phi} \ll r$. Since in our analysis r is regarded as arbitrarily large, the distinction is not important here.

There are two physical ingredients to the DE theory. First, because the rods are so strongly entangled, significant rotation of a test rod with a fixed centre is impossible, and so rotational diffusion can occur only if the rod slides along its length within the instantaneous cage, rotating slightly as it does so. This snake-like motion has been christened *reptation*. In consequence the escape time from the cage t_c (here called the reptation time) is given by the time taken for a rod to diffuse along its length, so that on dimensional grounds t_c is of order $(D_0^r)^{-1}$ where D_0^r is the rotational diffusivity of an isolated rod.

Second, the DE theory supposes that without reptating a test rod is unable to rotate further than the constraint provided by its nearest neighbours, with the implication that further rotation of a test rod will generate a 'log-jam' where no further rotation is possible. On this basis, in the time available before a test rod reptates away from its constraint, the maximum angle that it can turn through (the cage size d_c) is of order $1/\hat{\phi}$ and

$$\frac{D^r}{D_0^r} = \frac{\beta}{\hat{\phi}^2}, \tag{9}$$

where β is an unknown constant of order unity.

In spite of the simplicity of the DE proposal, the log-jam mechanism is not itself attractive for this fluid-like system for the following reasons. In the absence of Brownian motion, if a steady external mechanical couple is applied by some means to a single suspended rod, then in circumstances where a log-jam occurs the associated stress must be transmitted to the solid boundaries of the container of the suspension. The stationary solvent cannot itself sustain the non-hydrostatic stress, and since the rods are small (arbitrarily so in the limit), an infinite cluster of touching rods extending to the boundary would have to form when the test rod rotates

through a small finite angle. In fact however in this concentration regime (below the nematic transition) each rod has non-zero room in which to manoeuvre so (as shown in §4.3) only a finite cluster can arise. Furthermore such a tight constraining mechanism would appear to prevent flow of the suspension altogether (as in a suspension of closely packed spheres which does display solid-like rheology).

We therefore discount the log-jam and raise the possibility that cooperative diffusive motions of a test rod and its surrounding cage permit a rotation of larger order than $1/\hat{\phi}$ before the rod reptates. Fixman (1985*a*) has also made this suggestion, noting that if a test rod makes a small rotation this initiates a *local* perturbation to the system giving rise to a quasi-elastic free energy stored within the cage, and that this free energy can then spread through the neighbouring rods. Fixman goes on to conclude on the basis of numerical simulation (discussed in §4.3) that the effective angular rotation is only $O(\hat{\phi}^{-\frac{1}{2}})$ for $24 < \hat{\phi} < 146$, and provides (Fixman 1985*b*) a model exhibiting this behaviour.

The substance of our conclusion (unlike Fixman's) is that DE result above is correct, though the constant β has a value (about 400) in excess of unity, and (like Fixman) that no log-jam occurs. Before embarking upon an analysis of this complex system we start by considering simpler quasi-one- or two-dimensional rod suspensions where similar techniques might be expected to be appropriate. These systems also provide means of checking the correctness of (5), and finding a quantitative estimate for t_c.

4.1. *A one-dimensional rod suspension*

Consider first the system of §3.3 in which the impenetrable point particles diffusing along an infinite line (the x-axis) are imagined to be the projections of long rods perpendicular to the line. The rods are now imagined to have an unhindered diffusivity D_0 along their length l. The rods are supposed parallel to the y-axis (see figure 4). Then a rod spends the time of order $t_c = l^2/D_0$ in 'escaping' from the line.

For times $t < t_c$ the finiteness of the rods is not apparent so (5) should apply and if x_0 is the x-displacement of a test rod from its initial position then

$$d_c = \langle x_0^2 \rangle^{\frac{1}{2}}(t_c) = \left[\int_0^{t_c} \frac{2D_0 \, dt'}{\mathcal{N}[(4\pi D_0 t')^{\frac{1}{2}}]} \right]^{\frac{1}{2}} \sim \left(\frac{4}{\pi}\right)^{\frac{1}{4}} \left(\frac{l}{n}\right)^{\frac{1}{2}},$$

where n is the number density of rods along the line. Thus in this artificial system the effective diffusivity in the x-direction is

$$\frac{D}{D_0} \propto \left(\frac{1}{\pi}\right)^{\frac{1}{2}} \frac{1}{nl} \propto \frac{1}{\hat{\phi}}, \tag{10}$$

where $\hat{\phi} = nl$ is the effective line concentration of rods. In consequence, if $\hat{\phi} \gg 1$, $D \ll D_0$. It is interesting to note however that the nearest-neighbour distance in this system is of order $1/n$, but that $d_c \gg 1/n$. Thus the cooperation of neighbours generates a much larger cage size than the interparticle separation. The reptation phenomenon occurs, but no 'log-jam' explanation is required or appropriate.

This model system is unsatisfactory as it stands in that only the dynamics of rods crossing a specific line have been considered. In the next section we analyse a reptating system in which every particle is treated equally.

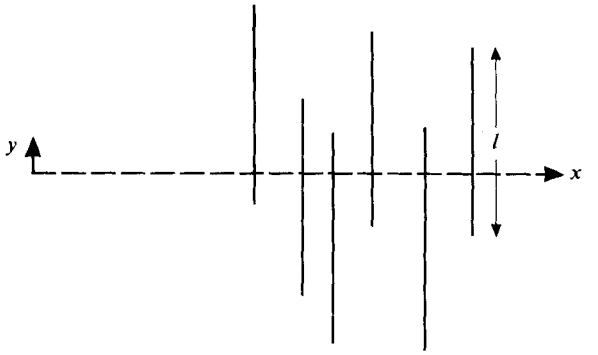

FIGURE 4. Definition sketch for a 'one-dimensional' rod suspension.

4.2. *Diffusion in a two-dimensional system of rods*

We consider next a two-dimensional suspension of Brownian rods of length l and width a confined to the (x, y)-plane, that are externally constrained by some means so that each always lies parallel to the y-axis. Let the area density of rod centres be n, and suppose that the rods are dilute but strongly overlapping so that $a \ll n^{-\frac{1}{2}} \ll l$ (the semidilute approximation). Let D_0 be the undisturbed x-diffusivity of an isolated rod. The motion of a rod along its length is unaffected by interactions and therefore the y-diffusivity has the value $\alpha^2 D_0$ where α is a constant independent of n. On hydrodynamic grounds the 'best' value for α is $\sqrt{2}$, but more importantly for the model calculation here, variation of α permits variation of the reptation time t_c and hence can provide an independent check on the appropriateness of the estimate suggested in §1 as the time at which the test rod first expects to evade its neighbours. Our aim is to analyse the x-diffusion of the rods. We anticipate that via the reptation mechanism this motion will ultimately be diffusive in character, and we seek to determine the dependence of the diffusivity on the effective area concentration of rods $\hat{\phi} = nl^2$.

Approximate result

Suppose first that $\alpha = 0$ so that no reptation occurs. Then for use of (5) we need to evaluate the expected number $\mathcal{N}(x)$ of rods required to move when a test rod translates through x. At first sight it might be thought that $\mathcal{N}(x)$ is simply the expected number of rod centres to be found in the area xl swept out by the test rod. This conclusion is incorrect, however, since the test rod sweeps up other rods that overlap it, and increases its own effective length with x. In fact a trapezoidal, not rectangular, area of rods is involved (sketched in figure 5). If $\mathscr{L}(x)$ is the effective length of a rod after displacement through a distance x, then when the test rod moves a further distance $\mathrm{d}x$ a new rod will be struck if its centre lies in an area $(\mathscr{L} + l)\,\mathrm{d}x$ and so

$$\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}x} = n(\mathscr{L} + l), \quad \mathcal{N}(0) = 1.$$

Further, the corresponding increase in $\mathscr{L}$ occurs (however large $\mathscr{L}$) near the rod's instantaneous ends and may be estimated as

$$\mathrm{d}\mathscr{L} = \text{Probability (new rod is struck)} \times \text{(Expected overlap)}$$

