J. Fluid Mech. (1985), *vol.* 159, *pp.* 323–345
Printed in Great Britain

Evaporation from a plane liquid surface into a turbulent boundary layer

By P. W. M. BRIGHTON
UKAEA, Safety and Reliability Directorate, Wigshaw Lane, Culcheth, Warrington WA3 4NE

(Received 18 December 1984)

A new analytic solution is presented for predicting evaporation rates from plane liquid surfaces into a neutral turbulent boundary layer. Conditions of passive dispersion are assumed. Molecular diffusivity is incorporated into the boundary conditions. Both smooth and rough surfaces are considered. A comparison with a wide variety of experimental data is made; this tends to reveal inadequacies and inconsistencies in the data, rather than test the theory. The effects of a roughness change at the boundary of the liquid surface and of high vapour pressures can be included for practical purposes by simple formulae. A criterion is derived for the validity of the neglect of buoyancy effects.

1. Introduction

A body of liquid with a free surface exposed to the atmosphere tends to vanish through evaporation as vapour diffuses from its surface and is carried away by the turbulent flow of the wind. This process has long been of interest to meteorologists and hydrologists in connection with water in lakes and reservoirs. Recently it has also become of importance in assessing the risks to society from industrial sites handling large quantities of hazardous flammable or toxic materials. Accidents can result in the formation of pools of liquefied gases or volatile liquids, and the evolution of vapour from these can create gas clouds capable of endangering the public (Health and Safety Executive 1978, 1981; COVO Steering Committee 1982).

Current methods of evaluating evaporation rates from a pool fall into two classes. The first class use simple formulae for mean evaporation rates with power-law dependences on wind speed and pool size. These are ultimately derived from the work of Sutton (1934), and do not incorporate knowledge of turbulent diffusion gained in the last half-century. Often they do not involve the relevant parameters in a dimensionally correct manner. Also they disagree as to the dependence of turbulent mass transfer on the molecular diffusivity of the vapour, which must be important in the viscous sublayer at the surface.

Secondly, there are methods involving numerical solution of equations for turbulent mass transfer using various closure assumptions. While potentially the most flexible, these methods are also the most expensive to apply, and their complexity may be unwarranted for practical purposes in view of the continuing debate over those closure assumptions.

The aim in this paper is to present an analytic solution based, like Sutton's (1934) theory, on representing the turbulent diffusion by an eddy diffusivity varying with height and replacing the logarithmic wind profile by a power law. However we follow Hunt & Weber's (1979) analysis of diffusion from a point source in using a power-law exponent dependent on the height to which the vapour diffuses. Unlike previous analytic studies, our treatment incorporates the effects of molecular diffusion near the surface by using near-wall logarithmic laws based on thorough reviews of experimental data in equilibrium layers by Kader (1981) for smooth-wall flows and by Brutsaert (1982, chap. 4) for rough-wall flows (appropriate to pools with waves). This results in a modified form of boundary condition for the diffusion problem, and consequently the solution does not have the simple power-law dependences on wind speed, pool size and molecular diffusivity found in the earlier studies. Nevertheless, a closed-form solution is obtained.

We attempt to compare our theoretical results with the published experimental data, but find that inconsistencies and inadequacies of these data do not allow a stringent test, though the general agreement is satisfactory.

The theory described above is based on a fundamental assumption that the vapour behaves as a passive contaminant in the atmosphere. This assumption is invalid if the vapour pressure is a significant fraction of atmospheric pressure, since the vertical velocity at the liquid surface then becomes large enough to alter the boundary-layer structure. It is shown that the theory can be extended to cover this case satisfactorily in a simple manner. The assumption of passive behaviour is also invalid if gravitational effects (i.e. natural convection) become important – criteria for the validity of the theory are derived, but we do not attempt to extend it to this complex situation.

2. Formulation of the problem

2.1. *Basic definitions*

Consider the evaporation from a pool of slightly volatile liquid whose surface occupies the region $0 \leqslant x \leqslant d$ on the horizontal plane $z = 0$. A neutrally stable turbulent airstream flows over this pool in the x-direction with friction velocity u_* and roughness length z_0, which are assumed to be uniform along the whole x-axis. The aim is to calculate the local evaporation rate $J(x)$ (in units of mass area^{-1} time^{-1}) as a function of x dependent on the parameters u_* and z_0: the pool temperature, which determines the saturated vapour pressure of the liquid, is assumed to be maintained constant in time and space.

It is supposed that the density of air saturated with the vapour is not altered so much as to change the mean-velocity profile or the turbulent structure of the airstream; the evaporation rate must also be small enough to preserve the boundary-layer structure. These conditions imply that the vapour is dispersed as a passive contaminant, so that the analytical methods of turbulent-diffusion theory may be used without the intractable complication of including the dynamics of a stratified turbulent flow. The vapour concentration in the air is determined by the condition that at the liquid surface it takes the value for saturated vapour, given, assuming that the perfect-gas law holds, by

$$c_{\mathrm{s}} = \frac{M_{\mathrm{v}} P_{\mathrm{v}}}{RT} \quad \text{(in units of mass/volume).} \tag{2.1}$$

Here M_{v} is the molecular weight of the vapour, P_{v} is the saturated vapour pressure at the temperature T of the liquid surface, and R is the gas constant.

On dimensional grounds we expect that the local evaporation rate should be given by

$$J(x, d, z_0, u_*, c_{\mathrm{s}}, \nu, D) = c_{\mathrm{s}} u_* j\left(\frac{x}{z_0}, \frac{d}{z_0}, Re_0, Sc\right), \tag{2.2}$$

where ν is the kinematic viscosity of the air and D is the molecular diffusivity of the vapour in air. The roughness Reynolds number is given by

$$Re_0 = u_* z_0/\nu. \tag{2.3}$$

Note that we extend this description to smooth-wall flows, when z_0 is defined by a constant value of $Re_0 = 0.13$ (Monin & Yaglom 1971, §5.3). Sc is the laminar Schmidt number given by

$$Sc = \nu/D. \tag{2.4}$$

In (2.2) we have suppressed reference to parameters describing the geometrical characteristics of the roughness elements, but at present there is little knowledge of the dependence on these (Brutsaert 1982, §4.4).

