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Mass transfer from small particles suspended in turbulent fluid

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Small rigid spherical particles are suspended in fluid, and material is being transferred from the surface of each sphere by convection and diffusion. The fluid is in statistically steady turbulent motion maintained by some stirring device. It is assumed that the Péclet number of the flow around a particle is large compared with unity, so that a concentration boundary layer exists at the particle surface, and that the Reynolds number of the flow around the particle is sufficiently small for the velocity distribution near the particle surface to be given by the Stokes equations.

The flow around a particle is a superposition of (*a*) a streaming flow due to a translational motion of the particle relative to the fluid with a velocity proportional to the density difference, and (*b*) a flow due to the velocity gradient in the ambient fluid. An expression for the mean transfer rate which is asymptotically exact for large Péclet numbers is obtained in terms of statistical parameters of these two superposed flow fields. As a consequence of the partial suppression of convective transfer by particle rotation, the only relevant parameters are the mean translational velocity of the particle in the direction of the ambient vorticity vector and the mean ambient rate of extension in the direction of the ambient vorticity. The former is shown to be zero in common turbulent flow fields, and an expression for the latter in terms of the mean dissipation rate ϵ is obtained from the equilibrium theory of the small-scale components of the turbulence. The final non-dimensional expression for the transfer rate is $0{\cdot}55(a^2\epsilon^{\frac{1}{2}}/\kappa\nu^{\frac{1}{2}})^{\frac{1}{3}}$, where a is the particle radius. This is found to agree well with some previously published sets of data for values of $a^2\epsilon^{\frac{1}{2}}/\nu^{\frac{3}{2}}$ less than 10^2.

1. Introduction

Control and prediction of the rate at which mass of some diffusible quantity is transferred across a phase boundary are common requirements in chemical engineering. There are many situations in which a high rate of transfer is preferred, and this leads naturally to manufacture of one of the phases in the form of numerous small particles. The particles with their large interfacial area should of course remain in contact with the disperse phase, which we shall suppose to be fluid, and this is achieved when the particles are sufficiently small to remain in suspension in the fluid. The transfer rate can then be made even larger by stirring the fluid. The fluid motion in the stirred tanks used in laboratories and in industry is usually turbulent. The underlying basic problem in such a case is thus the determination of the average rate of transfer of mass across the surface of a small particle immersed in fluid whose motion relative to the particle is fluctuating and given in statistical terms. This is the problem to be addressed

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theoretically in the present paper, which is a sequel to a previous investigaton (Batchelor 1979) of the rate of mass transfer from a particle immersed in fluid with a velocity distribution relative to the particle which is *steady*.

Mathematically we shall need to consider the solution of the equation

$$\frac{\partial C}{\partial t} + \mathbf{u}.\nabla C = \kappa \nabla^2 C \tag{1.1}$$

for the concentration C in the fluid, with the inner boundary condition taken, as in the previous paper, to be

$$C = C_1 \text{ (const.)} \quad \text{at the particle surface } A.$$

Turbulent mixing times are relatively short, and so it is appropriate to take the outer boundary condition as

$$C \to C_0 \quad \text{far from the particle surface.}$$

In some practical set-ups the ambient concentration level might rise slowly with time, but we shall assume C_0 to be constant. The instantaneous rate of transfer from the particle surface is

$$Q = -\kappa \int_A \mathbf{n}.\nabla C \, dA,$$

of which the non-dimensional measure is the Nusselt number

$$N = \frac{Q}{4\pi a \kappa (C_1 - C_0)}, \tag{1.2}$$

where a is a particle dimension. The fluid velocity $\mathbf{u}$ in (1.1) depends on both the particle density and the turbulent flow, and will be described specifically in § 2.

We shall make the following assumptions about the conditions in the stirred tank.

(*a*) The particles are rigid and spherical, with radius a, and are far enough apart to have no hydrodynamic interaction. This is primarily an assumption of convenience, to make possible the analytical determination of the velocity and concentration distributions in the neighbourhood of a particle. It applies with fair accuracy to many practical cases.

(*b*) The Péclet number of the motion relative to a particle is large compared with unity. Péclet numbers in laboratory and industrial stirred tanks are in fact usually large, as we shall see later when comparing the theoretical result with the available data, as a consequence of the smallness of the molecular diffusivity of most solutes in liquid. Analytically the assumption is a great help, because it implies the existence of a thin concentration boundary layer at the particle surface.

(*c*) The Reynolds number of the motion in the neighbourhood of a particle is small compared with unity. One of the purposes of this assumption is to enable us to use the Stokes equations for the calculation of the velocity distribution near a particle. However, the velocity distribution, and hence also the rate of mass transfer from the particle surface, varies rather slowly with Reynolds number for values of this number

below unity,† and the mass transfer results obtained herein may be expected to apply approximately when the Reynolds number of the motion near a particle is of order unity. The restrictiveness of assumption (*c*) is discussed at the end of the paper.

Assumptions (*b*) and (*c*) together imply that the Prandtl or Schmidt number for the fluid and the diffusible quantity is large. Schmidt numbers for solutes in liquid are in fact typically large; for example $\nu/\kappa = 1{\cdot}0 \times 10^3$ for NaCl in water, $2{\cdot}6 \times 10^3$ for ammonium nitrate in ethanol, and 300–600 for anion exchange resins in aqueous acids. Note the implication of assumption (*c*) that the gradient of velocity is approximately constant across the thin concentration boundary layer.

(*d*) The turbulent motion in the fluid containing the particles is statistically steady, although not necessarily homogeneous. It follows that in most set-ups, including a stirred tank and flow through cylindrical tubes and flow in open cylindrical channels, a particle 'samples' different parts of the flow field in turn and the fluid velocity in the neighbourhood of a particle, and relative to it, is statistically steady.

Note that no assumption is being made about the relative density of the particles and the fluid, except of course that the particles must remain suspended in the fluid for a time sufficiently long to allow an appreciable transfer of mass between the two phases to occur.

The above assumptions are all fairly conventional, and do not specify a new problem. But hitherto no firm theoretical results have been put forward. Those who have been concerned with the reduction of observational data on the transfer from particles in turbulent fluid have usually looked for a match of the data with either one of two alternative power-law forms of the relation between the non-dimensional average mass transfer rate N and the particle Péclet number P. One of these relations, viz. $N \propto P^{\frac{1}{3}}$, has been regarded as suggested by the available asymptotic ($P \to \infty$) expression for the mass transfer rate for a particle held in a steady uniform stream (and if the velocity in the fluid in which the particle is immersed were steady and varied linearly with position, the transfer rate would still vary as $P^{\frac{1}{3}}$ – see Batchelor 1979). The other, viz. $N \propto P^{\frac{1}{2}}$, is a consequence of a surface-renewal model of the transfer mechanism according to which the transfer from the particle surface takes place by diffusion into stationary fluid for a certain time characteristic of the turbulent flow and then the surface layer is suddenly replaced by pure solvent and the diffusion begins again. The steady-rate relation is exact but is not directly applicable to a particle suspended in turbulent fluid, whereas the surface-renewal relation is derived from a very crude model; neither of the underlying concepts is satisfactory as a theoretical basis for the analysis of data.