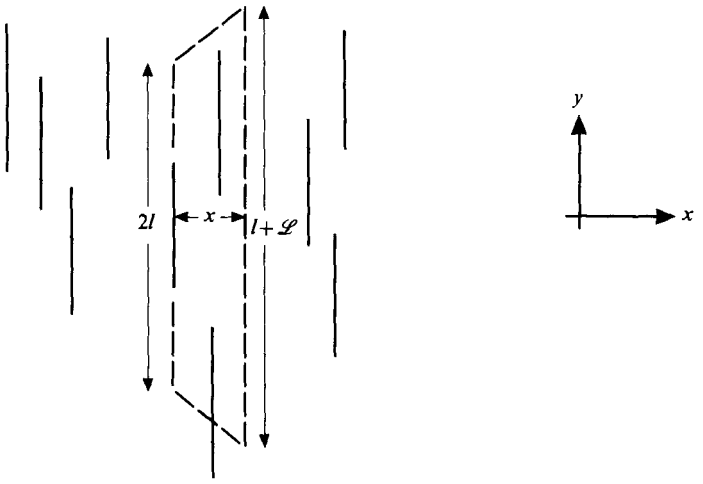

FIGURE 5. Definition sketch for a 'two-dimensional' rod suspension. The trapezoidal region marked is the area within which a rod centre must fall if it is to be struck by the test rod.

and, since all overlaps between 0 and l are equally probable and both ends must be accounted for

$$\mathrm{d}\mathscr{L} = 2n\,\mathrm{d}x\int_0^l y\,\mathrm{d}y = nl^2\,\mathrm{d}x.$$

Now $$\mathscr{L}(0) = l,$$

and thus $$\mathscr{L}(x) = l + nl^2x,$$

and so $$\mathscr{N}(x) = 1 + 2\hat{\phi}\frac{x}{l} + \tfrac{1}{2}\hat{\phi}^2\left(\frac{x}{l}\right)^2.$$

Equation (6) then gives for the effective diffusivity

$$\frac{D(t)}{D_0} = \frac{1}{2\pi\tau}\left[\log\left(1 + 2(4\pi\tau)^{\frac{1}{2}} + 2\pi\tau\right) - \sqrt{2}\log\frac{2-\sqrt{2}+(4\pi\tau)^{\frac{1}{2}}}{2+\sqrt{2}+(4\pi\tau)^{\frac{1}{2}}} + \sqrt{2}\log\frac{2-\sqrt{2}}{2+\sqrt{2}}\right], \quad (11)$$

where $\tau = \hat{\phi}^2 D_0 t/l^2$ is a dimensionless time. Asymptotic limits are

$$\frac{D(t)}{D_0} \sim \begin{cases} 1 & \tau \to 0, \\ \dfrac{1}{2\pi\tau}\log\tau & \tau \to \infty. \end{cases}$$

We note that $\langle x_0^2\rangle \to \infty$ as $t \to \infty$ though only logarithmically. Thus again a test rod can move arbitrarily far, and no phenomenon analogous to the log-jam occurs. A graph of $D(t)$ is plotted in figure 6.

Numerical realization

The numerical solution for the problem of particles on a ring discussed in §3.4 is easily adapted for this more complicated system. A set of N rods is confined to a

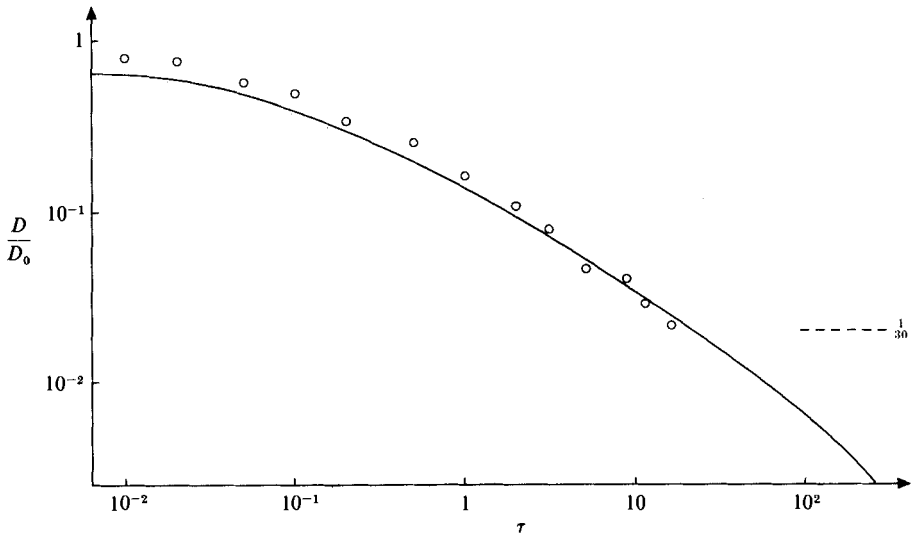

FIGURE 6. Diffusivities for a non-reptating ($\alpha = 0$) two-dimensional rod suspension. ——, equation (11); ○, numerical simulation of 30 rods with $\hat{\phi} = 0.1$; – – –, level at which numerical results cease to apply.

rectangular region with periodic boundaries in both the x- and y-directions. At each time-step random increments $h(t)$ to the x- and y-positions of each rod centre of relative strengths 1 and α are applied in accordance with (2). Two rods are then considered to overlap if their x-positions lie within a distance a of one another and their y-coordinates differ by l or less. In that case a soft potential (described in §3.1) pushes them apart again. In the simulations the length of the rods was taken as unity and $N = 30$ rods were confined to a periodic box of size 50 in x and 6 in y. It follows that $\hat{\phi} = 0.1$.

For $\alpha = 0$ no y-motion takes place and so the formula (11) above should be appropriate. In figure 6 we show the comparison of the numerical and approximate solutions. The two results agree to within 8% (which is less than the expected statistical error in the simulation) over the whole range of $\tau \leqslant 8$. For larger values of τ the diffusivity D ($\leqslant 0.05 D_c$) is so small that almost every rod in the simulation has become involved and the estimate of $\mathcal{N}(x)$ for an unbounded system has ceased to be valid. Indeed at such large times the effective rod length $\mathscr{L}$ is approximately 6 and thus the system should look like the ring of §3.1 with a diffusivity $\frac{1}{30}D_0$ (as marked in figure 6). Thus for the non-reptating system with $\alpha = 0$ the result (11) for $D(t)$ seems an acceptable approximation.

Reptation

For (small) non-zero α, rods are now able to escape from their cages. In line with the suggestion of §1 we suppose that t_c is the time at which a test rod expects to have moved sufficiently far to escape its nearest neighbour. In this system both a test rod and its neighbour diffuse independently in y with diffusivity $\alpha^2 D_0$, and hence after time t their centres have moved apart by an expected distance y given as

$$\langle y^2 \rangle = 4\alpha^2 D_0 t.$$

Now at the initial instant all centre separations y between 0 and l are equally

probable so that the probability that the initial separation lies in the range y, $y+\mathrm{d}y$ is $\mathrm{d}y/l$, and thus the reptation time t_c is

$$t_c = \frac{1}{4\alpha^2 D_0}\int_0^l \frac{(l-y)^2\,\mathrm{d}y}{l} = \frac{l^2}{12\alpha^2 D_0}. \tag{12}$$

The corresponding value of τ is then $\hat{\phi}^2/12\alpha^2$ and the diffusivity is given by (11) as

$$\frac{D}{D_0} = \frac{6\alpha^2}{\pi\hat{\phi}^2}\left[\log\left(1+2\left(\frac{\pi}{3}\right)^{\frac{1}{2}}\frac{\hat{\phi}}{\alpha}+\frac{\pi}{6}\frac{\hat{\phi}^2}{\alpha^2}\right)-\sqrt{2}\log\frac{2-\sqrt{2}+\left(\frac{\pi}{3}\right)^{\frac{1}{2}}\frac{\hat{\phi}}{\alpha}}{2+\sqrt{2}+\left(\frac{\pi}{3}\right)^{\frac{1}{2}}\frac{\hat{\phi}}{\alpha}}+\sqrt{2}\log\frac{2-\sqrt{2}}{2+\sqrt{2}}\right]$$

$$\sim \frac{12}{\pi}\frac{\alpha^2}{\hat{\phi}^2}\log\frac{\hat{\phi}}{\alpha} \quad \text{for } \frac{\hat{\phi}}{\alpha}\to\infty. \tag{13}$$

We show in table 1 the results for values of $\hat{\phi}/\alpha$ from 1 to 8, where they are compared with those from a numerical simulation.

