The effect of fluid motions on the absorption of molecules by suspended particles

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The rate at which a particle in suspension can capture diffusing solute molecules can be increased by stirring the fluid. It is shown that the increase is closely related to the total power expended, per unit volume of fluid, by the stirring device. The increase in diffusion current to a particle is related to the local rate of deformation of the fluid Ω (which, in turn, determines the dissipation) by a function $F(\Omega a^2/D)$, where a is the particle radius and D the diffusion constant for the molecule in question. The function F has been determined experimentally by investigating the corresponding problem in heat transfer. In a fluid of viscosity η, stirring which is vigorous enough to double the mean diffusion current to a particle must entail a power dissipation, per unit volume, not less than $500\eta D^2/a^4$. For particles a few microns in size, or smaller, in water, effective stirring is not feasible. The results can be used also to predict the effect of stirring on the coagulation of similar particles. To double, by stirring, the rate at which particles of radius b form dimers requires a stirring power proportional to b^{-6}, and is not feasible in water if b is less than 10^{-5} cm.

To what extent can stirring a solution increase the rate of absorption of the solute molecules by particles suspended in the fluid? This question arose in a study of the acquisition of attractant molecules by bacterial cells (Berg & Purcell 1977). I wish to deal with it here in a more general context, the only restriction being that the absorbing particles are not too large and are far apart relative to their size. Practically speaking, I shall be interested in particle sizes ranging from 10^{-6} cm to 10^{-2} cm.

To begin with a well-defined problem, consider a dilute suspension of spherical particles, each of radius a, in a solution of some molecular species X which is characterized by the diffusion constant D. Assume that any X-molecule that reaches the surface of one of the particles is permanently absorbed or possibly adsorbed; the *distinction is here irrelevant. In any case the particle is supposed to remain at all times* a perfect sink for X-molecules. If the distance between neighbouring particles is much larger than a, the mean rate at which a particle collects X-molecules, which we shall call the current J_0, is given by

$$J_0 = 4\pi a D c_\infty. \tag{1}$$

Here c_∞ is the concentration, in X-molecules per unit volume, far from an absorber. This asymptotic concentration is to be maintained by addition of material as needed. In the vicinity of an absorbing particle the concentration varies with the distance r from the centre of the spherical particle according to

$$c = (1 - a/r) c_\infty. \tag{2}$$

All this applies if the fluid is motionless. Agitation of the fluid surrounding an absorbing sphere, if vigorous enough, can increase the steady current J above the value J_0. It can do so by bringing close to the absorber parcels of fluid with the higher concentration found further out, thus increasing the concentration gradient around the absorber. Indeed, that is the *only* way stirring can increase the current collected by the absorber. It cannot convey an X-molecule directly to the surface; the last stage, so to speak, of the molecule's journey must be accomplished by diffusion alone.

If a region of size a next to the absorber were suddenly to be enriched in X-molecules, it would be depleted by diffusion in a time of the order of magnitude a^2/D. Therefore, if the motion of the fluid is to have any significant effect upon the current J, it must involve velocities v such that

$$a/v \lesssim a^2/D. \tag{3}$$

A uniform fluid velocity, however large, would have no effect at all; the absorbing sphere would simply be carried along with the fluid. Equation (3) must be viewed as a condition on the gradients of the velocity field in the neighbourhood of the particle. We require that at least some components of the tensor grad $\mathbf{v}$ be of magnitude D/a^2 or larger. The condition may be expressed as

$$|\partial v_i/\partial x_j| \approx \beta D/a^2 \quad \text{with} \quad \beta \gtrsim 1. \tag{4}$$