In the following pages we shall see that the average rate of transfer from the surface of a particle immersed in turbulent fluid can be shown rigorously to be proportional to $P^{\frac{1}{3}}$ and that, rather remarkably for a problem involving random velocity fluctuations, the proportionality constant can be determined fully with the aid of the equilibrium

† Calculations by Ryskin & Fishbein (1976) show that, for a rigid sphere in steady translational motion with velocity U_0 through fluid at rest at infinity, the rate of mass transfer from the sphere at $U_0 a/\nu = 1$ is only 7 % greater than at zero Reynolds number, for a given large Péclet number. Another, less directly relevant, result obtained by Ryskin (1980) is that the extra rate of energy dissipation caused by the presence of a rigid sphere in an axisymmetric steady pure straining motion with axial rate of extension E is only about 1 % greater when $a^2E/\nu = 0{\cdot}5$ than at zero Reynolds number.

theory for the small-scale components of the turbulent flow and a knowledge of one parameter of the turbulence.

2. The fluid motion near a particle

The rate of transfer of mass from the particle surface is determined by the velocity distribution in the fluid near the particle. Only the fluid velocity relative to the particle is relevant. The fluid motion in the neighbourhood of the particle may be due partly to movement of the particle through the fluid under the action of an applied force, and partly to the existence of an *ambient* motion of the fluid (i.e. a motion of the fluid in the absence of the particle). These two sources make independent contributions to the flow field (although not to the mass transfer) when the Reynolds number of the local fluid motion is small.

Consider first the relative translational motion of the particle and the surrounding fluid. The gravitational force on a particle, after allowance for buoyancy, is

$$\tfrac{4}{3}\pi a^3(\rho_p - \rho_f)\,\mathbf{g},$$

where ρ_p and ρ_f are the density of the particle and the fluid respectively. Inasmuch as the element of fluid containing the particle may be accelerating, as it takes part in the turbulent motion in the tank, there is in addition an effective force on the particle relative to axes moving with this element which also is proportional to $\rho_p - \rho_f$. These two forces together, one of which is steady and one fluctuating, cause a translational motion of the particle relative to the fluid which is resisted by viscous stresses. Thus one contribution to the fluid motion near the particle, and relative to it, is the flow field due to the particle being held stationary in a uniform stream with velocity $-\mathbf{V}(t)$ say; and $|\mathbf{V}|$ is proportional to $\rho_p - \rho_f$. The disturbance velocity at position $\mathbf{X}$ in the fluid resulting from the presence of the rigid spherical particle with centre at $\mathbf{Y}$ is then the familiar solution of the Stokes equation:

$$\mathbf{u}^{(T)}(\mathbf{x}) = \mathbf{V}.\left\{\left(\frac{3a}{4r}+\frac{a^3}{4r^3}\right)\mathbf{I}+\left(\frac{3a}{4r}-\frac{3a^3}{4r^3}\right)\frac{\mathbf{xx}}{r^2}\right\}, \tag{2.1}$$

where $\mathbf{x} = \mathbf{X}-\mathbf{Y}$ and $|\mathbf{x}| = r$, the superscript (T) indicates translational motion, and $\mathbf{I}$ denotes the unit second-rank tensor.

Consider now the contribution to the fluid motion near the particle which is due to the ambient flow field and which exists even when $\rho_p = \rho_f$. The ambient fluid velocity $\mathbf{U}$ at point $\mathbf{X}$ in the neighbourhood of the instantaneous position $\mathbf{Y}$ of the particle centre may be represented approximately by the Taylor series

$$\mathbf{U}(\mathbf{X}) = \mathbf{U}(\mathbf{Y})+(\mathbf{X}-\mathbf{Y}).\{\nabla\mathbf{U}\}_{\mathbf{X}=\mathbf{Y}}+\ldots. \tag{2.2}$$

The statistical properties of the velocity gradient tensor $\nabla\mathbf{U}$ and the higher-order spatial derivatives are among the small-scale features of the turbulent motion, and so are determined by the two parameters ϵ and $\nu(=\mu/\rho_f)$, where ϵ is the local mean rate of dissipation of mechanical energy, according to the Kolmogoroff equilibrium theory. The ratio of two consecutive spatial derivatives is thus a length of order $(\nu^3/\epsilon)^{\frac{1}{4}}$, statistically speaking, and so for values of $|\mathbf{X}-\mathbf{Y}|$ which are a few times the particle radius a the ratio of the further unwritten terms on the right-hand side of (2.2) to the second term is of order $a\epsilon^{\frac{1}{4}}/\nu^{\frac{1}{4}}$. This ratio can also be written as $(a^2E/\nu)^{\frac{1}{4}}$, where E is

a measure of the mean local rate of extension in the ambient flow field, which is recognizable as the square root of a Reynolds number of the flow about a particle immersed in an ambient pure straining motion. The assumption of a small Reynolds number of the flow near the particle, which we have already made, thus implies that the particle dimension is small compared with the smallest eddy size in the turbulent flow (and equally that a^2/ν is small compared with the time scale of the small eddies) and that the fluid velocity in the ambient flow field is approximately a linear function of position.

The velocity gradient tensor can be decomposed into its symmetrical and unsymmetrical parts:

$$\nabla \mathbf{U} = \mathbf{E} + \boldsymbol{\Omega},$$

where the antisymmetric part $\boldsymbol{\Omega}$ represents a rigid-body rotation with angular velocity $\frac{1}{2}\boldsymbol{\omega}$ and $\boldsymbol{\omega}$ is the ambient vorticity. A couple-free rigid sphere tends to take up the same angular velocity as that in the ambient flow field, and the relaxation time for this adjustment may readily be shown to be $\rho_p a^2/\mu$, i.e. ρ_p/ρ_f times a^2/ν. But a^2/ν is small compared with the time scale of the small eddies when the Reynolds number of the flow about a particle is small, as already noted; and so when ρ_p/ρ_f is of order unity, as it is for liquid suspending media, the response to changes in the ambient vorticity is effectively instantaneous. Thus the particle rotates with the ambient fluid at all times.