Each simulation with non-zero α showed an approach to an asymptotic value of D as $t\to\infty$, and the values are given in table 1. The figures are subject to statistical errors of about 10% because relatively few simulations could be run in a reasonable amount of computer time. For even larger values of $\hat{\phi}/\alpha$ the asymptotic value was reached at very large values of t and the finiteness of the number of rods in the simulation became important. We note that the quantitative estimate (13) for the reptation time produces extraordinarily good agreement between theory and numerical experiment as $\hat{\phi}/\alpha$ increases. In view of the statistical errors, the apparent closeness of the agreement must be regarded as fortuitous, but it is again when many rods are simultaneously involved (i.e. the concentration is high) that agreement is best.

It is also noteworthy that the results indicate the cage size d_c scaling as $(\log\hat{\phi}/\alpha)^{\frac{1}{2}}\alpha/\hat{\phi}$, whereas the nearest-neighbour separation would give $d_c\sim\alpha/\hat{\phi}$. Thus the cooperation by the cage increases d_c (and hence the diffusivity), albeit by only a logarithmic factor for this problem.

The striking conclusions from this simulation then are (*a*) that (5) provides a good approximation for the behaviour of the rod within the cage, and (*b*) that the naïve estimate for t_c obtained from nearest-neighbour interactions is surprisingly good.

4.3. *Reptation in a three-dimensional system of rods*

We turn finally to the physically realistic case of a three-dimensional system of semidilute rods and endeavour to determine their effective rotational diffusivity D^r in terms of the effective volume concentration $\hat{\phi} = nl^3(\gg 1)$. DE have pointed out that D^r must also depend in general on the degree of orientation of the rods (as described by an orientation distribution $f(\boldsymbol{p})$, where $\boldsymbol{p}$ is a unit vector along a test rod). We shall also determine the functional dependence on f, which proves to be very weak.

We suppose that the short-time rotational diffusivity of a rod is D_0^r. It may then be shown by slender-body theory for Stokes flows, together with the Stokes–Einstein relation, that for diffusion along the rod $D_0^{\parallel} = \frac{1}{6}D_0^r l^2$, and for diffusion perpendiculr to it $D_0^{\perp} = \frac{1}{12}D_0^r l^2$ (see e.g. Batchelor 1970).

The reptation time for this system is given in §4.2 as the time at which a test rod

$\hat{\phi}/\alpha$	D/D_0 (equation (13))	D/D_0 (Numerical simulation)	τ_∞
1	0.41	0.52 ± 0.05	60
2	0.25	0.24 ± 0.02	300
4	0.12	0.13 ± 0.01	800
8	0.055	0.055 ± 0.005	2000

TABLE 1. Calculated long-time diffusivities for a two-dimensional suspension of rods. τ_∞ is an approximate time at which the asymptote for D is reached.

first escapes the constraint of its nearest neighbour. Now the nearest neighbour in this context is the rod that impedes the angular rotation of the test rod most severely and is therefore more likely to be close to the end of the test rod than to its centre. In order to escape this first constraint a rod must diffuse a distance of order l along its length, and this takes an expected time $\gamma(D_0^r)^{-1}$ where γ is a constant of order unity. We show by detailed analysis in Appendix A that $\gamma = \frac{1}{8}$. In addition, the possibility exists that the constraint may itself disappear because the constraining rod reptates out of the way. This takes an expected time $1/4D_0^r$. The expected time at which the former of these events occurs is of course shorter than both, and is approximately $1/12D_0^r$.

We have thus estimated t_c and hence from (6)

$$\frac{D^r}{D_0^r} = 12\int_0^{1/12D_0^r} \frac{\mathrm{d}t'}{\mathcal{N}[(4\pi D_0^r t')^{\frac{1}{2}};f]} = \frac{6}{\pi}\int_0^{(\pi/3)^{\frac{1}{2}}} \frac{\theta'\,\mathrm{d}\theta'}{\mathcal{N}(\theta';f)}. \tag{14}$$

and it remains finally to determine $\mathcal{N}(\theta;f)$.

Determination of $\mathcal{N}$

Consider first the isotropic orientation distribution with $f = \text{const} = 1/4\pi$. Exact evaluation of $\mathcal{N}$ is a difficult problem in combinatorial graph theory, but some progress may be made by order-of-magnitude estimation. Suppose that a test rod with fixed centre, and at fixed azimuth, rotates through an angle θ. Then it sweeps out an area $\frac{1}{4}\theta l^2$. A second rod is therefore struck directly by the first if it intersects this area. Now the expected number of rods which intersect an area A is $\frac{1}{2}nlA$, and hence the expected number of rods struck by a test rod is $\frac{1}{8}\hat{\phi}\theta$.

The rods so far accounted for are, of course, just the 'first generation'. Each of these may be expected to hit others. A crude over-estimate for $\mathcal{N}$ would be that for each step of $8/\hat{\phi}$ in θ the number of rods involved doubles, and hence that $\mathcal{N}(\theta) = 2^{\frac{1}{8}\theta\hat{\phi}}$. This is plainly an overstatement when $\theta\hat{\phi}$ is large since it counts several times over some rods which are reached by different routes. Furthermore, because successive generations of rods are inclined to one another, the area each must sweep out decreases for each successive generation. A better estimate for $\mathcal{N}$ when $\theta\hat{\phi}$ is large may be obtained as follows.

Initially each rod has enough room to turn through an angle of about $8/\hat{\phi}$ before it hits another. Thus if the test rod rotates through an angle of order unity a series of chains of about $\theta\hat{\phi}/8$ links radiating from the test rod must also be caused to move. Now each link in the chain is randomly aligned to the previous one, and hence the disturbance of the suspension spreads to a radius of order $(\theta\hat{\phi})^{\frac{1}{2}}l$ from the test rod. An upper bound for $\mathcal{N}$ (which seems likely to be attained in an order-of-magnitude

sense) is then given by the number of rods in a sphere of this radius, which scales as $\hat{\phi}^{\frac{5}{2}}\theta^{\frac{3}{2}}$ as $\hat{\phi} \to \infty$. It follows from (5) that as $t \to \infty$

$$\langle \theta^2 \rangle \propto \int_0^t \frac{t'^{-\frac{3}{4}} \mathrm{d}t'}{\hat{\phi}^{\frac{5}{2}}} \propto \frac{t^{\frac{1}{4}}}{\hat{\phi}^{\frac{5}{2}}},$$

and hence that the first rod can attain an arbitrary orientation ($\theta \sim 1$) at a (large but) finite time.

In summary, we have that $\mathcal{N}$ is a monotone increasing function with

$$\mathcal{N}(\theta) = \begin{cases} \mathcal{N}_1(\theta\hat{\phi}) & \text{for } \theta\hat{\phi} = o(\hat{\phi}) \quad \text{as } \hat{\phi} \to \infty, \\ \alpha\theta^{\frac{3}{2}}\hat{\phi}^{\frac{5}{2}} & \text{for } \theta\hat{\phi} = O(\hat{\phi}) \quad \text{as } \hat{\phi} \to \infty. \end{cases}$$

Now (14) gives

$$\frac{D^{\mathrm{r}}}{D_0^{\mathrm{r}}} = \frac{6}{\pi\hat{\phi}^2} \int_0^{(\frac{\pi}{9})^{\frac{1}{2}}\hat{\phi}} \frac{\psi \, \mathrm{d}\psi}{\mathcal{N}(\psi/\hat{\phi})},$$

and the contribution to the integral from $\psi = O(\hat{\phi})$ is of order $\hat{\phi}^{-\frac{1}{2}}$ (and thus negligible) as $\hat{\phi} \to \infty$. It follows that asymptotically

$$\frac{D^{\mathrm{r}}}{D_0^{\mathrm{r}}} = \frac{\beta}{\hat{\phi}^2} + O(\hat{\phi}^{-\frac{5}{2}}),$$

where (using the fact that $\mathcal{N}_1(\psi) \to \infty$ rapidly as $\psi \to \infty$) we may put

$$\beta = \frac{6}{\pi} \int_0^\infty \frac{\psi \, \mathrm{d}\psi}{\mathcal{N}_1(\psi)}.$$

The constant β here is formally of order unity as $\hat{\phi} \to \infty$.