On the scale of the particle size a, the Reynolds number R_e for the flow is $av\rho/\eta$, or in view of (4), $\beta D\rho/\eta$, where η is the fluid's viscosity and ρ its density. If we use the Einstein–Smoluchowski relation $D = kT/6\pi\eta r_{\text{eff}}$ to express the molecular diffusion constant D in terms of an effective molecular radius r_{eff}, the Reynolds number can be written as

$$R_e = \beta kT\rho/6\pi\eta^2 r_{\text{eff}}. \tag{5}$$

We are concerned with normal temperatures, ordinary liquid densities and viscosities not smaller than that of water, 10^{-2} dyne s/cm². Then even if r_{eff} is as small as 2 Å, (5) gives $R_e = 10^{-3}\beta$. We shall not be concerned with very large values of the numerical factor β. It will turn out that, in practice, a value of β large enough to make $R_e > 1$ is attainable only for particles some millimetres in size or larger. With the understanding that our conclusions might need modification for a greater than, say, 1 mm, we can be sure that the velocity field in the vicinity of the absorber is characterized by a Reynolds number much smaller than one. Inertial forces can therefore be neglected. Of course, the primary motion driven by the stirring mechanism may be, and usually will be, a highly turbulent large-scale flow, the kinetic energy of which is continually transferred into eddies of smaller and smaller size until viscous friction ultimately takes over at the scale usually called the Kolmogorov length. Our conclusion about the Reynolds number is tantamount to the observation that the Kolmogorov length for the flow is much larger than the size of our absorbing particles. This is important, for it means that the only features of the flow that we shall need to consider are not strongly dependent on the structure of the large-scale motion driven by the stirring mechanism.

To see what kind of flow would be capable of altering the distribution of X-molecules around an absorber, imagine that the diffusion is 'turned off' when the distribution has attained the form it would have in the stationary fluid, given by (2). To change such a distribution by deforming the incompressible fluid clearly requires a *shearing* deformation. The velocity gradients in a shearing deformation are just those that form the viscous stress tensor

$$\sigma'_{ij} = \eta(\partial v_i/\partial x_j + \partial v_j/\partial x_i). \tag{6}$$

In fact, these are the *only* combinations of first derivatives of velocity that need to be considered. A rotation, involving combinations like $\partial v_i/\partial x_j - \partial v_j/\partial x_i$, obviously has no effect on a spherically symmetric distribution. But it would have no effect on the current to the absorber even if the distribution were not spherically symmetric because, inertial forces being negligible as we have already seen, the absorbing particle would merely rotate with the local fluid. We conclude that the effect of fluid motion upon the distribution of X-molecules around the absorbing particle is entirely determined by the components of the viscous stress tensor that appear in (6).

The same components also determine completely the rate at which energy is being dissipated by viscous friction, in a unit volume of fluid. Let us denote that rate by S. It is given explicitly (Landau & Lifshitz 1959, p. 54) by

$$S = \frac{\eta}{2} \left[\left(\frac{\partial v_x}{\partial y} + \frac{\partial v_y}{\partial x} \right)^2 + \left(\frac{\partial v_y}{\partial z} + \frac{\partial v_z}{\partial y} \right)^2 + \left(\frac{\partial v_z}{\partial x} + \frac{\partial v_x}{\partial z} \right)^2 \right]. \tag{7}$$

S is the total rate at which kinetic energy is turning into heat, per unit volume. For continuous stirring the integral of S over the entire volume stirred gives the mechanical power output of the stirring device. This suggests a remarkably simple relation between the total power invested, by whatever means, in agitating the fluid and the effectiveness of stirring on the microscopic scale. Can it be that the details of fluid motion on intermediate scales are irrelevant and all that matters in determining the current enhancement J/J_0 is the total power expended? (In the case of an ordinary rotary agitator or blender that power is just the product of the torque and shaft speed.)

Before drawing so sweeping a conclusion we must be able to rule out the possibility that two different velocity fields could have equal values of $\langle S \rangle$, the space and time average of the quantity S given by (7), but nevertheless differ in the resulting current enhancement factor J/J_0 for the same size of absorbing particle. Two independent arguments against that possibility can be made. The first is an appeal to the theory of isotropic turbulence, according to which as we go down the hierarchy of eddy scales the turbulent velocity field becomes statistically isotropic and independent of the large-scale pattern. This should hold *a fortiori* at scales below the Kolmogorov length. In that case the specification of $\langle S \rangle/\eta$ would suffice to determine all kinematic features of the flow on the scale a, including its effect on J/J_0.