On the other hand, a rigid sphere cannot follow the straining motion in the ambient flow field, and a disturbance motion is generated in the fluid. This disturbance velocity is determined by the instantaneous value of the symmetric rate-of-strain tensor $\mathbf{E}$, and is given (see Batchelor 1967, p. 249) by

$$\mathbf{u}^{(E)}(\mathbf{x}) = \mathbf{x}.\mathbf{E}.\left\{-\frac{a^5}{r^5}\mathbf{I} - \frac{5a^3}{2r^3}\left(1-\frac{a^2}{r^2}\right)\mathbf{xx}\right\}. \tag{2.3}$$

The complete expression for the fluid velocity in the neighbourhood of the particle, relative to the velocity of the particle centre, is thus

$$\mathbf{u}(\mathbf{x}) = -\mathbf{V} + \mathbf{u}^{(T)} + \boldsymbol{\Omega}.\mathbf{x} + \mathbf{x}.\mathbf{E} + \mathbf{u}^{(E)}, \tag{2.4}$$

where the two disturbance flow fields associated with the translational motion of the particle and the ambient extensional motion are given by (2.1) and (2.3) respectively.

If the Péclet number of the fluid motion about the particle is large, as we have assumed, the variations in concentration of the diffusible material occur mainly within a thin layer adjoining the particle surface. We are consequently interested in the form taken by the expression (2.4) at values of r such that $r-a \ll a$, viz.

$$\mathbf{u}(\mathbf{x}) \approx -\frac{3}{2}\frac{\xi}{a}\mathbf{V}.(\mathbf{I}-\mathbf{ll}) + (a+\xi)\boldsymbol{\Omega}.\mathbf{l} + 5\xi\mathbf{l}.\mathbf{E}.(\mathbf{I}-\mathbf{ll}) + O(\xi^2), \tag{2.5}$$

where $\xi = r-a$ and $\mathbf{l} = \mathbf{x}/r$. The rate of transfer from the particle surface must now be determined by solving equation (1.1) for C within the concentration boundary layer, with the fluid velocity $\mathbf{u}$ given by (2.5). The parameters $\mathbf{V}$, $\mathbf{E}$ and $\boldsymbol{\Omega}$ are all stationary random functions of time, with statistical properties which will be considered later.

3. The partial suppression of transfer by particle rotation

The mechanism by which convection greatly increases the transfer rate at large Péclet numbers is evident: fluid elements adjoining the particle surface receive solute material by diffusion from the particle and move round the surface towards some stagnation point where they move away from the surface, their place being taken by other fluid elements which come near to the surface at another stagnation point. It is essential to this process that fluid elements come near to the particle surface, remain near to it for a time, and then move away. If fluid elements moved round the particle in closed paths the effect of convection would be much weaker; and if all fluid elements in the neighbourhood of a particle moved in closed paths the Nusselt number would tend to a constant, as $P \to \infty$, of the same order of magnitude as in the case of pure diffusion. Now it was shown in the previous study of transfer from a particle in a *steady* linear ambient velocity field (Batchelor 1979) that, when the ambient vorticity is non-zero, the paths of fluid elements near the particle surface are nearly closed, being slightly irregular helices of very small pitch, and that there is a corresponding suppression of the convective transfer associated with some of the components of the ambient rate-of-strain tensor. The ambient straining motion can always be decomposed into an axisymmetric straining with the axis of symmetry in the direction of the ambient vorticity and another straining motion with zero rate of extension in the direction of the ambient vorticity; and only the former causes fluid elements to approach the particle and later move away from it, with a correspondingly large contribution to the transfer rate of order $P^{\frac{1}{3}}$. It is not difficult to see by similar arguments that, if the ambient flow field is a super-position of a steady uniform stream and a steady rigid-body rotation, only the component of the stream velocity in the direction of the ambient vorticity leads to the paths of fluid elements being open and to a transfer rate of order $P^{\frac{1}{2}}$.

It is important now to enquire whether there is a similar partial suppression of convective transfer due to the existence of ambient vorticity in the present case in which the ambient flow parameters $\mathbf{V}$, $\mathbf{E}$ and $\boldsymbol{\Omega}$ all vary with time. To this end we inspect the form taken by the fluid velocity near the particle surface when the tensors $\mathbf{I}$, $\mathbf{V}$, $\mathbf{E}$ and $\boldsymbol{\Omega}$ are expressed in terms of components in a Cartesian co-ordinate system with the x_3 axis parallel to the ambient vorticity and the x_1 axis in an arbitrary orthogonal direction. With the further introduction of spherical polar co-ordinates r, θ, ϕ such that $\theta = 0$ in the direction of the ambient vorticity and $\theta = \frac{1}{2}\pi$, $\phi = 0$ in the direction of the x_1 axis, we find from (2.5)

$$\begin{aligned} u_\theta &= (u_1 \cos\phi + u_2 \sin\phi)\cos\theta - u_3 \sin\theta \\ &= \frac{3}{2}\frac{\xi}{a}\{V_3 \sin\theta - (V_1 \cos\phi + V_2 \sin\phi)\cos\theta\} \\ &\quad + 5\xi\{-\tfrac{3}{4}E_{33}\sin 2\theta + \tfrac{1}{4}\sin 2\theta\,(E_{11}\cos 2\phi - E_{22}\cos 2\phi + 2E_{12}\sin 2\phi) \\ &\quad + \cos 2\theta(E_{31}\cos\phi + E_{23}\sin\phi)\}, \end{aligned} \tag{3.1}$$

$$\begin{aligned} u_\phi &= u_2 \cos\phi - u_1 \sin\phi \\ &= \frac{3}{2}\frac{\xi}{a}(V_1 \sin\phi - V_2 \cos\phi) + \Omega(a+\xi)\sin\theta + 5\xi\{\tfrac{1}{2}(E_{22} - E_{11})\sin\theta \sin 2\phi \\ &\quad + E_{12}\sin\theta\cos 2\phi + \cos\theta\,(E_{23}\cos\phi - E_{31}\sin\phi)\}, \end{aligned} \tag{3.2}$$

where $\Omega(=\frac{1}{2}|\boldsymbol{\omega}|)$ is the angular speed of rotation of the particle and the ambient fluid about the x_3 axis. The component u_r (which is of order ξ^2) may be found from the mass-conservation relation

$$u_r = \frac{\xi}{2a\sin\theta}\left\{-\frac{\partial(u_\theta \sin\theta)}{\partial\theta} - \frac{\partial u_\phi}{\partial\phi}\right\}. \tag{3.3}$$