This is the asymptotic dependence of D^{r} on $\hat{\phi}$ predicted by DE on the basis that a test rod will rotate only as far as its nearest neighbour. The theory above shows that given sufficient time a test rod can diffuse even further, but that in the available reptation time only an angle of order $1/\hat{\phi}$ is achived. Furthermore in order to determine the value of the numerical constant β it suffices to evaluate $\mathcal{N}$ for θ of order $1/\hat{\phi}$, i.e. only the first few generations of interaction of the rods.

In order that the $\hat{\phi}^{-\frac{5}{2}}$ term be negligible in comparison with the $\hat{\phi}^{-2}$ term retained it is necessary that $\phi^{\frac{1}{2}} \gg 1$. Since $\hat{\phi}/8$ appears a more appropriate estimate of the volume concentration it is likely that ϕ itself needs to be very large ($\gg 64$ say) before the reptation mechanism becomes important. It is notable that the numerical simulation of Doi *et al.* (1984) similarly requires that $\hat{\phi}$ exceed about 100 before the $\hat{\phi}^{-2}$ behaviour is seen, and suggests that the conclusion of Fixman (1985*a*) that D^{r} is proportional to $\hat{\phi}^{-1}$ based on numerical simulation with $20 < \hat{\phi} < 150$ may not truly represent the asymptotic dependence as $\hat{\phi} \to \infty$ (see also figure 8).

Dependence on the orientation distribution f

The question arises as to how these estimates are affected if f is non-uniform. As a simple scalar measure of the anisotropy let

$$\lambda = \tfrac{1}{2}\langle 3(\boldsymbol{p}\cdot\boldsymbol{e}_x)^2 - 1 \rangle \equiv \frac{1}{2} \int_{\text{orientations}} (3(\boldsymbol{p}\cdot\boldsymbol{e}_x)^2 - 1) f(\boldsymbol{p}) \, \mathrm{d}^2\boldsymbol{p}, \tag{15}$$

where $\boldsymbol{e}_x$ is a unit vector in the x-direction. $\lambda = 0$ when $f = \frac{1}{4}\pi$ and the distribution is isotropic, and $\lambda = 1$ when all the rods are aligned. Then the expected number of

rods which intersect an area A now depends upon the direction of the normal to A and is of order $nlA(1-|\lambda|)$. Hence the number of 'first generation' rods struck by a test rod is of order $\theta\hat{\phi}(1-|\lambda|)$. Thus only if the rods are sufficiently aligned that $1-|\lambda| \ll 1$ is the asymptotic dependence on $\hat{\phi}$ of the estimate above affected. Specifically provided that the mean angle of deviation of a test rod from full alignment exceeds $\hat{\phi}^{-1}$ then

$$\frac{D^r[f]}{D_0^r} = \frac{\beta[f]}{\hat{\phi}^2} \quad \text{where } \beta = \frac{6}{\pi}\int_0^\infty \frac{\psi\,\mathrm{d}\psi}{\mathcal{N}_1(\psi;f)}. \tag{16}$$

For systems that are evenly more strongly aligned, the theory above breaks down, and presumably the diffusivity of each rod (for such time as f remains sharply peaked) is approximately D_0^r.

We turn finally to a numerical evaluation of $\beta[f]$.

Determination of $\mathcal{N}_1(\psi)$

The dominant contribution to β comes from the first few generations of interacting rods. In particular, after three generations the integrand in (16) has fallen to about $\frac{1}{8}$th of its largest value. In consequence a fair approximation may be obtained by examining the first few generations with some care, and using a cruder approximation for later generations. Suppose then that the test rod rotates through an angle $\psi/\hat{\phi}$. Define generation zero as the test rod, and generations $r = 1, 2\ldots$ as the set of rods struck by generation $r-1$; let $\nu_r(\psi)$ be the expected number of rods in generation r. Suppose that the test rod advances from θ to $\theta+\mathrm{d}\theta$ and that each rod of generation r consequently sweeps out an area $l^2A_r\,\mathrm{d}\theta$. Then write the mean number of rods of generation $r+1$ that strike unit area swept out by generation r as nlM_r. It follows that

$$\frac{\mathrm{d}\nu_{r+1}}{\mathrm{d}\psi} = \frac{1}{\hat{\phi}}\frac{\mathrm{d}\nu_{r+1}}{\mathrm{d}\theta} = M_r A_r \nu_r.$$

Noting that $\nu_0(\psi) = 1$ and that $\nu_r(0) = 0, r > 0$, the ν_r can be determined iteratively when A_r and M_r are known. We show in Appendix A that approximate values for A_r and M_r are

$$M_r = M, \quad A_r = \tfrac{1}{3}(0.67K)^r \quad (r \geqslant 1),$$

in which the constants M and K are given by (A 2) and (A 3) as

$$M = \frac{2}{\pi}\iint_{\text{orientations}} f(\boldsymbol{p})f(\boldsymbol{p}')\,|\boldsymbol{p}\wedge\boldsymbol{p}'|\,\mathrm{d}^2\boldsymbol{p}\,\mathrm{d}^2\boldsymbol{p}',$$

and

$$K = \frac{2}{\pi}\iint_{\text{orientations}} f(\boldsymbol{p})f(\boldsymbol{p}')\,E(|\boldsymbol{p}\wedge\boldsymbol{p}'|)\,\mathrm{d}^2\boldsymbol{p}\,\mathrm{d}^2\boldsymbol{p}',$$

and E is a complete elliptic integral. It follow that

$$\mathcal{N}(\psi) = \sum_{r=0}^{\infty}\nu_r(\psi) = 1 + \tfrac{3}{4}\sum_{r=0}^{\infty}\frac{1}{r!}\left(\frac{M\psi}{3}\right)^r (0.67K)^{\frac{1}{2}r(r-1)},$$

and the sum is easily computed from the first few terms.

We show in figure 7 the variation of $\mathcal{N}$ for modest values of ψ for the isotropic orientation distribution $f = \frac{1}{4}\pi$. This value will be an overestimate of $\mathcal{N}$ because as ψ increases some rods are counted more than once. A numerical evaluation of the integral (16) for β is straightforward and gives $\beta = 410$.

The largeness of this 'order-one' coefficient deserves comment. The more

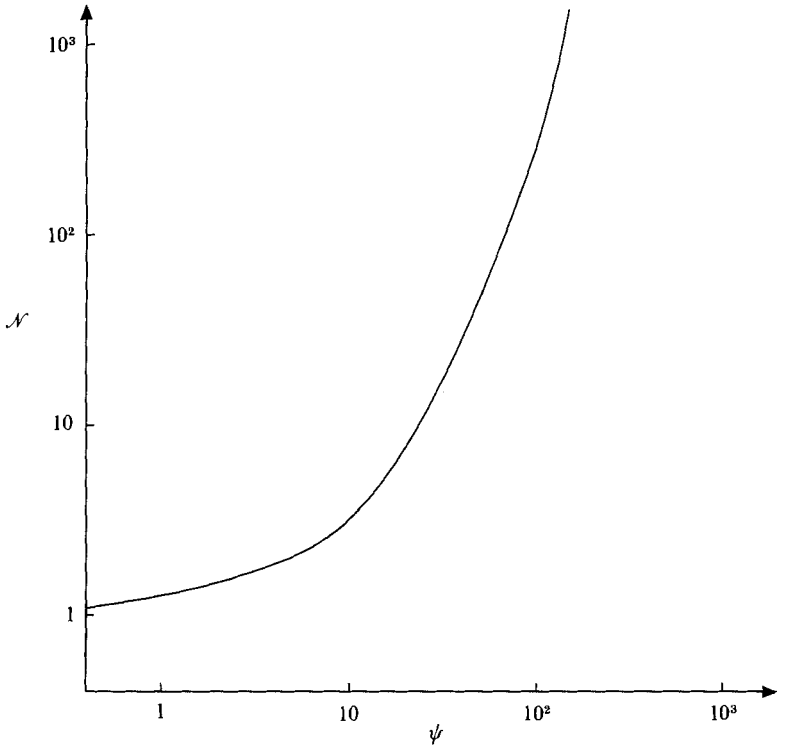

FIGURE 7. Variation of $\mathcal{N}(\psi)$ for a three-dimensional system of randomly aligned rods.

important reason is that in defining $\hat{\phi}$ the rod length l rather than the half-length $\frac{1}{2}l$ was used. In consequence a typical rotational freedom of only $\hat{\phi}/8$ occurs for each rod. The quantity β scales with the sixth power of the rod length and thus redefining $\hat{\phi}$ as $(n\frac{1}{2}l)^3$ would reduce β to about 6.4. This additional factor arises from the cooperation of the cage in giving a test rod more room for manoeuvre than the distance to its nearest neighbours.