A different argument can be based on our observation that the variables on which J/J_0 must depend are just the deformation rates $\partial v_i/\partial x_j + \partial v_j/\partial x_i$. In fact, J/J_0 must be an even function of these quantities, for reversing the sign of all the space derivatives could not change J/J_0. We therefore expect the fractional increase in current $J/J_0 - 1$ to be proportional to the square of a deformation rate, for rates sufficiently small. But then it will differ from $\langle S \rangle$ only by some constant factor depending on the parameters a, D and η. In that case the total power input would determine J/J_0 even if the stirring were not uniform throughout the volume. It will turn out, however, that for deformation rates high enough to achieve a significant increase in current $J/J_0 - 1$ increases more slowly than the square of the local deformation rate. Consequently, for given total power invested, the stirring will be most effective if the dissipation is uniform throughout the stirred volume. I shall discuss that special case first.

Suppose that we are able to determine the factor J/J_0 by which the current to a spherical absorber of radius a is increased if the particle finds itself in a region where one

component of the viscous stress tensor, say $\eta(\partial v_x/\partial y + \partial v_y/\partial x)$, has a locally uniform non-zero value and other components are zero. Denote this value by $\eta\Omega$; i.e. let

$$\Omega = \partial v_x/\partial y + \partial v_y/\partial x. \tag{8}$$

(By 'locally uniform' I mean that Ω would be constant throughout a region much larger than a if the particle were not there. Of course the flow is different in the immediate neighbourhood of the spherical particle.)

The value of J/J_0 can depend only on the kinematics of the flow and the diffusion constant D, i.e. only upon Ω, a and D. The dimensionless combination in which these variables will appear can only be $\Omega a^2/D$, or powers thereof. The energy dissipated per unit volume is $\frac{1}{2}\eta\Omega^2$. In this case, for given a and D, a particular value of J/J_0 will be associated with a certain value of the mean stirring-power density $\bar{P}$.

Let us denote by u the dimensionless combination $\Omega a^2/D$, and let $J/J_0 = F(u)$. The function $F(u)$ could be found by solving the following problem. Consider first the irrotational velocity field with uniform shearing stress:

$$\mathbf{v}_0(\mathbf{r}) = \tfrac{1}{2}\Omega(\hat{\mathbf{x}}y + \hat{\mathbf{y}}x). \tag{9}$$

Now immerse in this fluid a small sphere of radius a, located on the z axis, and find the new velocity field $\mathbf{v}(\mathbf{r})$ which approaches $\mathbf{v}_0(\mathbf{r})$ asymptotically. This velocity field is zero on the surface of the sphere $r = a$ and for $r > a$ satisfies the equations for incompressible flow at very low Reynolds number: div $\mathbf{v} = 0$ and $\nabla^2(\text{curl }\mathbf{v}) = 0$. Having found $\mathbf{v}(\mathbf{r})$, solve the diffusion equation

$$D\nabla^2 c + \mathbf{v}\cdot(\text{grad }c) = 0 \tag{10}$$

with $c = 0$ at $r = a$ and $c = c_\infty$ at infinity. Then $F(u)$ will be given by $(a/c_\infty)(\partial c/\partial r)_{r=a}$ with u given by $\Omega a^2/D$.

Rather than attempt that solution, I have resorted to an experimental determination of $F(u)$ through an investigation of the identical problem in heat transfer. If we replace c by temperature and D by the thermal diffusivity of the fluid α (= thermal conductivity/heat capacity per unit volume), what was the diffusive current J becomes the current of heat to or from the sphere, the temperature difference between the sphere and remote liquid being c_∞. The problem is one of heat transfer in forced convection. One might even hope to find the problem already solved in the literature. But that hope fades when one realizes that if scaled up to macroscopic dimensions the system lies far outside any regime of practical interest in heat transfer. We must deal with fluid velocities near the sphere as small as $v \approx D/a$. Replacing D by α, which is typically not much greater than $10^{-3}\,\text{cm}^2/\text{s}$, we see that for $a \approx 1$ cm velocity gradients as small as $10^{-3}\,\text{s}^{-1}$ will be important. In a normal liquid, free convection driven by gravity would swamp any motion as slow as that, even for rather small temperature differences. For our purposes, fortunately, convection can be suppressed by using a liquid of high viscosity.