At points within the concentration boundary layer, where $\xi/a \ll 1$, the fluid velocity is a uniform azimuthal rotation with a superimposed small fluctuation. The mass transfer will be determined, to leading order in P, by the net drift of fluid elements in the polar direction, because this drift motion carries solute round the particle surface and eventually away from the surface at either the equator or one of the poles (depending on the sense of the drift). In the case of a steady ambient flow field investigated in the previous paper, this poleward drift was obtained by averaging u_θ over one rotation of a fluid element about the x_3 axis; and none of the terms in (3.1) which are sinusoidal in ϕ or 2ϕ survived this averaging. In the present case V_i, E_{ij} and Ω are functions of time t, and fluctuate over a time-scale Ω^{-1}, so the net drift of a material fluid element must be determined by replacing ϕ by $\phi - \Omega t$ in (3.1) and averaging over a time long compared with Ω^{-1}. But the average of terms like $V_i \sin(\phi - \Omega t)$ and $E_{ij}\sin(\phi - \Omega t)$ over a long time is zero when V_i, E_{ij} and Ω are stationary random functions of t. It follows that the average poleward velocity of a material fluid element near the particle surface is

$$\frac{3}{2}\frac{\xi}{a}\langle V_3\rangle \sin\theta - \tfrac{15}{4}\xi\langle E_{33}\rangle \sin 2\theta, \tag{3.4}$$

where the angle brackets denote an average over a time long compared with Ω^{-1}.

It appears therefore that, relative to the particle surface, the mean motion of fluid elements in the concentration boundary layer is a poleward drift which is exactly the same as if the particle were stationary and immersed in a steady ambient flow consisting of a uniform stream with velocity $-V_3$ in the direction of the x_3 axis (i.e. with velocity $-\boldsymbol{\omega}.\mathbf{V}\boldsymbol{\omega}/\boldsymbol{\omega}^2$) and a pure straining motion with symmetry about the x_3 axis and rate of extension $E_{33}(=\boldsymbol{\omega}.\mathbf{E}.\boldsymbol{\omega}/\boldsymbol{\omega}^2)$ in the direction of that axis. All other components of $\mathbf{V}$ and $\mathbf{E}$ simply cause oscillations in the motion of a fluid element with zero mean.

The argument to show that only these components V_3 and E_{33} cause the mass transfer rate to be of order $P^{\frac{1}{3}}$ when $P \gg 1$ is now similar to that given in the previous paper for the case of a steady ambient velocity distribution. For the purposes of this argument we introduce axes which rotate with the particle and the ambient fluid. The new velocity components $\overset{*}{u}_\theta$ and $\overset{*}{u}_\phi$ are obtained from (3.1) and (3.2) by replacing ϕ by $\phi - \Omega t$ and by deleting the second term on the right-hand side of (3.2). We write

$$C = \langle C\rangle + C', \quad \overset{*}{\mathbf{u}} = \langle\overset{*}{\mathbf{u}}\rangle + \overset{*}{\mathbf{u}}',$$

where the angle brackets again denote an average over a time long compared with Ω^{-1}, $\langle\overset{*}{u}_\theta\rangle$ is given by (3.4), $\langle\overset{*}{u}_\phi\rangle$ is zero, and C' and $\overset{*}{\mathbf{u}}'$ have zero mean. Now the boundary-layer form of the equation for C is

$$\frac{\partial C}{\partial t} + \overset{*}{\mathbf{u}}.\nabla C = \kappa\frac{\partial^2 C}{\partial\xi^2}, \tag{3.5}$$

and taking a mean of all terms in this equation gives

$$\langle \overset{*}{\mathbf{u}} \rangle . \nabla \langle C \rangle + \langle \overset{*}{\mathbf{u}}' . \nabla C' \rangle = \kappa \frac{\partial^2 \langle C \rangle}{\partial \xi^2}. \tag{3.6}$$

The corresponding equation for the concentration fluctuation C' is found by subtracting (3.6) from (3.5) to be

$$\frac{\partial C'}{\partial t} + \langle \overset{*}{\mathbf{u}} \rangle . \nabla C' + \overset{*}{\mathbf{u}}' . \nabla C' - \langle \overset{*}{\mathbf{u}}' . \nabla C' \rangle - \kappa \frac{\partial^2 C'}{\partial \xi^2} = - \overset{*}{\mathbf{u}}' . \nabla \langle C \rangle. \tag{3.7}$$

We propose to show that the solution of this equation satisfying the boundary conditions

$$C' = 0 \quad \text{at} \quad \xi = 0 \quad (\text{where} \quad C = C_1),$$

$$C' \to 0 \quad \text{as} \quad \xi \to \infty \quad (\text{where} \quad C \to C_0),$$

is such that $|C'/(C_1 - C_0)| \ll 1$. Since C' vanishes outside the concentration boundary layer, the appropriate normal position variable in (3.7) is ξ/δ, where δ is a measure of the thickness of the boundary layer (and $\delta/a = O(P^{-\frac{1}{3}})$). We therefore write (3.7) as

$$\frac{\Omega}{E} \frac{\partial C'}{\partial \tau} + \frac{1}{E} (\langle \overset{*}{\mathbf{u}} \rangle . \nabla C' + \overset{*}{\mathbf{u}}' . \nabla C' - \langle \overset{*}{\mathbf{u}}' . \nabla C' \rangle) - \frac{a^2}{\delta^2} \frac{1}{P} \frac{\partial^2 C'}{\partial (\xi/\delta)^2} = - \frac{\overset{*}{\mathbf{u}}' . \nabla \langle C \rangle}{E}, \tag{3.8}$$

where $\tau = \Omega t$, E is a measure of the rate of strain in the boundary layer (so that ξE is a measure of the fluid velocity relative to the particle surface), and $P = a^2 E/\kappa$. Now $\langle \overset{*}{\mathbf{u}} \rangle . \nabla C'/E$ and $\overset{*}{\mathbf{u}}' . \nabla C'/E$ are both of order $C'\delta/a$ at points within the boundary layer, showing that when $P \gg 1$ the first term on the left-hand side of (3.8) is dominant (provided that Ω/E is not small) and that (3.8) reduces approximately to

$$\frac{\Omega}{E(C_1 - C_0)} \frac{\partial C'}{\partial \tau} = - \frac{\overset{*}{\mathbf{u}}' . \nabla \langle C \rangle}{E(C_1 - C_0)} = O\left(\frac{\delta}{a}\right). \tag{3.9}$$

The integration with respect to τ can be carried out explicitly (since $\overset{*}{\mathbf{u}}'$ is sinusoidal in τ), giving C' in terms of $\langle C \rangle$, but it is sufficient to note that $C'/(C_1 - C_0)$ is small, and of order $P^{-\frac{1}{3}}$.