In table 2 we show also the values of K, M and β for more strongly peaked orientation distributions f. It is impractical to explore the full function space of possibilities for f, but a representative sample of distributions may be obtained by choosing

$$f(\boldsymbol{p}) \propto \exp\{\tfrac{1}{2}\mu(3(\boldsymbol{p}\cdot\boldsymbol{e}_x)^2-1)\},$$

where μ is a constant ($\mu = 0$ isotropic: $\mu = \infty$ fully aligned). The scalar measure of the anisotropy λ is given by (15). It is striking that β is a very weak functional of f: indeed for small λ,

$$\beta = 410(1+\lambda^2),$$

and since the dependence is quadratic the distribution must be strongly peaked for β to be changed significantly. Thus those approximate calculations which have taken D^r as independent of f (e.g. DE) should be acceptably accurate.

The result for β here can be compared with that given by other methods. Doi *et al.* (1984) quote a value of 540 from a numerical simulation. The discrepancy is probably accounted for by our overestimation of $\mathcal{N}$ (which then underestimates β). A simulation of a different sort has also been performed by Frankel & McGuire (1983) giving a value for β of about 1000, but with only modest values of $\hat{\phi}$ (25–50). The

μ	λ	M	K	β
0	0	0.498	0.743	410
0.1	0.021	0.498	0.743	410
0.3	0.063	0.497	0.744	420
1.0	0.220	0.484	0.754	430
2.0	0.439	0.439	0.787	480
3.0	0.601	0.382	0.832	570
4.0	0.717	0.333	0.873	690
5.0	0.786	0.297	0.900	810
∞	1	0	1	

TABLE 2. Variation of diffusivity with orientation distribution for a three-dimensional suspension of rods

dynamics in this simulation is however of free motion of particles with collisions rather than Brownian motion and no exact comparison can therefore be expected.

A third simulation has been performed by Fixman (1985*a*) for which a different dependence on $\hat{\phi}$ is claimed, namely $D^r \propto \hat{\phi}^{-1}$. The results quoted by Fixman are for a system of rods whose centres are constrained not to move so that a test rod can never escape the cage. The autocorrelation function of the rod orientation is then found to asymptote to a fixed value as $t \to \infty$ (called C_p by Fixman), and the mean angular displacement θ of a test rod is then given as

$$\langle \theta^2 \rangle = 2(1 - C_p).$$

We show in figure 8 Fixman's data for $\langle \theta^2 \rangle$ for varying $\hat{\phi}$ on a log–log plot. The 'best' slope appears to be about -1.6, intermediate between the DE value (-2) and that of Fixman's (1985*b*) model (-1).

It is notable, however, that both Doi *et al.*'s (1984) simulation and our analysis suggest that only for values of $\hat{\phi}$ exceeding about 80 can the $\hat{\phi}^{-2}$ behaviour be expected, and keeping only the data points for large $\hat{\phi}$ in figure 8 does support an exponent closer to -2 than -1. We can also compare at this point Fixman's model (1985*b*) with ours. Fixman assumes that for $0 < t < t_c$ the equilibration of the cage 'proceeds outward from the test rod at substantially the same rate as unhindered angular diffusion of the rod'. This assumption amounts in our terms to a comparatively modest linear (or quadratic) growth of $\mathcal{N}$ with θ rather than the exponential growth suggested above. We have noted in earlier sections (4.1, 4.2) that such functional dependence gives rise to a diffusivity D^r larger, as a function of $\hat{\phi}$, than implied by nearest-neighbour separations, and this discrepancy in $\mathcal{N}$ may well give rise to the conclusion that $D^r \propto \hat{\phi}^{-1}$.

A number of experiments to measure D^r have been performed (Zero & Pecora 1982; McGuire, McTague & Rondelez 1980) and these appear to support the DE theory but with a value for β in the range 1000 to 2000. One likely source for the discrepancy between theory and experiment is that the theory does not include hydrodynamic interactions between rods. A naïve expectation is that distant rods may act as a porous medium so far as the fluid is concerned and thereby (as noted by Batchelor 1971) generate a logarithmic correction to the diffusivity D^r. In consequence the result $D^r \propto \hat{\phi}^{-2}$ should be modified by inclusion of a $\log \hat{\phi}$ term. A careful analysis of this question is itself a major task and lies outside the scope of this paper.

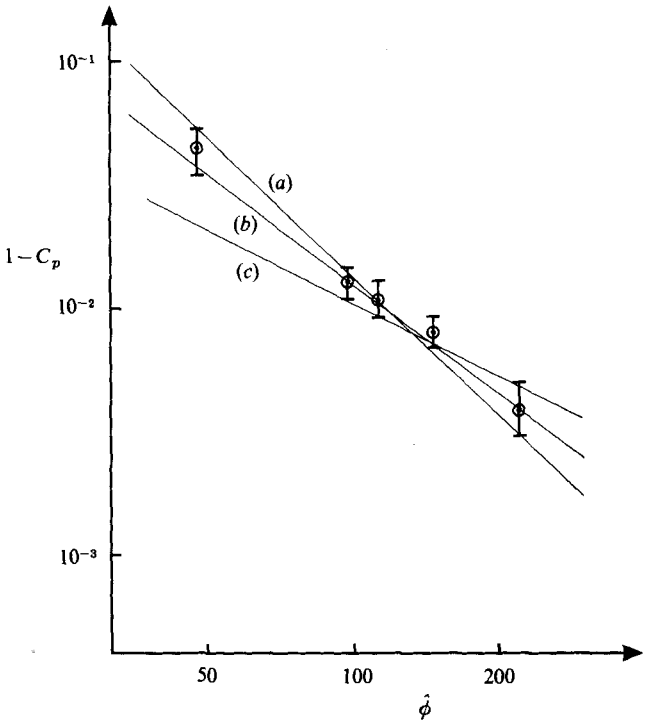

FIGURE 8. A numerical simulation of rods in three dimensions but with fixed centres. The long-time orientational autocorrelation C_p plotted against $\hat{\phi}$. ⊙, data from Fixman (1985*a*); lines (*a*), (*b*), (*c*) have slopes -2, -1.6, -1 respectively.

5. Diffusion in a suspension of rigid spheres

We consider in this section the self-diffusion of a suspension of rigid Brownian spheres of number density n and radius a. This problem has been considered for small concentrations by Batchelor (1983) who showed that

$$\frac{D}{D_0} = 1 - 2.10\phi + O(\phi^2).$$

The experiments of Kops-Werkhoven *et al.* (1982) show reasonable agreement with this result for concentrations $\phi \lesssim 0.15$. The formula above makes allowance for hydrodynamic interactions between spheres. The corresponding result when hydrodynamic interactions are neglected is

$$\frac{D}{D_0} = 1 - 2\phi + O(\phi^2) \tag{17}$$

(see Rallison & Hinch 1986 and references therein). Rallison & Hinch also give formulae from which the full time-dependence of $\langle x^2 \rangle(t)$ may be calculated for small ϕ.

For non-dilute systems light-scattering experiments of Kops-Werkhoven & Fijnaut (1982) have determined $D(\phi)$ for general ϕ, and show that beyond a critical value of ϕ, ϕ_c say, the self-diffusivity becomes very small, possibly zero. We seek here to compare the theoretical prediction from (5) with the experimental results.