2.2. *The diffusion–advection equation*

To describe the vapour concentration field we use a dimensionless variable $\chi(x,z)$ defined as the ratio of the mass concentration of the vapour to the saturated-vapour value (2.1). Thus χ takes the value 1 at the liquid surface and tends to zero at large distances, assuming no background concentration of vapour. χ is an ensemble-mean quantity, and it is assumed that conditions have reached a statistically steady state so that χ is independent of time. Only the mean quantity χ is considered in this paper.

We use a boundary-layer version of the diffusion–advection equation with variable eddy diffusivity:

$$U(z)\frac{\partial \chi}{\partial x} = \frac{\partial}{\partial z}\left(K'(z)\frac{\partial \chi}{\partial z}\right). \tag{2.5}$$

The velocity profile for a neutral turbulent boundary layer (above the viscous sublayer) is

$$U(z) = \frac{u_*}{\kappa}\ln\frac{z}{z_0}, \tag{2.6}$$

where κ is von Kármán's constant. The eddy diffusivity K' is assumed proportional to the eddy viscosity K, with

$$\sigma = K/K', \tag{2.7}$$

the turbulent Schmidt number. The eddy viscosity corresponding to the profile (2.6) with Reynolds stress independent of z is

$$K = \kappa u_* z. \tag{2.8}$$

Although the use of a diffusion equation is well known to be dubious in many cases of turbulent dispersion, the work of Chatwin (1968) and Hunt & Weber (1979) shows that for dispersion from the surface in a logarithmic boundary layer it gives a good approximation to the results of Lagrangian similarity theory (Batchelor 1964), which does not involve any concept of eddy diffusivity. This success may be due to the fact that, since the eddy diffusivity is proportional to distance from the wall, it is also proportional to the local depth of the vapour layer; this automatically incorporates the idea that, as a plume grows in size, larger eddies become most important in dispersing it. In homogeneous turbulence, on the other hand, this means that a uniform eddy diffusivity cannot describe the dispersion of a puff of contaminant (Batchelor 1952).

The neglect of the terms for diffusion in the x-direction in (2.5) is justified if the vertical scale of the problem is much smaller than the horizontal scale: the validity of this will be discussed below. The equation is also valid for evaporation from a pool of finite width provided the width is much greater than the depth of the vapour layer. Vertical diffusion then proceeds independently along each line traversing the pool in the x-direction. Since (2.5) is parabolic, solutions are not influenced by the position of the downstream edge. Thus in this model there should be no dependence of the local dimensionless evaporation rate j of (2.2) on the parameter d/z_0.

2.3. *Previous solutions for evaporation*

Equation (2.5) was originally used to describe evaporation by Sutton (1934). He used the power-law wind profile

$$U(z) = U_1(z/z_1)^n, \tag{2.9}$$

in which the index n was regarded as dependent solely on the atmospheric stability and the ground roughness. Also he assumed that the eddy viscosity $K(z) \propto z^{1-n}$ so that the shear stress $\rho_A K \partial U/\partial z$ was constant with height (ρ_A being the air density). The turbulent Schmidt number (2.7) was taken as a constant. At the liquid surface Sutton applied the boundary condition $\chi(x, 0) = 0$ for $x < 0$ and 1 for $x \geqslant 0$. Under these circumstances (2.5) can be solved analytically, yielding a similarity solution in which the evaporation rate

$$J(x) = -\lim_{z \to 0} c_S K' \frac{\partial \chi}{\partial z} \tag{2.10}$$

is proportional to x^{-m}, with $m = n/(1+2n)$. Sutton recommended the value $n = \frac{1}{7}$, giving $m = \frac{1}{9}$, to fit windspeed measurements in neutral conditions.

Pasquill (1943) modified Sutton's approach by introducing a dependence of K' on Sc. This was based on arguments due to Sutton involving an empirical expression for the turbulent autocorrelation function for the vertical component of fluctuating velocity. This derivation bears little relation to current concepts of the role of molecular viscosity and diffusivity in turbulent transport, but led Pasquill to the conclusion that J is proportional to $Sc^{-\frac{2}{9}}$, for which he found some experimental support.

To estimate evaporation rates from pools of liquid in hazard analysis, several subsequent authors (Opschoor 1978; Shaw & Briscoe 1978; Lees 1980, §15.2.2; Cremer and Warner Ltd *in* COVO Steering Committee 1982, Part 2, §7.0) have applied Sutton's results in the form

$$\bar{J} = kc_S U_1^{\frac{7}{9}} d^{-\frac{1}{9}} Sc^{-r}, \tag{2.11}$$

where $\bar{J}$ is the mean evaporation rate per unit area of a square or circular pool of area d^2. If any reference height is stated, U_1 is taken as the wind velocity at 10 m. The exponent r is assigned values ranging from 0 to $\frac{2}{3}$. Values of k are derived from various sources of experimental information.

Equation (2.11) is unsatisfactory because it does not conform to the basic dimensionless form (2.2) involving the parameters u_* and z_0 defining the boundary-layer structure. The diversity of opinion about the dependence on Sc is also unsatisfactory. This may not matter for practical purposes if these correlations are applied to situations close to the original experimental conditions, but in hazard analysis it is frequently necessary to extrapolate to much larger pool sizes. Such extrapolation needs to be based on physically justified scaling principles.

Calder (1949) improved Sutton's approach by recognizing that the power-law index n should be chosen so as to match the fundamental logarithmic profile (2.6) for values of z characteristic of the local plume depth, rather than applying a fixed value for given atmospheric conditions as in all the work mentioned above. This approach was revived by Hunt & Weber (1979) in describing diffusion from a point or line source.

To obtain satisfactory agreement with Lagrangian similarity theory, Hunt & Weber also used the linear eddy-diffusivity profile (2.8) instead of the z^{1-n} dependence used by previous workers. This feature plays a key role in our solution because it implies that concentration profiles become logarithmic near the surface, whereas in Sutton's formulation they remain finite. This allows us to introduce the effects of molecular diffusivity in a small region near the surface by matching our solutions to relations for equilibrium logarithmic concentration profiles with dependence on *Sc*.

The abovementioned solutions to the evaporation problem have applied the condition $\chi = 1$ directly to the turbulent-diffusion equation with no allowance for molecular effects near the boundary. The Schmidt-number dependence in (2.11) has been introduced by other arguments of doubtful validity.

The turbulent-diffusion equation has also been solved numerically by Reijnhart, Piepers & Toneman (1980) with allowance for molecular effects near the wall. This is similar to the present treatment, but they did not obtain any analytic solutions. Other numerical solutions for evaporation of water including stability and roughness-change effects, which can be important for lakes and reservoirs, are reviewed by Brutsaert (1982, chap. 7).