Thus to leading order in P the concentration and its time-mean are equal and satisfy the equation

$$\langle \overset{*}{u}_r \rangle \frac{\partial \langle C \rangle}{\partial \xi} + \frac{\langle \overset{*}{u}_\theta \rangle}{a} \frac{\partial \langle C \rangle}{\partial \theta} = \kappa \frac{\partial^2 \langle C \rangle}{\partial \xi^2} \tag{3.10}$$

obtained by dropping the term containing C' in (3.6). The velocity components in this equation are given by

$$\langle \overset{*}{u}_\theta \rangle = \frac{3}{2} \frac{\xi}{a} \langle V_3 \rangle \sin\theta - \tfrac{15}{4} \xi \langle E_{33} \rangle \sin 2\theta, \tag{3.11}$$

with $\langle \overset{*}{u}_r \rangle$ following from the starred and averaged version of (3.3) (with $\langle \overset{*}{u}_\phi \rangle = 0$). It appears therefore that no leading order in P the mean concentration, and so also the mean rate of transfer from the particle, is the same as in the case of a stationary spherical rigid particle immersed in ambient flow consisting of a uniform stream with steady velocity $-\langle V_3 \rangle$ in the direction of the x_3 axis and a steady pure straining motion which is axisymmetric about the x_3 axis and has rate of extension $\langle E_{33} \rangle$ in the direction

of that axis. The rotation of the particle and the ambient fluid has the effect of suppressing the convective transport due to all components of the streaming and straining ambient motions except V_3 and E_{33} and also that due to fluctuations in these two quantities.

4. The formal expression for the mean transfer rate

An explicit expression for the mean rate of transfer from the surface of the particle may now be obtained from the above prescription by using results available for steady ambient flow with axial symmetry and described in the previous paper (Batchelor 1979). It may be shown, by the method developed by Levich (1962) for cases of steady flow over stationary particle surfaces with large Péclet number and large Prandtl (or Schmidt) number, that the rate of mass transfer from the part of the surface of a spherical particle between the polar angles $\theta = \theta_1$ and $\theta = \theta_2$ bounding a region of one-signed tangential stress is

$$Q = 1{\cdot}616\pi\kappa^{\frac{2}{3}}a^{\frac{5}{3}}(C_1 - C_0)\left\{\int_{\theta_1}^{\theta_2} \sin^{\frac{3}{2}}\theta\, F^{\frac{1}{2}}\, d\theta\right\}^{\frac{2}{3}}, \tag{4.1}$$

where $\mu F(\theta)$ is the tangential stress in the polar direction at the particle surface.

In the case of the steady axisymmetric ambient flow field represented by (3.11), we have

$$F(\theta) = \frac{3}{2}\frac{\langle V_3\rangle}{a}\sin\theta - \tfrac{15}{4}\langle E_{33}\rangle \sin 2\theta. \tag{4.2}$$

The tangential stress is one-signed between $\theta = 0$ and $\theta = \pi$ if $|\beta| \leqslant 1$, where

$$\beta = 5a\langle E_{33}\rangle/\langle V_3\rangle,$$

so the rate of transfer across the whole particle surface is given in this case by (4.1) with $\theta_1 = 0$, $\theta_2 = \pi$. On the other hand, if $|\beta| > 1$ the tangential stress changes sign at $\theta = \cos^{-1}\beta^{-1}$ and the total transfer rate is the sum of two expressions like (4.1) in one of which $\theta_1 = 0$, $\theta_2 = \cos^{-1}\beta^{-1}$ and in the other of which $\theta_1 = \cos^{-1}\beta^{-1}, \theta_2 = \pi$. The total transfer rate is evidently a function of β, and may be written conveniently as

$$N = 0{\cdot}404L(\beta)\left\{\frac{a(\frac{9}{4}\langle V_3\rangle^2 + \frac{225}{4}a^2\langle E_{33}\rangle^2)^{\frac{1}{2}}}{\kappa}\right\}^{\frac{1}{3}}, \tag{4.3}$$

where L is a dimensionless function of β to be found by evaluating numerically integrals like the one in (4.1). It was pointed out in the previous paper that the known values of L for $|\beta| = 0$, 1 and ∞ suggest a range of variation of L of no more than 14 per cent. We shall be concerned especially with the particular case $\langle V_3\rangle = 0$, corresponding to $|\beta| \to \infty$, for which $L = 1{\cdot}225$ and

$$N = 0{\cdot}968\left(\frac{a^2|\langle E_{33}\rangle|}{\kappa}\right)^{\frac{1}{3}}, \tag{4.4}$$

which is the result for steady axisymmetric ambient pure straining motion found first by Gupalo & Ryazantzev (1972). At the other extreme, $|\beta| = 0$, the result is $L = 1{\cdot}351$ and

$$N = 0{\cdot}625\left(\frac{a|\langle V_3\rangle|}{\kappa}\right)^{\frac{1}{3}}, \tag{4.5}$$

as found first by Levich (1962).

Further progress with the determination of the mean transfer rate for a particle suspended in turbulent fluid thus requires an investigation of the values of $\langle V_3 \rangle$ and $\langle E_{33} \rangle$. These mean values depend on the properties of the turbulence and, in the case of $\langle V_3 \rangle$, on the excess density of the particle. The x_3 axis, it will be recalled, is in the direction of the instantaneous ambient vorticity, and since these particular axes have served their purpose we now change to the more general notation

$$V_3 = \frac{\mathbf{V}.\boldsymbol{\omega}}{|\boldsymbol{\omega}|}, \quad = V_\omega \text{ say, and } E_{33} = \frac{\boldsymbol{\omega}.\mathbf{E}.\boldsymbol{\omega}}{|\boldsymbol{\omega}|^2}, \quad = E_\omega \text{ say.}$$