5.1. *Evaluation of $\mathcal{N}(x)$ for a system of spheres*

The calculation of $\mathcal{N}(x)$ follows much the same lines as that for the system of rods discussed in §4.2. When a test sphere advances rectilinearly through a distance x, an advancing 'front' of spheres is pushed before it, and this front will be approximately circular for both small and large values of x. We suppose then for simplicity that the front is *always* circular with radius $\mathscr{R}(x)$. Then, when the test sphere advances a further distance $\mathrm{d}x$, a new sphere is struck if its centre lies in a volume $\pi(\mathscr{R}+a)^2\,\mathrm{d}x$ and so

$$\frac{\mathrm{d}\mathcal{N}}{\mathrm{d}x} = n\pi(\mathscr{R}+a)^2 \quad \text{with } \mathcal{N}(0) = 1. \tag{18}$$

$\mathscr{R}$ also increases with x because new overlapping spheres increase the area of the front. We can approximate this increase by requiring that

$$\mathrm{d}(\pi\mathscr{R}^2) = \text{Probability (new sphere is hit)} \times \text{(Expected area of overlap)}.$$

Now if $\mathscr{R} \gg a$ an overlapping sphere is hit if its centre lies in a volume $2\pi\mathscr{R}\,2a\,\mathrm{d}x$, and its expected area of overlap is $\frac{1}{2}\pi a^2$, hence

$$\frac{\mathrm{d}}{\mathrm{d}x}(\pi\mathscr{R}^2) \sim n\,2\pi\mathscr{R}\,2a\,\tfrac{1}{2}\pi a^2 = \phi\tfrac{3}{2}\pi\mathscr{R} \quad \text{as } \mathscr{R}/a \to \infty.$$

On the other hand for the first encounter when $\mathscr{R} = a$, a second sphere is struck if its centre lies in a volume $\pi(2a)^2\,\mathrm{d}x$ and, as shown in Appendix B, the expected area overlap is $\frac{3}{4}\pi a^2$. Thus

$$\frac{\mathrm{d}}{\mathrm{d}x}(\pi\mathscr{R}^2) \sim n\,4\pi a^2\,\tfrac{3}{4}\pi a^2 = \phi\tfrac{9}{4}\pi\mathscr{R} \quad \text{as } \mathscr{R}/a \to 1.$$

These results may be combined to give (within the approximation of circularity for the front)

$$\mathrm{d}\mathscr{R}/\mathrm{d}x = \tfrac{3}{4}\phi\alpha(\mathscr{R}/a), \quad \mathscr{R}(0) = a, \tag{19}$$

where

$$\alpha \sim \begin{cases} 1 & (\mathscr{R}/a \to \infty), \\ \frac{3}{2} & (\mathscr{R}/a \to 1). \end{cases} \tag{20}$$

The solution of the differential equations (18) and (19) then determines $\mathcal{N}(x)$.

5.2. *Evaluation of t_c for a system of spheres*

In order to escape the influence of its nearest neighbours a test sphere must be able to move a distance comparable with its radius a, so that the cage size $d_c = \gamma a$, where γ is a number of order unity. The choice of γ is less clear, but a value may be selected by means of the following observation. To side-step a second sphere directly in its path, the test sphere must suffer a relative sideways displacement at least as great as its diameter $2a$, and thus on average both the test sphere and the obstacle are required to move through at least half this distance. The simplest choice for γ is therefore $\gamma = 1$ and $d_c = a$. We shall show later that for this choice of d_c (and only for this choice) the self-diffusivity first vanishes at (or at least close to) the concentration for which the spheres are randomly close-packed – which provides support for the hypothesis.

For the calculation here, therefore, d_c is in principle given and t_c is to be

determined. If no finite solution for t_c exists then the test sphere can never escape the cage and so the long-time self-diffusivity is zero.

5.3. *Determination of the effective diffusivity*

With the choice $d_c = a$, (5) gives for the x-component of the test-sphere displacement

$$\frac{\langle x^2 \rangle}{a^2} = \frac{1}{\pi a^2} \int_0^{(4\pi D_0 t/a^2)^{\frac{1}{2}}} \frac{x' \, dx'}{\mathcal{N}(x')}. \tag{21}$$

t_c is the value of t (if such exists) for which the right-hand side of this equation first reaches unity, and then

$$\frac{D}{D_0} = \frac{a^2}{2D_0 t_c}.$$

It is convenient to solve the equations above by the following device: let $r = \mathscr{R}/a$ and regard $x = x(r)$ and $\mathcal{N} = \mathcal{N}(r)$. Then from (19) and (18)

$$\tfrac{3}{4}\phi \frac{x}{a} = \int_1^r \frac{dr'}{\alpha(r')}, \quad \mathcal{N}(r) = \int_1^r \frac{(1+r')^2 \, dr'}{\alpha(r')} + 1.$$

To make further progress it is necessary to make some assumption about the form of the (monotonic) function $\alpha(r)$ consistent with the asymptotes (20): a simple and convenient choice is

$$\alpha(r) = (1 - \tfrac{1}{3}r)^{-1}.$$

It follows that

$$\tfrac{3}{4}\phi \frac{x}{a} = r - \tfrac{1}{3}\log r - 1$$

and

$$\mathcal{N}(r) = \tfrac{1}{3}r^3 + \tfrac{5}{6}r^2 + \tfrac{1}{3}r - \tfrac{1}{3}\log r - \tfrac{1}{2},$$

and hence from (21)

$$\frac{\langle x^2 \rangle}{a^2} = \frac{16}{9\pi\phi^2} \int_1^r \frac{(r' - \frac{1}{3}\log r' - 1)(r' - \frac{1}{3}) \, dr'}{r'(\frac{1}{3}r'^3 + \frac{5}{6}r'^2 + \frac{1}{3}r' - \frac{1}{3}\log r' - \frac{1}{2})}, \tag{22}$$

where r is given implicitly by

$$r - \tfrac{1}{3}\log r - 1 = \frac{3\phi}{4}\left(\frac{4\pi D_0 t_c}{a^2}\right)^{\frac{1}{2}}. \tag{23}$$

Now as r increases, the integral in (22) is a monotonic increasing function with asymptotic value of 0.73 as $r \to \infty$. Hence beyond a critical concentration ϕ_c, given as

$$\phi_c = [16 \times 0.73/9\pi]^{\frac{1}{2}} = 0.64,$$

$\langle x^2 \rangle$ cannot exceed a^2 for any time t, and hence the diffusivity D must vanish. As noted above, this value for ϕ_c is close to the 'random close-packing' value $\phi_c = 0.63$ generated by Monte Carlo simulations of rigid spheres (see the discussion in Batchelor & O'Brien 1977), and indeed within the approximations made here is indistinguishable from it.

For concentrations ϕ close to ϕ_c, t_c and hence r become very large and (22) may be written

$$\frac{\langle x^2 \rangle}{a^2} \sim \frac{\phi_c^2}{\phi^2} - \frac{16}{9\pi\phi^2} \int_r^\infty \frac{3 \, dr'}{r'^2} \quad \text{as } r \to \infty.$$

The solution of this equation for r gives the asymptotic estimate

$$\frac{D}{D_0} \sim \frac{27\pi^3}{128}\phi_c^5 \left(1 - \frac{\phi}{\phi_c}\right)^2 \quad \text{as } \phi \to \phi_c. \tag{24}$$

For lower concentrations ϕ it is a straightforward matter of interpolation from a numerical evaluation of the integral in (22) to determine the value of $r(\phi)$ at which $\langle x^2\rangle/a^2 = 1$, and hence from (23) the corresponding t_c, giving D.

These results are plotted in figure 9 along with the data of Kops-Werkhoven & Fijnaut (1982) from light-scattering experiments. The agreement is good, at any rate for higher concentrations, which is perhaps surprising in view of the fact that no explicit account is taken in the theory of the effect of hydrodynamic interactions between spheres. For low and moderate concentrations the theory is poor and in particular does not coincide with (17).

An alternative interpretation of the results for D/D_0 may be made by means of Batchelor's (1983) observation that the long-time sedimentation coefficient $s(\phi)$ of a tracer sphere (at zero Péclet number) in a suspension of neutrally buoyant spheres is proportional to $D(\phi)$. Thus the result shown in figure 9 for the thermodynamic transport coefficient D/D_0 may alternatively be regarded as a calculation of the hydrodynamic property s/s_0 (see also Rallison & Hinch 1986). Unfortunately the available experiments on tracer sedimentation rates (Kops-Werkhoven & Fijnaut 1982) cover only the small-ϕ concentration regime, where the theory here is inappropriate.