2.4. *Power-law approximation to the logarithmic profile*

The diffusion–advection equation (2.5) cannot be solved analytically with the profiles given by (2.6)–(2.8). The power-law profile (2.9) provides a good approximation to the logarithmic profile (2.6) if

$$U_1 = \frac{u_*}{\kappa}\ln\frac{z_1}{z_0}, \quad n = \left(\ln\frac{z_1}{z_0}\right)^{-1} \tag{2.12}$$

over a range of z defined by

$$n\left|\ln\frac{z}{z_1}\right| \ll 1 \quad \text{or} \quad z_1\,\mathrm{e}^{-1/n} = z_0 \ll z \ll z_1\,\mathrm{e}^{1/n} \tag{2.13}$$

(Hunt & Weber 1979). To achieve the appropriate approximation in a particular problem z_1 is chosen to match the typical depth of the vapour layer over the lengthscale of interest – in this case the pool length d. (It does not matter that the power-law profile is not valid as z becomes zero because near the wall the advection term becomes negligible, as will be seen later.) Hence (2.5)–(2.8) become

$$U_1\left(\frac{z}{z_1}\right)^n\frac{\partial\chi}{\partial x} = \frac{\partial}{\partial z}\left(\frac{\kappa u_* z}{\sigma}\frac{\partial\chi}{\partial z}\right), \tag{2.14}$$

which can be solved analytically. To provide an estimate for z_1 we use the following results from the theory of line sources.

Hunt & Weber showed that the solutions of (2.14) for instantaneous and continuous line sources display features matching all the properties deducible from Lagrangian similarity theory without invoking the use of an eddy diffusivity (Batchelor 1964). Their solutions also agree with properties of solutions of (2.5) with the logarithmic profile established by Chatwin (1968). This agreement extends to the zeroth- and first-order terms in an expansion in powers of $n \ll 1$, as the profile given by (2.9) and (2.12) matches (2.6) to that accuracy.

For a continuous line source of uniform strength q per unit length, Batchelor's (1964) result for the downwind ground level concentration is

$$\chi(x,0) \propto \frac{q}{\bar{z}\ln(c\bar{z}/z_0)}, \tag{2.15}$$

where $\bar{z}(x)$ is the path of the centroid of an instantaneous puff of contaminant given implicitly by

$$x = \frac{\sigma}{\kappa^2}\bar{z}\left(\ln\frac{c\bar{z}}{z_0} - 1\right). \tag{2.16}$$

The constant c was evaluated by Chatwin (1968) as $e^{-\gamma}$, where $\gamma = 0.5772\ldots$ is Euler's constant. The turbulent Schmidt number σ was taken as 1 by Chatwin and by Hunt & Weber, but our requirement of matching with logarithmic concentration profiles near the wall means that $\sigma = 0.85$ (see below). Fackrell & Robins (1982) found that a value for σ of approximately 0.8 was needed to match their careful measurements of mean concentrations and vertical fluxes from a ground-level point source.

Note that, in terms of the small parameter n of (2.12), equations (2.15) and (2.16) give

$$\chi(x,0) \propto \frac{q}{x}\,\frac{1+n[\ln(c\bar{z}/z_1)-1]}{1+n\ln(c\bar{z}/z_1)} \tag{2.17}$$

without further approximation. The reference height z_1 is still arbitrary, but the choice $z_1 = c\bar{z}(x_1)/e$ makes Hunt & Weber's ground-concentration solution (see their equation (4.12))

$$\chi(x,0) = \frac{\sigma q}{\kappa u_* x(1+n)} \tag{2.18}$$

match (2.17) in magnitude and slope at $x = x_1$. (Hunt & Weber in fact chose $z_1 = \bar{z}(x_1)$, but this affects the result only at $O(n^2)$.)

For a liquid surface the appropriate value of z_0 is uncertain because of the possible presence of gravity waves: a value of 2×10^{-4} for 'smooth sea' as quoted by Sutton (1955) would seem appropriate for accidental liquid spills. If the liquid surface is aerodynamically smooth then $z_0 = 0.13\nu/u_*$ (Monin & Yaglom 1971, §5.3) – for air $\nu \approx 1.5\times10^{-5}$ m^2/s, so $z_0 \approx 10^{-5}$ m for $u_* = 0.2$ m/s. The horizontal dimensions of interest for spills of hazardous liquids probably vary from 1 to 1000 m, so that the dimensionless pool length d/z_0 may lie between 10^3 and 10^8, if the maximum possible z_0 for 'rough' conditions is taken as 10^{-3} m. Figure 1 shows how the plume height $\bar{z}$ corresponding to these distances varies according to (2.16). The values of $n^{-1} = \ln(c\bar{z}/e z_0)$ are seen to vary from about 3 to over 12. However, as the larger values of d are likely to be associated with the larger values of z_0 and *vice versa*, values of d/z_0 are probably in a smaller range around 10^5, giving n close to Sutton's value $\frac{1}{7}$ and making the expansion for small n a reasonable approximation.

2.5. *General solution of the diffusion–advection equation*

Equation (2.14) can be solved for general distributions of the mass flux from the boundary by use of a Laplace transform in x. First it is convenient to render the variables dimensionless by taking

$$X = \frac{n\kappa^2 x}{\sigma z_1}, \quad Z = \frac{z}{z_1}, \tag{2.19}$$

so that

$$Z^n\frac{\partial\chi}{\partial X} = \frac{\partial}{\partial Z}\left(Z\frac{\partial\chi}{\partial Z}\right). \tag{2.20}$$

The Laplace transform $\tilde{\chi}(p, Z)$ is defined by

$$\tilde{\chi}(p, Z) = \int_0^\infty \mathrm{e}^{-pX} \chi(X, Z)\, \mathrm{d}X \tag{2.21}$$

and satisfies the ordinary differential equation

$$\frac{\mathrm{d}}{\mathrm{d}Z}\left(Z \frac{\mathrm{d}\tilde{\chi}}{\mathrm{d}Z}\right) - pZ^n \tilde{\chi} = 0. \tag{2.22}$$