5. The value of $\langle V_\omega \rangle$

The translational motion of the particle relative to the fluid results from the action of the external gravitational force on the excess density of the particle and the action of the effective force due to acceleration of the element of fluid in which the particle is immersed. Now the local vorticity in a turbulent motion is associated with the small eddies and the statistical distribution of the direction of the vorticity vector $\boldsymbol{\omega}$ is isotropic. It follows that the mean value of the component of the vertical fall velocity of the particle due to gravity in the direction of the local ambient vorticity is zero. The contribution to $\mathbf{V}$ due to acceleration of the fluid element containing the particle likewise has zero correlation with $\boldsymbol{\omega}$, because the mean value $\langle \boldsymbol{\omega}.(D\mathbf{U}/Dt) \rangle$ would not otherwise have the statistical invariance to reflexion of the axes of reference that is usually found experimentally to accompany isotropy of the small-scale components of the turbulence. Hence

$$\langle V_\omega \rangle = 0.$$

This result leads us to the conclusion that translational motion of the particle relative to the fluid – often referred to as particle 'slip' – has no effect on the mass transfer rate, to leading order in the (large) Péclet number. Bearing in mind the mechanism of suppression of convective transfer by particle rotation, this conclusion is not implausible, but it nevertheless has some strange consequences. For instance, if particles are falling under gravity with speed U_0, the effect of gentle turbulent stirring of the fluid is to *decrease* the average rate of mass transfer from a particle because the expression for N changes from (4.5) (in which $\langle V_3 \rangle$ is replaced by the steady fall speed) with no stirring to (4.4) as soon as the r.m.s. vorticity in the stirring motion is of order $U_0 P^{-\frac{1}{3}}/a$, where $P = aU_0/\kappa$; of course further increase of the intensity of the straining motion leads to indefinite increase of the transfer rate according to (4.4).

As noted earlier the relative translational velocity of a particle is proportional to its excess density. The above conclusion is thus equivalent to the mean mass transfer rate being independent of the excess density ratio $(\rho_p - \rho_f)/\rho_f$, to leading order in P. This is not inconsistent with the body of data obtained from stirred tanks by chemical engineers. After a careful survey of data on mass transfer from approximately spherical particles obtained in many laboratory investigations by themselves and previous workers, all of which referred to large Péclet number although in some cases the particle Reynolds number was smaller than unity and in some cases larger, Levins & Glastonbury (1972) concluded that 'the effect of particle density on the mass transfer coefficient is not generally large and can be ignored with little error in many

cases'. These authors also present data showing that the effect of quite a large density difference, as in the case of iron or copper particles in liquid, is to increase the mass transfer coefficient by a small but not negligible amount (see figure 17 of their paper). This might correspond to the density difference entering the theoretical expression for N in the departure from the asymptotic form at large P; the asymptotic form is of order $P^{\frac{1}{3}}$, and the fact that our neglected concentration fluctuation $C'/(C_1 - C_0)$ is of order $P^{-\frac{1}{3}}$ suggests that the relative error in the expression for N is of order $P^{-\frac{1}{3}}$, giving an absolute error which is independent of P and which might be numerically significant in certain cases.

6. The value of $\langle E_\omega \rangle$

The quantity $\langle E_\omega \rangle$ is a parameter of the turbulent motion in which the particle is immersed, and is independent of the properties of the particle. It is determined in particular by the small-scale properties of the turbulence. Statistical isotropy is one of these properties, but this has no direct consequences for the value of $\langle E_\omega \rangle$ since it is by definition invariant under rotation and reflexion of the axes of reference. $\langle E_\omega \rangle$ plays a familiar and important role in theoretical studies of turbulence as the mean rate of extension of vortex lines. It may be shown that for turbulence which is locally homogeneous and isotropic (see Batchelor 1953)

$$\langle E_\omega \rangle = \frac{7}{6\sqrt{15}} S \left(\frac{\epsilon}{\nu}\right)^{\frac{1}{2}}, \tag{6.1}$$

where S is minus the 'skewness factor' of the rate of extension in a fixed direction (that is, minus the mean cube of this rate of extension divided by the $\frac{3}{2}$ power of its mean square) and ϵ is the mean rate of dissipation per unit mass of fluid.

According to Kolmogoroff's local equilibrium theory S is an absolute constant for turbulent motion at high Reynolds number, but the theory has been modified in recent years (see Monin & Yaglom 1975) and the current view is that it is a very slowly increasing function of the Reynolds number. The measurements of S made by a number of experimenters have been compared recently by Tavoularis, Bennett & Corrsin (1978). These measurements, which are reproduced here in figure 1, show values of S ranging from 0·3 to 1·0 over a very wide range of Reynolds numbers of the turbulence. The Reynolds number referred to in figure 1, viz. R_λ ($= u'\lambda/\nu$, where u'^2 is the m.s. fluctuation in one velocity component – or the average of all three if they differ – and λ is the dissipation length parameter defined by $(15\nu u'^2/\epsilon)^{\frac{1}{2}}$), is the one commonly used by experimenters. Values of R_λ for laboratory stirred tanks will certainly be less than 10^4 and will often lie in the range 10^2–10^3. A value of S near 0·6 seems to be appropriate for the range of turbulence Reynolds numbers relevant here, and since we shall later need to take the $\frac{1}{3}$-power of S the consequences of some error are not very serious.

With S chosen to be 0·60 we have

$$\langle E_\omega \rangle = 0{\cdot}18(\epsilon/\nu)^{\frac{1}{2}}. \tag{6.2}$$

Another exact relation for isotropic turbulence is that the rate of extension in a fixed direction has zero mean and root mean square equal to $0{\cdot}26(\epsilon/\nu)^{\frac{1}{2}}$. Comparison with (6.2) shows that the mean rate of extension in the direction of the local vortex line is

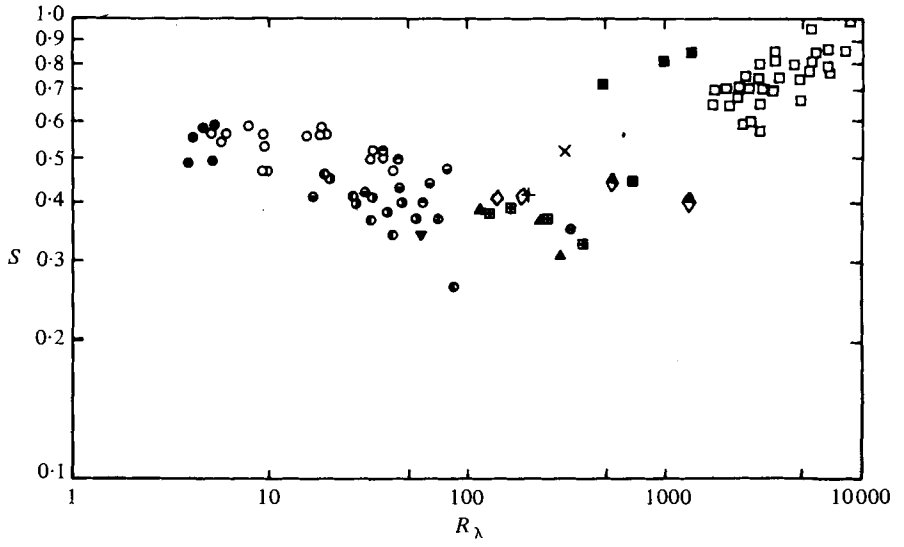

FIGURE 1. Measurements of the skewness factor of the rate of extension in a fixed direction in various turbulent flow systems and by various authors (from Tavoularis, Bennett & Corrsin 1978, who give details of the sources of the measurements). $S = -\langle(\partial u/\partial x)^3\rangle/\langle(\partial u/\partial x)^2\rangle^{\frac{3}{2}}$ and $R_\lambda = u'\lambda/\nu$.

quite close in magnitude to the r.m.s. rate of extension in a fixed direction. The reason for this is that, effects of viscosity aside, the direction of the vortex line is always being turned towards the direction in which the rate of extension is greatest, so that the rate of extension in the direction of the local vortex line is a biased sample of rates of extension with a preference for large positive values.