More speculatively, however, it may be legitimate to regard the change in tracer sedimentation coefficient with concentration as arising from the corresponding change in viscosity of the suspension surrounding the tracer sphere. In particular if we write

$$s(\phi) = [6\pi\mu(\phi)\,a]^{-1}, \quad \text{then } \frac{s}{s_0} = \frac{\mu_0}{\mu},$$

In fact, for general concentrations ϕ this identification of sedimentation and shear properties is not exact. The viscosity of the suspension is not defined on a lengthscale of a single particle and so the Stokes drag formula is not appropriate. In particular for small ϕ the well-known Einstein result gives for the viscosity

$$\frac{\mu_0}{\mu} = 1 - 2.5\phi + O(\phi^2),$$

which does not agree with (17).

Nevertheless, for high concentrations it may be argued (see e.g. Russel & Gast 1986; Batchelor 1983) that the same physical mechanism that reduces D to zero (the inability of a sphere to escape from its cage) must also produce a dramatic increase in the zero-shear-rate fluid viscosity. We therefore plot in figure 9 measured values of μ_0/μ from de Kruif *et al.* (1985). The extrapolated value of ϕ_c from their experiments is 0.63 ± 0.02 in agreement with our result here.

Additionally the nature of the viscosity singularity as $\phi \to \phi_c$ appears to be well-approximated by (24) as

$$\mu \propto \left(1 - \frac{\phi}{\phi_c}\right)^{-2}$$

and is certainly at least as good (for $\phi \to \phi_c$) as the *ad hoc* formula often used,

$$\mu = \left(1 - \frac{\phi}{\phi_c}\right)^{-2.5\phi_c},$$

in which the exponent is about -1.6.

It should be pointed out that the physical origin of the very high viscosities predicted here is not a supposed high rate of energy dissipation in the small gaps

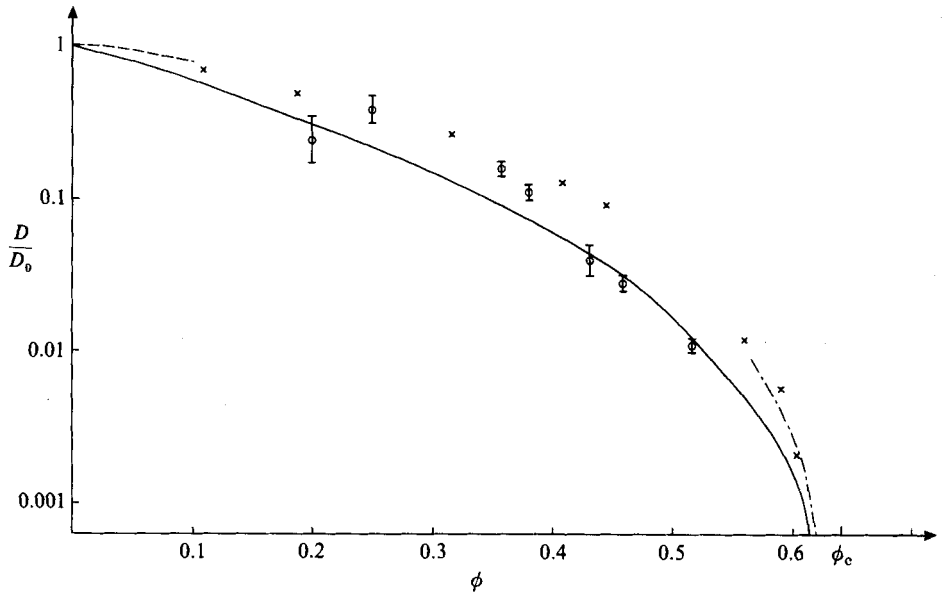

FIGURE 9. Diffusivity in a suspension of spheres. ——, theory; ϕ_c, calculated concentration for which $D = 0$; —·—·—, asymptotic theory for $\phi \to \phi_c$, equation (24); – – –, theory for small concentrations, equation (17); ○, experiments of Kops-Werkhoven & Fijnaut (1982); ×, experimental values of the zero-shear-rate viscosity μ_0/μ from de Kruif *et al.* (1985).

between particles (indeed no explicit account has been taken in the theory of the lubrication regions between spheres). The proposal is rather than when any given particle moves, it causes a large clump of adjacent Brownian spheres to move (on average), and the energy dissipation consequently takes place over a much larger region of the fluid.

In spite of the apparent agreement between theory and experiment in results for diffusivity and viscosity, there is no doubt that the physical picture here is an over-simplification. First, there is evidence from computer simulations (see Hansen & MacDonald 1976) and experiment (Pusey & Van Megen 1986) that the equilibrium state for a hard-sphere suspension is in fact crystalline if $\phi > 0.55$, and that even in the 'metastable liquid' phase with $\phi > 0.55$ (in which crystallization is prevented) computer experiments (Woodcock 1981) suggest that $D \to 0$ at $\phi_c = 0.59 \pm 0.01$. This decrease in D has also been seen recently in experiment (P. N. Pusey, private communication). A more careful calculation is needed to resolve this discrepancy in the predicted value of ϕ_c.

Secondly, there can be no doubt that these results would be modified by the inclusion of hydrodynamic interactions between particles. An indication of the importance of hydrodynamics is provided by measurements of the *short*-time diffusivity in a hard-sphere suspension, for this variation in diffusivity with concentration can be explained only by hydrodynamic effects. The experiments of Van Megen *et al.* (1987) and de Kruif *et al.* (1987) show a reduction by a factor of 4 in the short-time diffusivity when $\phi = 0.5$, though this is still a small effect in comparison with the hundredfold reduction in the long-time diffusivity. It appears then that at high concentrations the most important consequence of the lubrication forces between particles is that particle overlap is prevented – and this is correctly

modelled by our use of potential repulsive forces. But more detailed analysis is needed to incorporate hydrodynamic effects for tangential particle motions.

6. Conclusions

The central aim of this paper has been to exploit and quantify the idea of a 'cage' of neighbours in a concentrated suspension of Brownian particles. To that end we have proposed two approximate but physically appropriate results to calculate (*a*) the dynamics of a particle during the time that it is confined by a cage, and (*b*) the time at which it escapes the cage.

For very simple systems the first of these results (equation (5)) has been verified analytically (§§3.1, 3.2). For more complex systems, agreement with numerical simulations (§§3.4, 4.2) proves to be remarkably good where many particles are simultaneously involved. No general proof of the result is available at present however.

The second result (*b*) has been shown to be acceptably accurate, at any rate for a system of rods, by comparison with a numerical simulation (§4.2). In the simulation the reptation time could be varied arbitrarily, and where the time was sufficiently long for many rods to become involved in the cage dynamics good agreement was found.

By combining the two results, two systems of experimental interest were investigated. In a semidilute suspension of rods (§4.4) the calculation of the escape time is straightforward by the reptation mechanism, and the theory provides a method for calculating the cooperative diffusion of test rod and its surrounding cage. Fair agreement with experiment is obtained.

In §5 the same ideas were applied to a concentrated suspension of spheres where the calculation of the escape time is difficult, but the size of the cage is clear at the outset. Again good agreement with experiment is found at concentrations sufficiently high for many spheres to be involved in the cooperative motion of the cage.

There are at least three open-ended questions raised by this work. First the comparison of the results with experiment suggests that the fundamental equation (5) is valid in some asymptotic sense whenever a large number of particles are simultaneously interacting, but represents only an approximation when $\mathcal{N}$ is more modest. A theoretical proof of this conjecture would be valuable.

Secondly, we have treated here only systems of identical particles. It is plausible that analogous results will be available when two or more species are present.

Thirdly, we have considered only very simple rigid model particle shapes. The most important practical case of interest is that of polymer solutions where application of Doi–Edwards ideas have suggested viscosities that depend very strongly on molecular weight and concentration. Careful analysis of the diffusion of a flexible polymer molecule within its cage may suggest modifications of their results to bring them (even) more closely in line with experiment.

I am grateful to Professor S. F. Edwards and Drs E. J. Hinch, M. T. Barlow and P. N. Pusey for illuminating discussions about the work involved in this paper.

Appendix A. Statistical geometry for a three-dimensional suspension of rods

We evaluate here the statistical qualities of interest in §4.4. A test rod rotates through an angle $\mathrm{d}\theta$. The consequent mean area swept out by each rod of generation r is $l^2 A_r \mathrm{d}\theta$. The mean number of rods of generation $(r+1)$ striking unit area swept out by generation r is M_r. We seek to calculate A_r and M_r.