The liquid used was Dow–Corning 200 Fluid (dimethylsiloxane polymer) with a viscosity at 25 °C of 60 000 cS. This material has a thermal conductivity of 0·00037 cal/cm s °C and a thermal diffusivity of 0·00100 cm²/s. A velocity field approximating that described by (9), in a central region, was established by four slowly rotating cylinders (figure 1). In this geometry the value of Ω in the central region is approximately $1\cdot78\omega$, where ω is the angular speed of each cylinder, so that $u = 1\cdot78\omega a^2/\alpha$.
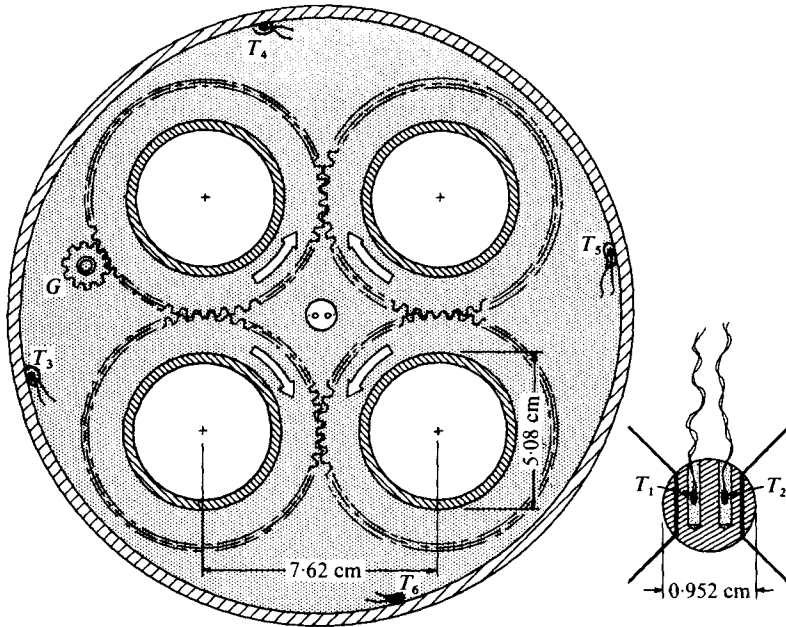
FIGURE 1. Plan view of the arrangement of the rotating cylinders and the spherical heat source in the bath of Dow–Corning 200 fluid. The axial length of the cylinders is 14 cm. The aluminium sphere, within which two thermistors are epoxied, was held by taut nylon filaments. The heat loss through these filaments and the leads to the thermistors was negligible. One of the thermistors, supplied from a constant-current source, served as the heater. Thermistors T_3, T_4, T_5 and T_6, connected together, served to measure the bath temperature. The spur gear G was driven by a stepping motor outside the bath.

The cylinders were driven, by means of the spur gear, by a stepping motor. Their speed ω ranged from 0·0017 to 0·120 rad/s, in various runs, covering a range in u of from 0·7 to 49. The aluminium sphere was located on the symmetry axis and midway, vertically, along the length of the cylinders. It contained *two* separate thermistors. One was used merely as a heater, the other to measure the temperature of the aluminium sphere. The temperature of the remote fluid was measured by several thermistors around the periphery.

With the cylinders turning at a constant speed ω, the temperature difference Δt between sphere and bath and the heating power p_h were measured after a steady state had been attained. For fixed ω, the relation between Δt and p_h was linear within the accuracy of the measurements, showing that free convection was playing a negligible role. The value of $F(u)$, where $u = \Omega a^2/\alpha$, is simply the ratio of the heating power required to maintain a temperature difference Δt between the source and the bath to the power required to maintain the same Δt with the cylinders stationary.