(Recall that $\chi(x, z) = 0$ for $x \leqslant 0$.) The general solution satisfying a condition of zero concentration at ∞ is

$$\tilde{\chi} = F(p)\, K_0(s), \tag{2.23a}$$

where

$$s = \frac{p^{\frac{1}{2}} Z^{\frac{1}{2}(n+1)}}{\frac{1}{2}(n+1)} \tag{2.23b}$$

and K_0 is a modified Bessel function (Abramowitz & Stegun 1972, §9.6). As $Z \rightarrow 0$ and $s \rightarrow 0$ this solution has the behaviour

$$\begin{aligned} \tilde{\chi} &\sim -F(p)\,[\ln \tfrac{1}{2}s + \gamma]\,[1 + O(s^2)] \\ &\sim -F(p)\,[\tfrac{1}{2}(n+1) \ln Z + \tfrac{1}{2} \ln p - \ln(1+n) + \gamma]. \end{aligned} \tag{2.24}$$

We define the dimensionless mass flux $j(X)$ by (cf. (2.2))

$$j(X) = \frac{J}{c_{\mathrm{s}} u_*} = -\lim_{z \rightarrow 0} \frac{\kappa}{\sigma} Z \frac{\partial \chi}{\partial Z}, \tag{2.25}$$

and so, using (2.24),

$$\tilde{j}(p) = \tfrac{1}{2}(n+1) \frac{\kappa}{\sigma} F(p). \tag{2.26}$$

2.6. *The boundary condition at the surface*

The surface boundary condition needed to fix the solution of the turbulent-diffusion equation is obtained by matching the concentration profile near the surface (2.24) to a wall profile that takes account of the presence of a laminar sublayer dominated by molecular transport processes. For the case of an aerodynamically smooth surface, Kader (1981) recommends the wall profile

$$\chi_0 - \chi = j\left[\frac{\sigma}{\kappa} \ln \frac{z u_*}{\nu} + \beta_1(Sc)\right], \tag{2.27a}$$

where χ_0 is the vapour concentration at $z = 0$ and is 1 at the pool surface. The function β_1 is determined by a combination of dimensional reasoning and empirical correlation as

$$\beta_1(Sc) = (3.85\, Sc^{\frac{1}{3}} - 1.3)^2 + \frac{\sigma}{\kappa} \ln Sc \tag{2.27b}$$

for $6 \times 10^{-3} \leqslant Sc \leqslant 4 \times 10^4$. As mentioned above, the values of the von Kármán constant κ and the turbulent Schmidt–Prandtl number σ used in this correlation are 0.40 and 0.85 respectively.

For rough surfaces a range of empirical and semiempirical relations has been reviewed by Brutsaert (1982, §4.4); for present purposes we propose to use Brutsaert's (1975) expression

$$\chi_0 - \chi = j\left[\frac{\sigma}{\kappa} \ln \frac{z}{z_0} + \beta_2(Sc)\right], \tag{2.28a}$$

with
$$\beta_2(Sc) = 7.3\, Re_0^{\frac{1}{4}}\, Sc^{\frac{1}{2}} - 5\sigma, \tag{2.28b}$$
which has been validated for $0.6 \leqslant Sc \leqslant 6$ and $Re_0 > 2$.

In terms of the dimensionless variables of the diffusion equation above, (2.27) and (2.28) can be expressed as

$$\chi_0 - \chi = j\left[\frac{\sigma}{\kappa}\ln Z + \frac{\sigma}{\kappa}n^{-1} + \beta(Sc)\right], \tag{2.29a}$$

where
$$\beta(Sc) = \beta_1(Sc) + \frac{\sigma}{\kappa}\ln 0.13 \tag{2.29b}$$

for a smooth surface, since then the effective roughness length is $z_0 = 0.13\,\nu/u_*$, and

$$\beta(Sc) = \beta_2(Sc) \tag{2.29c}$$

for a rough surface.

3. The solution for an evaporating pool

Matching the wall-region concentration profile (2.29*a*) with the near-wall form (2.24) of the Laplace transform of the general solution of the turbulent-diffusion equation yields a result for the surface mass flux in terms of the known distribution of surface concentration $\chi_0(X)$:

$$\tilde{j}(p) = \frac{(\kappa/\sigma)(1+n)\,\tilde{\chi}_0}{A - \ln p}, \tag{3.1a}$$

where A is a function of the power-law index n and the Schmidt number Sc:

$$A = n^{-1} + 1 + 2\ln(1+n) - 2\gamma + \frac{\kappa}{\sigma}(1+n)\,\beta. \tag{3.1b}$$

This matching occurs for values of z with $z \ll z_1$ and $z \gg z_0$: hence in view of (2.13) it is justified by the condition $n \ll 1$. In practice it appears that this condition need not be very strict, presumably because for $z \ll z_1$ the advection term becomes negligible in (2.5) and the accuracy of the power-law profile is irrelevant.

At the liquid surface, $\chi_0 = 1$: it is unnecessary to consider explicitly the vapour dispersion downwind of the pool end at $x = d$ since the governing equation (2.20) is parabolic. We do not consider here the form of the solution beyond $x = d$, and so the pool may be treated as semi-infinite. However, the pool length will be reflected in the choice of the power-law index n from (2.12) and figure 1, so that our solution is to be regarded as valid just for distances of order d. In effect, n can be regarded as a slowly varying function of x (Hunt & Weber 1979, §4). The Laplace transform of the function $\chi_0(X) = 1$ for all $X \geqslant 0$ is simply $\tilde{\chi}_0 = p^{-1}$; substitution in (3.1*a*) and manipulation of the inverse transform as described in Appendix A yields the formula for downwind evolution of the mass flux

$$j(X) = \frac{\kappa}{\sigma}(1+n)\,G(e^{A}X), \tag{3.2a}$$

where
$$G(\xi) = \int_0^\infty \frac{e^{-p\xi}\,dp}{p(\ln^2 p + \pi^2)}. \tag{3.2b}$$

We suppose that, to obtain the best overall result for a pool of length d, z_1 should be related to the depth of the vapour layer at some intermediate point $x = \alpha_2 d$ with