7. The rate of mass transfer from particles

We may return now to the expression (4.3) for N and substitute the above results for $\langle V_\omega\rangle$ and $\langle E_\omega\rangle$. Since $\langle V_\omega\rangle = 0$, the relation (4.4) is applicable, whence

$$N = 0{\cdot}55\left(\frac{a^2\epsilon^{\frac{1}{2}}}{\kappa\nu^{\frac{1}{2}}}\right)^{\frac{1}{3}}. \tag{7.1}$$

This expression for the mean rate of mass transfer from a spherical particle in fluid in statistically steady (but not necessarily homogenous) turbulent motion is asymptotically exact, for large values of the Péclet number $a^2\epsilon^{\frac{1}{2}}/\kappa\nu^{\frac{1}{2}}$, aside from the small error involved in the use of the empirical constant value of S. The absence of any undetermined constants from (7.1) is unusual for a theoretical relation representing one of the effects of turbulent motion.

Experiments to test (7.1) directly have not been made, but some comparison with data is possible. A number of empirical relations between the average transfer rate and parameters relevant to turbulent stirring of a suspension of particles have been put forward in the chemical engineering literature. It has been found in particular that the power input due to the stirring is the most relevant dynamic factor. One of the most extensive and systematic sets of observations has been made by Levins & Glastonbury (1972). They found that 357 experimental results for the transfer from effectively

neutrally buoyant spherical particles were 'correlated' by a relation which can be written as

$$N = 1 + 0{\cdot}41 \left(\frac{a^2 \overset{*}{\epsilon}{}^{\frac{1}{2}}}{\kappa \nu^{\frac{1}{2}}}\right)^{0{\cdot}41} \left(\frac{\kappa}{\nu}\right)^{0{\cdot}05} \left(\frac{D_S}{D_T}\right)^{0{\cdot}17}, \tag{7.2}$$

where D_S is the diameter of the stirring device and D_T is the diameter of the containing tank. In (7.2) $\overset{*}{\epsilon}$ is the total power input divided by the mass of fluid in the tank whereas in (7.1) ϵ denotes the time average of the local dissipation rate sampled by a moving particle. The turbulence in a stirred tank is not homogeneous, and if a particle does not sample uniformly all parts of the tank ϵ and $\overset{*}{\epsilon}$ might differ a little. The appearance of the parameters D_S and D_T in (7.2) may be a consequence of the non-uniformity of the sampling of different parts of the tank being a function of D_S/D_T. However, $(D_S/D_T)^{0{\cdot}17}$ was not different from unity by more than 20 per cent in any one of the experiments concerned and can be ignored in a broad comparison of (7.2) with theory. The particle Péclet number $a^2 \overset{*}{\epsilon}{}^{\frac{1}{2}}/\kappa\nu^{\frac{1}{2}}$ was large in all these experiments. The particle Reynolds number $a^2 \overset{*}{\epsilon}{}^{\frac{1}{2}}/\nu^{\frac{1}{2}}$ varied from about 0·06 to 120, and so did not always have the small value assumed in our theory. The agreement between the theory and the empirical relation is nevertheless fair over the whole of the range covered by the experiments.

In order to be able to compare their results with those of some previous investigators, Levins & Glastonbury also obtained from their data the following correlation, which *assumes* that $N - 1 \propto \kappa^{-\frac{1}{3}}$ and ignores any dependence on D_S/D_T:

$$(N-1)\left(\frac{\kappa}{\nu}\right)^{\frac{1}{3}} = 0{\cdot}44 \left(\frac{a^2 \overset{*}{\epsilon}{}^{\frac{1}{2}}}{\nu^{\frac{1}{2}}}\right)^{0{\cdot}41}. \tag{7.3}$$

The multiplying constant in (7.3) is a little smaller than that in (7.1) and the power of the Reynolds number $a^2 \overset{*}{\epsilon}{}^{\frac{1}{2}}/\nu^{\frac{1}{2}}$ in (7.3) is a little larger than that in (7.1). These two differences partially cancel, and they do so exactly (ignoring now any difference between ϵ and $\overset{*}{\epsilon}$) when $a^2\epsilon^{\frac{1}{2}}/\nu^{\frac{1}{2}} = 16$, which lies within the range of values covered in the experiments. Levins & Glastonbury noted that (7.3) agrees reasonably well with the earlier observations of Harriott (1962), which also referred to large Péclet numbers and a range of Reynolds numbers, some smaller than unity and some larger. Figure 2 shows the theoretical relation (7.1) (with the small difference between N and $N-1$ ignored), the empirical relation (7.3) that represents Levins & Glastonbury's data, and points representing Harriott's data (as reproduced by Levins & Glastonbury in their figure 16); ϵ and $\overset{*}{\epsilon}$ have here been regarded as equal. The agreement of (7.1) with Harriott's data is a little better than with Levins & Glastonbury's empirical relation, and is as close as the scatter of the data allows.

The comparison with data in figure 2 suggests that the formula (7.1) for the transfer rate is valid at values of $a^2\epsilon^{\frac{1}{2}}/\nu^{\frac{1}{2}}$ as large as 10^2. This calls for some explanation, since the theoretical relation is based on the formal assumption of small Reynolds number of the flow around a particle. It should first be noted, however, that a more significant choice of the Reynolds number of the extensional flow that is responsible for the mass transfer is $a^2\langle E_\omega\rangle/\nu$, which is smaller than $a^2\epsilon^{\frac{1}{2}}/\nu^{\frac{1}{2}}$ by a factor 0·18.