The results are given in figure 2 as a logarithmic plot of $F(u) - 1$ against the dimensionless variable u, which is $\Omega a^2/\alpha$ in the heat-transfer problem and $\Omega a^2/D$ in the diffusion problem. Of course these results, even if free of experimental error, would not represent an exact solution to the stated problem of a spherical source in an unbounded
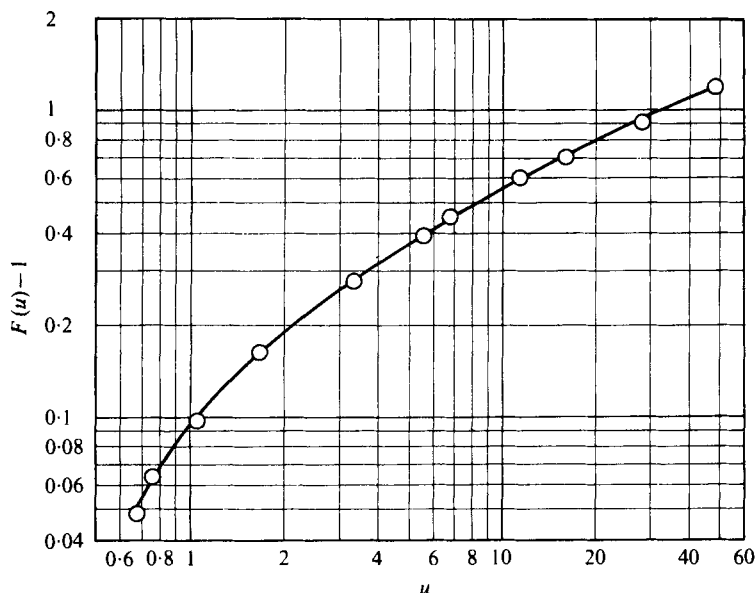
FIGURE 2. $F(u) - 1$ is the fractional increase in heat current for constant power caused by fluid motion characterized by the deformation rate Ω, the dimensionless variable u being defined as $\Omega a^2/\alpha$ (α = thermal diffusivity). It is also the fractional increase in diffusion current to a spherical sink for a given concentration of the bath, with u defined in that case as $\Omega a^2/D$. Circles are experimental points from the thermal model. The curve was drawn through them by eye.

medium. For one thing, the relation between Ω and the observed ω is only approximate; the flow is not precisely that specified in (9). Also, because of the high thermal conductivity of the metal cylinders, the outer thermal boundary of the system, to which the 'bath temperature' refers, is in effect some irregular surface not much further away from the source than the nearest part of a cylinder: a distance that may be roughly estimated as 8–10 times the radius a of the sphere. This increases the heat loss from the sphere by some 10–12 % compared with the case of an infinite medium. It could hardly have a larger effect on the relative increase in heat loss caused by stirring. I believe that the true $F(u)$ for a sphere immersed in the velocity field (9) is not likely to differ by more than 20 % from the curve through the experimental points in figure 2. Notice that the slope of the logarithmic curve is approaching 2 at the smallest values of u, confirming our expectation that $F(u) - 1$ would be quadratic in u in the neighbourhood of $u = 0$.

Suppose that we say, more or less arbitrarily, that stirring is effective if it more than doubles the current to the absorbers, i.e. if $F(u) > 2$. According to figure 2 that requires a value of u not less than 30. Setting $\Omega a^2/D = 30$, we find that the minimum stirring power S_{min} required, per unit volume, is

$$S_{min} = \tfrac{1}{2}\eta\Omega^2 = 450\eta D^2/a^4. \tag{11}$$

Considering the experimental inaccuracies mentioned above and the flatness of the curve, the value of u for which the true $F(u)$ equals 2 could conceivably be as low as 20. In that case the coefficient in (11) would be 200.