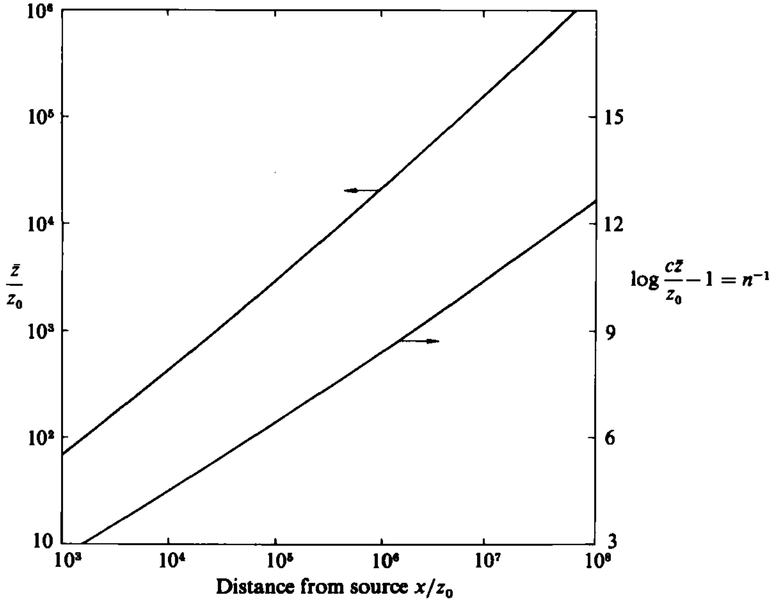

FIGURE 1. Variation of particle displacement $\bar{z}$ and power-law index n with distance from source. $\bar{z}$ is defined by $x = (\sigma/\kappa^2)\,\bar{z}[\ln(c\bar{z}/z_0) - 1]$.

$0 < \alpha_2 < 1$. Also, recalling the discussion following (2.17), we take

$$z_1 = \alpha_1 c\bar{z}(\alpha_2 d)/\mathrm{e}, \tag{3.3}$$

the function $\bar{z}(x)$ being defined by (2.16) (see figure 1). ($\alpha_1 = 1$ is the value needed to produce optimum results for the line-source problem.) With these definitions, the dimensionless distance (2.19) corresponding to the end of the pool is

$$X_1 = \frac{n\kappa^2 d}{\sigma z_1} = \frac{(1 - n\ln\alpha_1)\,\mathrm{e}}{\alpha_1\alpha_2 c}. \tag{3.4}$$

To evaluate the mean dimensionless evaporation rate, or mass-transfer coefficient, the quantity of prime practical interest, we now integrate over X, regarding n as a constant for a particular pool size. The result is

$$\bar{j} = \frac{1}{X_1}\int_0^{X_1} j(X)\,\mathrm{d}X = \frac{\kappa}{\sigma}(1+n)\,\bar{G}(\mathrm{e}^{A}X_1), \tag{3.5a}$$

where

$$\bar{G}(\xi) = \frac{1}{\xi}\int_0^{\xi} G(\xi')\,\mathrm{d}\xi'. \tag{3.5b}$$

The evaluation of the functions $G(\xi)$ and $\bar{G}(\xi)$ is described in Appendix B, where it is found that four terms of a formal series expansion give results within $\frac{1}{2}\%$ of an accurate numerical integration. Evaluation of $\bar{j}$ for α_1 between 1 and 4 and α_2 between $\frac{1}{4}$ and 1 produces variations of 4 % at most over the range of parameters studied (shown in figure 2). Thus no significant errors result from taking the fixed values $\alpha_1 = 1$, $\alpha_2 = \frac{1}{2}$, which are plausible physically. This is done in the results presented in §4. Hence there are effectively no disposable constants in the theory. Note that this insensitivity to the point at which the velocity profiles are matched serves to justify carrying out the integration of (3.5a) without varying n.

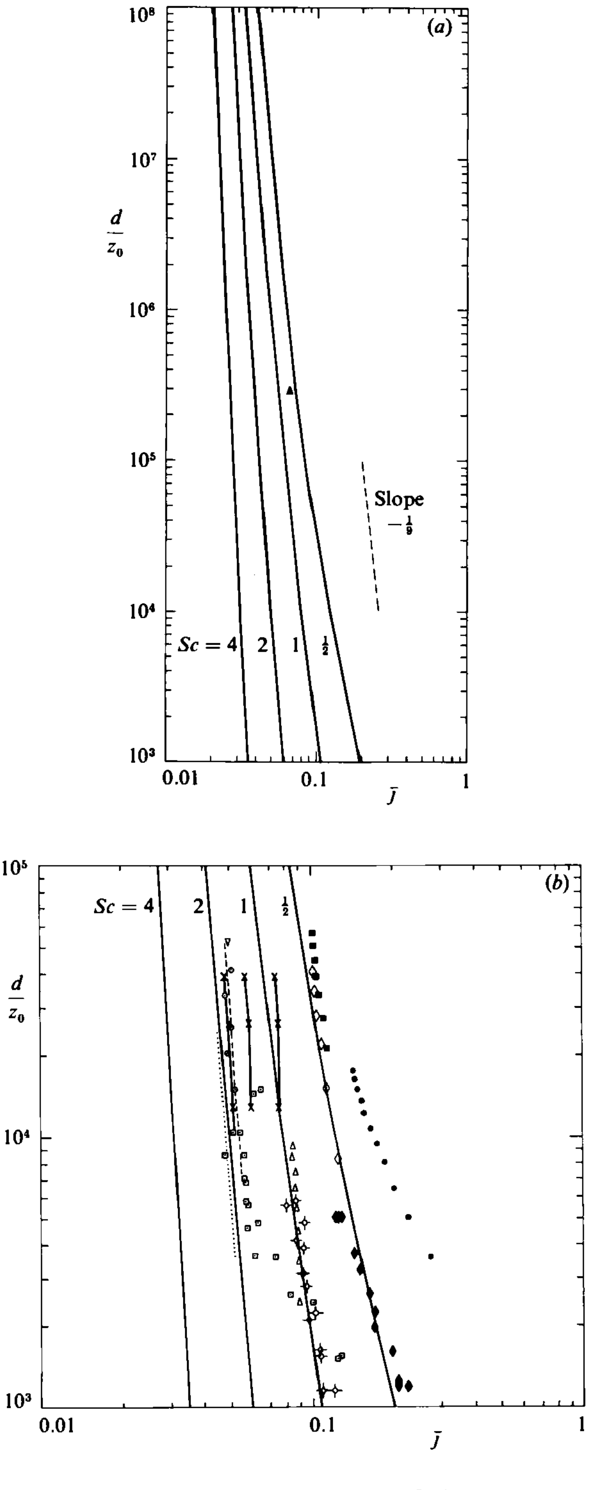

FIGURE 2. For description see facing page.