The assumption of small Reynolds number of the flow around a particle was used in two different ways in the foregoing theory. Firstly, it allowed us to calculate the velocity distribution from the Stokes equations. It was remarked in the introduction

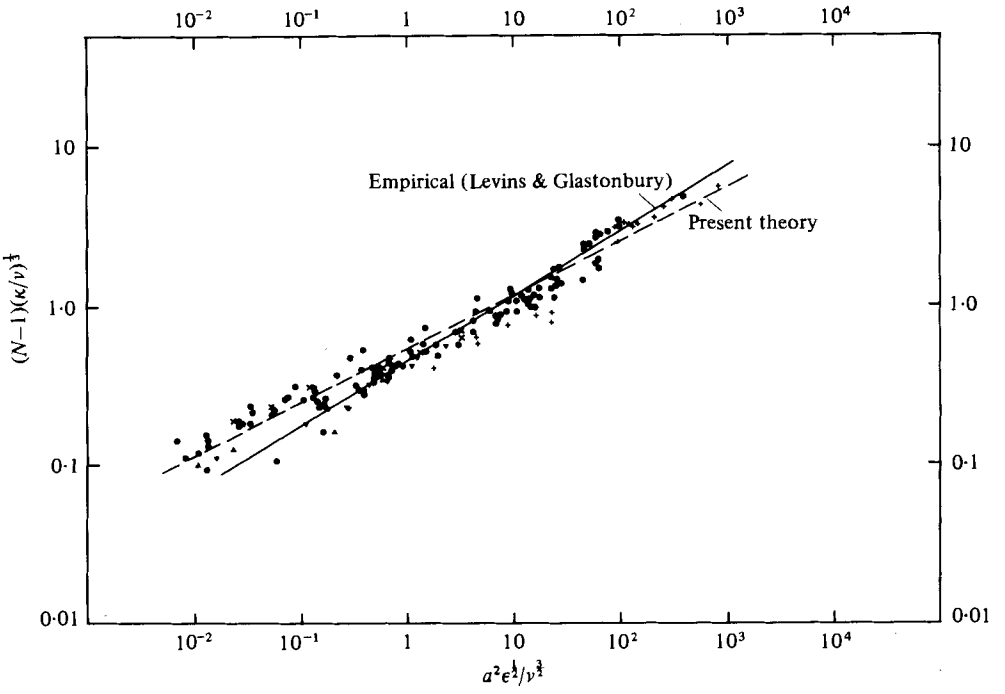

FIGURE 2. The Nusselt number N as a function of the particle Reynolds number $a^2\epsilon^{\frac{1}{3}}/\nu^{\frac{2}{3}}$. The full line is the empirical relation (7.3) found by Levins & Glastonbury (1972) to fit their own data. The points represent data obtained by Harriott (1962). The broken line is the theoretical relation (7.1).

Harriott's data	ν/κ
● ion exchange in water	$0{\cdot}52 \times 10^3$
▲ ion exchange in 0·21 % methocel	3·67
▼ ion exchange in 0·35 % methocel	11·3
× ion exchange in glycerine	108
+ benzoic acid in water	1·3

that the distribution of stress over the surface of a particle (which is the only relevant aspect of the flow field) is unlikely to depart significantly from that found from the Stokes equations until the Reynolds number exceeds unity. We know now that the type of flow around the particle that is relevant is that due to a particle in a linear ambient velocity distribution, rather than that due to translational motion of the particle through the fluid, and this strengthens the expectation of insensitivity of the calculated stress distribution to the particle Reynolds number (essentially because the distortion of the streamlines due to the presence of the sphere is less in a pure straining motion). Secondly, the assumption of small Reynolds number allowed us to regard the ambient velocity gradient as uniform over the region occupied by a particle. It is known from observations of turbulent flow that the wavelength, in a Fourier analysis of the velocity distribution, at which the maximum contribution to the mean-square velocity gradient occurs is approximately $40(\nu^3/\epsilon)^{\frac{1}{4}}$ (corresponding to a wave-number $0{\cdot}15(\epsilon/\nu^3)^{\frac{1}{4}}$; and so, when $a^2\epsilon^{\frac{1}{3}}/\nu^{\frac{2}{3}} = 10^2$, the particle radius is about one-quarter of this wavelength. However this is not seriously in conflict with the

assumption of a uniform ambient velocity gradient over the region occupied by a particle because virtually the whole mean-square velocity gradient is contributed by Fourier components with wavelengths greater than $40(\nu^3/\epsilon)^{\frac{1}{4}}$ (the velocity-gradient spectral density increases as the one-third power of the wavenumber throughout the inertial sub-range, and then falls off to zero sharply at wavenumbers above $0{\cdot}15(\epsilon/\nu^3)^{\frac{1}{4}}$).

It is thus not surprising that the theory remains fairly accurate at values of $a^2\epsilon^{\frac{1}{3}}/\nu^{\frac{2}{3}}$ up to about 10^2. The small number of points in figure 2 representing Harriott's measurements at values of $a^2\epsilon^{\frac{1}{3}}/\nu^{\frac{2}{3}}$ above 10^2 suggest that the transfer rate then takes larger values than those given by the theoretical relation (7.1).

REFERENCES

Batchelor, G. K. 1953 *The Theory of Homogenous Turbulence.* Cambridge University Press.

Batchelor, G. K. 1967 *An Introduction to Fluid Dynamics.* Cambridge University Press.

Batchelor, G. K. 1979 Mass transfer from a particle suspended in fluid with a steady linear ambient velocity distribution. *J. Fluid Mech.* **95**, 369.

Gupalo, Y. P. & Ryazantzev, Y. S. 1972 Diffusion on a particle in the shear flow of a viscous fluid. Approximation of the diffusion boundary layer. *Appl. Math. Mech.* (*P.M.M.*) **36**, 475.

Harriott, P. 1962 Mass transfer to particles. Part I. Suspended in agitated tanks. *Amer. Inst. Chem. Eng. J.* **8**, 93.

Levich, V. G. 1962 *Physicochemical Hydrodynamics.* Prentice-Hall.

Levins, D. M. & Glastonbury, J. R. 1972 Particle–liquid hydrodynamics and mass transfer in a stirred vessel. Part II. Mass transfer. *Trans. Inst. Chem. Eng.* **50**, 132.

Monin, A. S. & Yaglom, A. M. 1975 *Statistical Fluid Mechanics*, vol. 2. Massachusetts Institute of Technology Press.

Ryskin, G. 1980 The extensional viscosity of a dilute suspension of spherical particles at intermediate microscale Reynolds numbers. *J. Fluid Mech.* (in the press).

Ryskin, G. M. & Fishbein, G. A. 1976 Extrinsic problem of mass exchange for a solid sphere and a drop at high Péclet numbers and $Re \leqslant 100$. *J. Engng Phys.* **30**, 49.

Tavoularis, S., Bennett, J. C. & Corrsin, S. 1978 Velocity-derivative skewness in small Reynolds number, nearly isotropic turbulence. *J. Fluid Mech.* **88**, 63.