Equation (11) was obtained for the special case in which the deformation was uniform throughout the volume. That will not be true in general. We must ask instead for the

value of the average stirring-power density $\langle S \rangle_{\min}$ which will ensure that the average factor of current increase $\langle F(u) \rangle$ is 2. Here the brackets denote a space and time average over the stirred volume. To calculate $\langle S \rangle_{\min}$ we should need in addition to the function $F(u)$ some knowledge of the distribution function for Ω^2, the square of the local deformation rate. For example, suppose that Ω^2, which I shall abbreviate by W, has an exponential distribution with mean value $\overline{W}$. Assume, in other words, that at any instant the fraction of the total volume in which Ω^2 exceeds a particular value W is $\exp(-W/\overline{W})$. Let W^* denote the value of Ω^2 determined by (11):

$$W^* = 900D^2/a^4. \tag{12}$$

Write the function $F(u) - 1$ as $f(W)$; then $f(W^*) = 1$. In the neighbourhood of W^*, $f(W)$ can be represented approximately by

$$f(W) = (W/W^*)^\nu, \tag{13}$$

using which we can find an approximation for the average value of $f(W)$:

$$\langle f(W) \rangle \simeq \overline{W}^{-1} \int_0^\infty (W/W^*)^\nu \exp(-W/\overline{W}) \, dW = (\overline{W}/W^*)^\nu \, \Gamma(\nu+1). \tag{14}$$

The mean stirring-power density required to double the average current will be determined by that value of $\overline{W}$, which I shall denote by $\overline{W}_1$, which makes $\langle f(W) \rangle = 1$.

From (14) we have

$$\overline{W}_1 = W^*[\Gamma(\nu+1)]^{-1/\nu}. \tag{15}$$

Inspecting figure 2, we find that the logarithmic derivative of $F(u) - 1$ around $u = 30$ is approximately 0·48, so that $\nu = 0·24$. Then (15) gives

$$\overline{W}_1 = 0·49W^*. \tag{16}$$

The result is rather insensitive to ν; for $\nu = 0·2$ the factor would be 1·53; for $\nu = 0·3$ it would be 1·43. Notice that for $\nu = 1$, i.e. for quadratic dependence of $F(u) - 1$ upon u, we get $\overline{W}_1 = W^*$, a result that would hold for any distribution of W.

It would take an extremely broad distribution of W to give a $\overline{W}_1$ significantly larger than $1·5W^*$. For a distribution narrower than the exponential distribution we should find $\overline{W}_1/W^*$ somewhere between 1·5 and 1·0. Referring to (11) we now have for $\langle S \rangle_{\min}$

$$\langle S \rangle_{\min} = 450(\overline{W}_1/W^*)\eta D^2/a^4. \tag{17}$$

In view of the uncertainty in the numerical coefficients in (11) and (12), our ignorance of the actual distribution function for Ω^2, and the approximation introduced by (13), I shall adopt, as a rounded-off estimate of the mean stirring power required to double the current, the formula

$$\langle S \rangle_{\min} = 500\eta D^2/a^4. \tag{18}$$

I believe it unlikely that this is in error by more than 50 % either way.

For a spherical particle of radius 1 μm in water, with $D = 10^{-5}$ cm²/s, which might be typical for a fairly small molecule, the stirring-power density for doubling the rate of absorption is 0·5 W/cm³. Clearly that is violent stirring. Among other things, it would cause a temperature rise of more than 0·1 °C per second! For particles of radius 10 μm on the other hand, the modest investment of 50 μW of mechanical power per cm³ would suffice to double the rate of capture of diffusing molecules. Considering the

strong dependence on particle size, we can predict without much qualification that for particles smaller than a few microns effective stirring will be hardly feasible, while for particles larger than a few microns it will be easy. Of course that assumes values for η and D not grossly different from those in the foregoing example. But note that according to the Einstein–Smoluchowski relation the product ηD will tend to be a constant for a given solute molecule. Then the entire numerator in (18) will vary only as η^{-1}.

Our result can be applied to the coagulation of similar particles which are themselves diffusing, as in a colloidal suspension. Consider a suspension of isolated spherical particles (monomers) of radius b any two of which will stick together when they come in contact, forming a dimer. Beginning with monomers only, dimers will be formed at a rate determined by the concentration of monomers and their diffusion coefficient. To what extent can the rate of formation of dimers be increased by stirring the suspension?