With the chosen values of α_1 and α_2, (3.4) becomes

$$X_1 = \frac{2\mathrm{e}}{c} = 9.681.... \tag{3.6}$$

The basic boundary-layer approximation of neglecting streamwise diffusion in (2.5) can now be justified by the fact that

$$\frac{z_1}{d} = \frac{\kappa^2 cn}{2\,\mathrm{e}\,\sigma} \approx 0.02n. \tag{3.7}$$

Thus the power-law profile condition $n \ll 1$ is the main factor limiting the accuracy of the solution.

4. Comparison of results with experimental data

4.1. *Smooth surfaces*

Figure 2 (*a*) shows the variation of the mean mass-transfer coefficient $\bar{j}$ as a function of the pool-length parameter d/z_0 for four different values of *Sc*. Figure 2 (*b*) shows these graphs enlarged in the region for which the bulk of published experimental data is available. To meet the conditions of an aerodynamically smooth surface both upwind and over the pool, only data from wind tunnels are relevant. The experimental data must be treated with caution, because in most cases assumptions must be made about the values of u_* and there remain considerable inconsistencies between different sets of data.

In his theoretical and experimental study of the evaporation problem, Pasquill (1943) compared his results with those of several earlier investigators (Hine 1924; Hinchley & Himus 1924 (see also Himus 1929); Millar 1937; Wade 1942). He used these experiments as approaching the theoretical case of a liquid surface flush with a solid surface with a fully developed turbulent flow. Pasquill found that, while his own data matched his version of Sutton's (1934) theory closely, the earlier investigations showed greater evaporation rates, in some cases by a factor of two. Pasquill ascribed this excess to the existence of ridges at the upstream end of the liquid pools in some of the experiments and to the presence of ripples on the surface. He obviated these difficulties himself by using pieces of saturated filter paper in place of pans of liquid. Pasquill measured the mean air speed at a height of 10 mm above the evaporating surface, making it possible to derive a reliable value of u_* by using the smooth-wall logarithmic profile. Pasquill presented his result for bromobenzene ($Sc = 2.16$) as a table of smoothed values of the ratio of observed and predicted evaporation rates. We have converted these values to the dimensionless form required by (2.2). Pasquill used three different shapes of filter paper, but did not tabulate separate data for each. Our back calculation therefore leads to alternative results as

FIGURE 2. (*a*) Variation of mean mass-transfer coefficient $\bar{j}$ with non-dimensional pool length d/z_0 (smooth surface). (*b*) Part of (*a*) enlarged to show comparison with data: ▲, Elias (1929, 1930), $Pr = 0.71$ (from Pasquill 1943); □, Gray (1974), $Sc = 2.2$; ●, Hinchley & Himus (1924), $Sc = 0.60$ (from Pasquill 1943); ◇, Hine (1924), $Sc = 1.85$ (from Pasquill 1943); ▽, Mackay *et al.* (1980), $Sc = 2.7$; ■, Millar (1937), $Sc = 0.60$ (from Pasquill 1943); ◆, O'Brien & Stutzman (1950), $Sc = 0.61$; -○-, *ibid.*, $Sc = 1.68$; -◇-, *ibid.*, $Sc = 1.84$; ---, Pasquill (1943), $Sc = 2.16$, circles & large squares; ····, *ibid.*, rectangles; ×—×, Reijnhart *et al.* (1980), theoretical, $Sc = 1.0$, 1.4, 1.7; ○, Reijnhart & Rose (1980), $Sc = 1.7$; △, Wade (1942), $Sc = 1.79$ (from Pasquill 1943).

seen in figure 2(*b*). Pasquill does show individual data points in his figure 4, where there is a slight systematic variation with the size of paper. To make our comparison, we have taken d as the downwind length for squares and rectangles and as the square root of the area for circles: this procedure was adopted in processing all the experimental data discussed below. Pasquill's data agrees well with our predictions at the very similar Schmidt number of 2.

For the other experiments reviewed by Pasquill, the velocity measurements were either bulk averages or values from rather large instruments not particularly near the liquid surface. There were no specific attempts to create an equilibrium logarithmic boundary-layer profile over the evaporating surface; often there was little distance for full development of a channel-flow velocity profile. It is therefore impossible to deduce values of u_* at all precisely: all we have been able to do is to estimate it from the relation between u_* and the bulk velocity for pipe flow as given by Tennekes & Lumley (1972, equation (5.2.36)), obtaining an effective pipe radius by equating the areas to those of the rectangular or square cross-section used; or, in cases where velocities are given as point values (Hine 1924; Millar 1937), to use these in the logarithmic profile.

Using Pasquill's (1943) table 7 comparing these data with his theory, we have obtained the results inserted in figure 2(*b*). Like Pasquill, we find that the results of Hine (1924) and Hinchley & Himus (1924) are up to twice those predicted. Millar's (1937) results for water ($Sc = 0.6$) are slightly higher than our predictions for $Sc = 0.5$. Wade's (1942) results are about 50 % higher than we predict. In all cases the variation of d/z_0 is in reasonable agreement with the predicted trends.

The shortcomings criticized above in the experiments other than Pasquill's apply also to more recent work of O'Brien & Stutzman (1950) and Gray (1974), which have been included in Figure 2(*b*) after making the same assumptions regarding u_* as above. O'Brien & Stutzman's results for water are close to our curve for $Sc = 0.5$, but for organics of higher molecular weight they obtain mass-transfer rates about 50% higher than predicted. Gray's results for *m*-xylene ($Sc = 2.2$) are high for $d/z_0 < 4000$ but are close to ours for $Sc = 2$ at higher values. Gray's experiments show a much more marked variation with d/z_0 than any others.

Pasquill (1943) also considered that a useful comparison could be made with data of Elias (1929, 1930) for heat transfer from a heated copper plate mounted in an insulating wooden platform – though the leading edge of the plate was near that of the platform, invalidating the assumption of a developed boundary layer. The value of the heat-transfer coefficient extracted from Elias's data by Pasquill is shown in figure 2(*a*) and falls close to the value we predict using $Sc = 0.71$, the value of the Prandtl number.