Suppose then that $\boldsymbol{p}_r$ is a unit vector along a typical rod R_r of generation r, and that it sweeps out an area with normal $\boldsymbol{n}$ so that $\boldsymbol{p}_r \cdot \boldsymbol{n} = 0$. The probability density for the normal $\boldsymbol{n}$, $P(\boldsymbol{n})$, is given as

$$P(\boldsymbol{n}) = \int f(\boldsymbol{p}_r)\, \delta(\boldsymbol{n}\cdot\boldsymbol{p}_r)\, \mathrm{d}^2\boldsymbol{p}_r, \tag{A 1}$$

in which $f(\boldsymbol{p})$ is the given orientation distribution for the rods and δ is a Dirac delta function.

Estimate of M_r

Now a rod with orientation $\boldsymbol{p}_{r+1}$ with centre at distance $\frac{1}{2}\lambda l\boldsymbol{n}$ from unit area hits that area if $\boldsymbol{n}\cdot\boldsymbol{p}_{r+1} > |\lambda|$. Hence the expected number of rods intersecting unit area with normal $\boldsymbol{n}$ is

$$n \int_0^1 \text{Probability}\,(|\lambda| < \boldsymbol{n}\cdot\boldsymbol{p}_{r+1})\, \mathrm{d}\lambda$$

and hence averaging over all acceptable possibilities for $\boldsymbol{n}$,

$$\begin{aligned} M_r &= \left\langle \int f(\boldsymbol{p}_{r+1})\boldsymbol{p}_{r+1}\cdot\boldsymbol{n}\, \mathrm{d}^2\boldsymbol{p}_{r+1} \right\rangle_n \\ &= \frac{2}{\pi}\iint f(\boldsymbol{p}_r) f(\boldsymbol{p}_{r+1})\, |\boldsymbol{p}_r \wedge \boldsymbol{p}_{r+1}|\, \mathrm{d}^2\boldsymbol{p}_r\, \mathrm{d}^2\boldsymbol{p}_{r+1}. \end{aligned} \tag{A 2}$$

In the particular case where f is isotropic, the integrals are easily performed to give $M_r = \frac{1}{2}$. If all the rods are aligned, however $\boldsymbol{p}_{r+1} \wedge \boldsymbol{p}_r = 0$ and $M_r = 0$. Thus M_r depends strongly on f (see also table 2).

Estimate of A_1

Suppose a first-generation rod R_1 is struck at distance $\lambda_1 l$ from its centre, by a point distant $\lambda_0 l$ from the fixed centre of R_0. Now if R_0 rotates, its tip is more likely to be hit by R_1 than its unmoved centre. In fact the probability density for λ_0 is proportional to $|\lambda_0|$. In consequence the mean value of λ_0 is $\frac{1}{3}$. All points of R_1 are equally likely to be struck, so the density of λ_1 is uniform.

Let $\boldsymbol{n}$ be a normal to the plane of motion of R_0. The angle χ between R_1 and the direction of motion of R_0 is

$$\sin\chi = |\boldsymbol{p}_1 \wedge (\boldsymbol{p}_0 \wedge \boldsymbol{n})|.$$

When R_0 rotates by $\mathrm{d}\theta$, its contact point with R_1 moves a mean distance $d_0\,\mathrm{d}\theta$ where $d_0 = \frac{1}{3}l$, and hence the corresponding point of R_1 moves a mean distance $d_1 = \frac{1}{3}l\langle\sin\chi\rangle\,\mathrm{d}\theta$. Now R_1 will both rotate and translate as a result of the contact. A perpendicular force F applied to R_1 at $\lambda_1 l$ will generate a velocity and angular velocity proportional to $\frac{1}{12}D_0 l^2 F$ and $\lambda_1 l D_0 F$ respectively, so that when the point $\lambda_1 l$

advances by d_1 a typical point μl of R_1 advances by $d_1(1+12\lambda_1\mu)/(1+12\lambda_1^2)$. Hence on integration over μ, the total area A swept out by R_1 is given by

$$A = \begin{cases} \dfrac{d_1 l}{1+12\lambda_1^2} & 0 < \lambda_1 < \frac{1}{6} \quad \text{(all points of } R_1 \text{ move 'forwards')} \\ \dfrac{d_1 l(3\lambda_1 + 1/12\lambda_1)}{1+12\lambda_1^2} & \frac{1}{6} < \lambda_1 < \frac{1}{2} \quad \text{(some points of } R_1 \text{ move 'backwards')}. \end{cases}$$

On averaging over λ_1,

$$\langle A \rangle = 0.67 d_1 l = 0.22 l^2 \langle \sin\chi \rangle \, \mathrm{d}\theta.$$

Finally, on using the distribution (A 1) for $\boldsymbol{n}$

$$\langle \sin\chi \rangle = \frac{2}{\pi} \iint f(\boldsymbol{p}_0) f(\boldsymbol{p}_1) E(|\boldsymbol{p}_0 \wedge \boldsymbol{p}_1|) \, \mathrm{d}^2\boldsymbol{p}_0 \, \mathrm{d}^2\boldsymbol{p}_1 = K, \tag{A 3}$$

say, where E is a complete elliptic integral. For an isotropic distribution f, $K = \pi/4$, whereas for full alignment $K = 1$. Thus $A_1 = 0.22K$, where K is a constant only weakly dependent on f (see table 2).

Estimate of A_r, $r \geqslant 1$

It is clear from the complexity of the calculation above that careful determination of A_r $(r > 1)$ is exceedingly difficult. Since however higher generations contribute relatively little to the integral in (16) we can approximate (with fair accuracy) as follows.

Suppose for simplicity that rod rotations can now be neglected. Then all points of R_1 are equally likely to strike R_2, and d_2 (defined analogously to d_1 above) is given as

$$d_2 = 0.67 \langle \sin\chi \rangle d_1,$$

with a similar result for d_r. It follows that

$$A_{r+1} = (0.67K) A_r \quad (r \geqslant 1),$$

so that

$$A_r = (0.67K)^{r-1} \times 0.22K.$$

Estimate of the reptation time

Noting above that if a test rod is struck at $\lambda_0 l$ the probability density for λ_0 is proportional to $|\lambda_0|$, then since the distance by which the rod must reptate in order to escape the contact is $(1-|\lambda_0|)l$ the expected time taken to escape is

$$\langle t \rangle = \frac{1}{2D_0^{\parallel}} \int_0^{\frac{1}{2}} l^2(\tfrac{1}{2}-\lambda_0)^2 8\lambda_0 \, \mathrm{d}\lambda_0 = \frac{1}{8D_0^{\mathrm{r}}}.$$

On the other hand, the expected time at which R_1 releases the constraint is

$$\langle t \rangle = \frac{1}{2D_0^{\parallel}} \int_0^{\frac{1}{2}} l^2(\tfrac{1}{2}-\lambda_1)^2 \, \mathrm{d}\lambda_1 = \frac{1}{4D_0^{\mathrm{r}}}.$$

The expected time at which the earlier of these independent events occurs is approximately

$$t_{\mathrm{c}} = \frac{1}{12D_0^{\mathrm{r}}}.$$

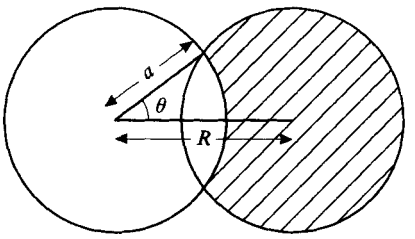

FIGURE 10. Area of overlap for two identical spheres.

Appendix B. Area overlap for a pair of colliding spheres

Suppose that a test sphere moves (perpendicular to the plane of the paper) and strikes a second identical sphere. The circular projections of the shapes are shown in figure 10. We seek to calculate the expected area A of overlap (shaded in figure 10).

Suppose the centre of the struck sphere lies at radial distance R from that of the test sphere (as shown). Then the probability density for R is $R/2a^2$ (since the area of each annulus is proportional to R). The overlap area A is easily calculated as

$$A = a^2(\pi - 2\theta + \sin 2\theta) \quad \text{where } \theta = \cos^{-1} R/2a,$$

and hence

$$\langle A \rangle = a^2 \int_0^{\pi/2} \sin 2\theta(\pi - 2\theta + \sin 2\theta)\, \mathrm{d}\theta = \tfrac{3}{4}\pi a^2.$$

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