The problem is essentially the same as the one we have just solved. The only difference is that, instead of a rapidly diffusing molecule and an absorbing particle so massive that its own Brownian motion could be neglected, we have here similar particles, whose Brownian motion *with respect to one another* is the effective diffusion process.

The diffusion coefficient for a particle of radius b in a fluid of viscosity η is $kT/6\pi\eta b$, but we must double this to obtain the value of D that characterizes the relative Brownian motion of two particles. We may think of the centre of one spherical particle as a diffusing molecule which is captured when it approaches within $2b$ of the centre of another particle. To adapt (18) to this problem, therefore, we replace D by $kT/3\pi\eta b$ and a by $2b$, obtaining

$$\langle S \rangle_{\min} = 0.35(kT)^2/\eta b^6. \tag{19}$$

In doing so we ignore the fact that, when the gap between two particles becomes small compared with the particle radius, the fluid dynamics must be somewhat different from the Stokes flow upon which the Einstein–Smoluchowski relation is based. In other words there will be in actuality some change in the effective diffusion constant D as two particles approach one another closely. Equation (19) is therefore a poorer approximation than (18), on which it is based. The important conclusion to be drawn, however, is very insensitive to the numerical coefficient in (19).

For particles of radius 10^{-5} cm in water (19) predicts that the mechanical stirring power required to double the initial rate of dimer formation will be 6 mW/cm³ or 6 W/l. That is a moderate, though by no means negligible, degree of agitation. On the other hand, particles of half that radius would require an investment of mechanical power 64 times greater, or about ½ h.p./l! Depositing energy at that rate in water by continuous stirring would present severe problems, including cavitation. I think that we may consider the requirement expressed in (19) prohibitive for particles of radius 0.5×10^{-5} cm. Thanks to the very strong dependence of stirring power on particle radius, we find a rather sharply defined limiting particle size below which effective stirring is not feasible. This limit lies somewhere between 0.5×10^{-5} and 1.0×10^{-5} cm.

Essentially the same conclusion, formulated less quantitatively, can be found in the classic papers of Smoluchowski (1916 *a, b*) on the coagulation of colloids. Smoluchowski considered the effect of stirring in connexion with some puzzling experimental results of H. Paine, for which he was able to give an elegant explanation. The crucial point, in Smoluchowski's words, is that 'The coagulating action of stirring increases at a quite extraordinary rate with particle size... In short, energetic stirring causes rapid coagula-

tion of microscopic particles, but leaves submicroscopic and amicroscopic particles unaffected.' (Smoluchowski 1916b, p. 599; my translation.)

In detail, Smoluchowski's analysis of the effect of fluid shear on the rate at which diffusing spheres come into contact was somewhat oversimplified and tended to overestimate the effect of a given rate of shearing deformation. If used to derive a relation like (19) his method would have given a considerably smaller numerical coefficient. He did not, in fact, remark on the quantitative relation between the stirring power dissipated in the fluid and the effectiveness of the motion in promoting coagulation. But he made the essential point and located the critical size somewhere between 'microscopic' and 'submicroscopic', a conclusion with which the one we have just reached appears consistent.

We have considered only spherical particles. A quantity strongly dependent on particle size must be expected to depend on particle shape. It would be interesting to know what relation corresponds to (19) for, say, rod-like particles. To derive it would be a formidable problem. For one thing, non-spherical particles will themselves tend to be oriented by the deformation of the fluid. Perhaps even more interesting would be the effect of stirring upon the coagulation of string-like objects. For such problems the methods of this paper appear to be hopelessly inadequate.

Note added in proof. It has been pointed out to me by G. Rybicki and W. Press that an axially symmetric deformation (e.g. polar flow inward with equatorial flow outward) could have served as well as the flow specified by (9) to establish a connexion between the deformation rate and the increase in diffusion current, and that the velocity field for such a flow around a sphere is obtainable from the formulae for a more general flow around a sphere derived in Batchelor (1967, p. 249). Although less convenient for the thermal experiment, the axially symmetric flow would be amenable to the relaxation method used to treat the problem of diffusion in a Stokes flow field as described in Berg & Purcell (1977). In that way values of $F(u)$ might be found by computation.

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