Also included in figure 2 are the wind-tunnel data on toluene of Reijnhart & Rose (1980), who were careful to develop a logarithmic boundary-layer profile and determine values of u_*. These data fall about where expected from our theory, and also match the numerical solutions of Reijnhart *et al.* (1980) mentioned above. They did not in fact use Kader's (1981) result (2.27*b*) as the wall boundary condition, but incorporated molecular diffusivity using a simpler analysis which happens to give similar values for Sc between 1 and 2. The results of Reijnhart *et al.* for $Sc = 1$, 1.4 and 1.7 are shown in figure 2(*b*), and appear to have a smaller slope than ours, but this may be due to our extraction of their results from a small-scale graph.

Reijnhart & Rose also conducted experiments with roughness elements upwind from the pool – these are discussed in §4.3.

The remaining experimental point on figure 2(*b*) is provided by Mackay, Paterson

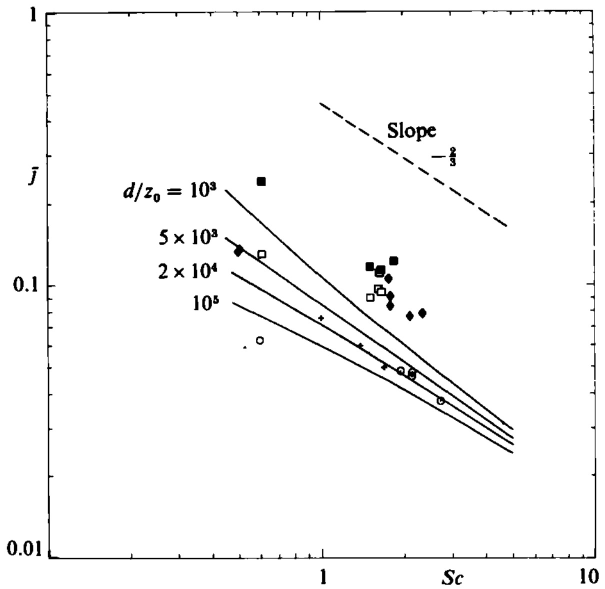

FIGURE 3. Dependence of mean mass-transfer coefficient $\bar{j}$ on Schmidt number *Sc* (smooth surface): ■, O'Brien & Stutzman (1950), $d/z_0 \approx 950$; □, *ibid.*, $d/z_0 \approx 5000$; ○, Pasquill (1943), $d/z_0 \approx 2 \times 10^4$; +, Reijnhart *et al.* (1980), theoretical, $d/z_0 \approx 2 \times 10^4$; ◆, Wade (1942), $d/z_0 \approx 5000$ (from Pasquill 1943).

& Nadeau's (1980) wind-tunnel measurement on cumene, for which the air velocity was recorded 30 mm above the liquid surface. The value of $\bar{j}$ is rather greater than we would predict for $Sc = 2.7$.

A potentially useful set of heat-transfer experiments was conducted by Browne & Antonia (1979), but unfortunately they do not give values of the friction velocity in their developing boundary layer. Snijders, Koppius & Nieuwvelt (1983) carried out a similar experiment with a tripped layer on a smooth plate with a section at a uniform raised temperature starting at 1.06 m behind the leading edge. They present detailed profiles and surface-flux measurements at a distance 0.443 m from the start of the heated section. The boundary-layer thickness was 35 mm. From their table 1, the value of d/z_0 was 9.73×10^4, giving $n = 0.173$. The local heat-transfer coefficient had a value of 5.87×10^{-2}. This compares with our theoretical value based on (3.2*a*) of 6.30×10^{-2}. The average heat-transfer rate is not reported, and so does not appear in figure 2(*b*).

4.2. *Variation with Schmidt number*

Pasquill (1943) presented further data of his own and from Wade (1942) in order to examine the dependence on Schmidt number. These are listed in his table 4 in the form of evaporation rates relative to water, and we have used them in a comparison with our results in figure 3 by assuming them to apply near the midrange values of d/z_0 shown in figure 2(*b*). Results of O'Brien & Stutzman (1950) have been included in a similar way. On the whole, all three experiments indicate a slower variation with *Sc* than we predict – again the calculations of Reijnhart *et al.* (1980) give results similar to ours. Taking each experiment separately, this might have been ascribed to some inadequacy, but the finding in three different cases seems significant: whatever the doubts about the absolute values measured, these experiments should be reasonably reliable for the relative evaporation rate of different substances.

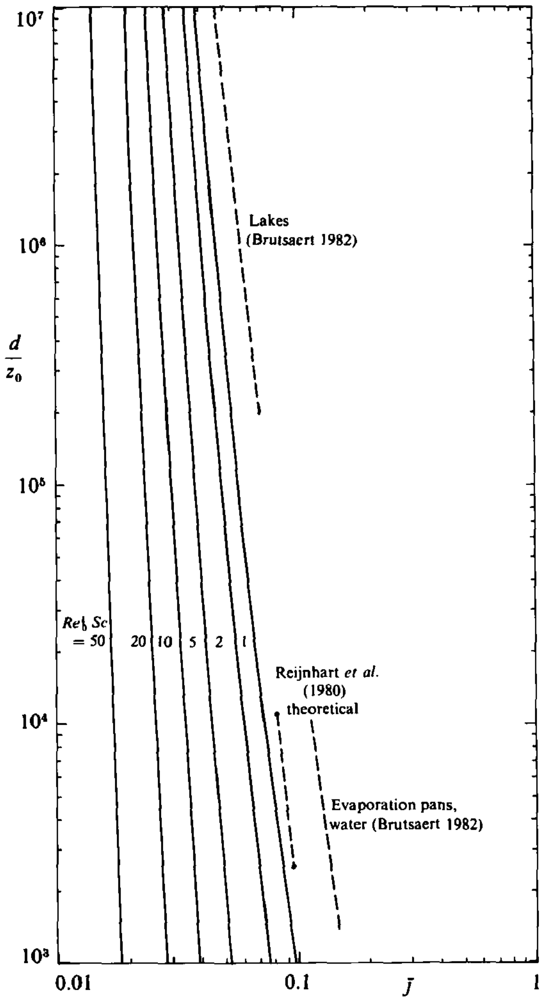

FIGURE 4. Variation of mean mass-transfer coefficient $\bar{j}$ with non-dimensional pool length d/z_0 (rough surface).

Unfortunately the values of Sc for other experimental liquids used span too small a range to shed much further light on the issue.

4.3. *Rough surfaces*

In most situations of practical interest it is likely that the liquid surface will be distorted by the presence of waves, and that it will be aerodynamically rough. For spills of liquid floating on the sea the roughness length will be related to that of the surrounding sea; for confined bodies of liquid the roughness will depend on the fetch available for the wind generation of waves, for which we know of no simple law. If evaporation occurs from a rough or porous land surface, then the roughness length may be characteristic of that surface, but the effective vapour pressure may be below the saturation value.

Figure 4 shows our calculated values for the mean mass-transfer coefficient $\bar{j}$ for evaporation from rough surfaces as a function of the dimensionless pool length d/z_0.

Because of (2.28*b*) the two parameters Re and Sc of (2.2) occur in the combination $Re_0^{\frac{1}{8}}\,Sc$. Since Re_0 must be greater than 2 for aerodynamically rough conditions, the minimum value of $Re_0^{\frac{1}{8}}\,Sc$ is about 1 for substances of practical interest.

The quality of data for testing these results is considerably lower than for small-scale smooth surfaces. Brutsaert (1982, §7.1) compared his version of Sutton's (1934) theory with an empirical mass-transfer formula due to Harbeck for reservoirs with areas between 4×10^{-3} and 120 km^2:

$$\bar{j} = 0.103d^{-0.1}. \tag{4.1}$$

This resulted from extensive measurements of means over a week or longer. Brutsaert recommended a value $z_0 = 2.28\times 10^{-4}$ m as a typical value for sea and lake surfaces deduced from measurements of the drag coefficient. The variation with windspeed was practically negligible except in high winds. With this value of z_0 we have inserted (4.1) on figure 4. If we assume a typical wind speed of 5 m/s at height 10 m then we find $Re_0 = 2.8$ for these conditions, giving $Re_0^{\frac{1}{8}}\,Sc = 1.0$. Our calculated mass-transfer coefficients are then satisfactorily close to (4.1), particularly in view of the scatter of Harbeck's results (Brutsaert 1982, figure 7.4), and of the fact that the profile of water-vapour concentration creates an unstable density gradient (see §6). We have also ignored in this comparison the existence of a roughness change at the shore.

Brutsaert gives a similar correlation for evaporation of water from shallow square pans between 0.1 and 6 m^2 in area,

$$\bar{j} = 0.129d^{-0.132}, \tag{4.2}$$

and we have plotted this in figure 4, again assuming $z_0 = 2.28\times 10^{-4}$ m, in the absence of actual experimental determinations. Again our predicted values are rather lower. Here, however, the effects of the roughness change and of the edges of pans are likely to be rather serious.

Results for evaporation of other liquids from pans of a similar size in the open air are given by Jones & McGugan (1978) and Jeulink (1983). Jones & McGugan were mainly concerned with comparison of results with evaporation of solvents from domestic waste, Jeulink with a study of the effectiveness of various fire-fighting foams in reducing evaporation. Hence detailed measurements for determining u_* and z_0 are again lacking. If one uses $z_0 = 2.28\times 10^{-4}$ m again to calculate u_* from the 10 m windspeed, one obtains the scattered values listed in table 1. On the whole these values are much lower than those indicated by the theory for appropriate values of $Re_0^{\frac{1}{8}}\,Sc$. The large values at low wind speeds might be due to natural convection (but see §6). Jeulink's results for 'iso-octane' have been omitted, since the precise isomer is not specified, creating an uncertainty in P_v of almost a factor of 3. (Here and elsewhere where vapour pressures were not evaluated by the original authors, we have used the Antoine equation with coefficients from Appendix A of Reid, Prausnitz & Sherwood (1977). In their chapter 11 they discuss means of estimating diffusion coefficients.)

There are several other ways in which one might process the results in table 1: one could assume a smooth surface, but more significant is the fact that the windflow in these experiments is far from the ideal configuration of a horizontally homogeneous boundary layer, since the upwind roughness lengths will be those characteristic of the terrain. Jeulink's experiments were conducted amongst 'sandhills' partly overgrown by small trees. It is possible to estimate u_* over the liquid surface from the simple relations of Hunt & Simpson (1982, §7.3.1). This implies that values of u_* may be $\frac{1}{3}$ of those used in table 1, and this would account for the low values listed.

Authors	Substance	Mean 10 m windspeed	$\bar{j}$
Jones & McGugan (1978), $d/z_0 = 4.39 \times 10^3$	isopropanol	0.5	0.2335
	acetone	6.7	0.0164
	perchloroethylene	10	0.0241
Jeulink (1983), $d/z_0 = 1.94 \times 10^4$	*n*-hexane	0.8	0.0650
	n-hexane	0.8	0.0522
	benzene	0.8	0.0626
	toluene	1.5	0.0460
	toluene	1.5	0.0498
	benzene	1.5	0.0299
	n-hexane	3	0.0365
	n-hexane	3	0.0332
	toluene	3	0.0209
	benzene	4.5	0.0422

TABLE 1. Summary of evaporation-pan experiments, assuming logarithmic velocity profile, $z_0 = 2.28 \times 10^{-4}$ m

We conclude that, in most of these experiments, there is insufficient detail to do more than confirm the order of magnitude of our predicted values.

Some rather more careful experiments involving roughness effects were conducted by Reijnhart & Rose (1980) in which a rough surface was placed upwind of an evaporation pan in a wind tunnel. Unfortunately, velocity profiles were measured only upwind, not over the pool itself. They achieved a good match with numerical solutions of the Reijnhart *et al.* (1980) model by accounting for the roughness change by the *ad hoc* procedure of using a new equilibrium smooth-wall velocity profile whose average velocity over the boundary-layer depth was equal to the average velocity upwind. In this case this gives a similar result for the change in friction velocity to that of Hunt & Simpson (1982). Thus these experiments do not in fact yield any data relevant to rough-wall evaporation.

Finally, figure 4 includes numerical results from Reijnhart & Rose (1980) using the Reijnhart *et al.* model for rough walls. This case was treated by taking the eddy diffusivity as $\kappa u_*(z+z_0)$, avoiding occurrence of a singularity at the wall, with no allowance for molecular diffusion. This is similar to our solution with $\beta = 0$, which according to (2.28*b*) would occur for $Re_0^{\frac{1}{2}}\, Sc = 0.339$, and this is in accord with figure 4. Reijnhart & Rose found that use of this solution for evaporation with the upwind roughness gave completely erroneous results, implying that evaporation would increase as z_0 increased at fixed u_*, instead of decreasing as found experimentally and predicted by including the roughness change.

5. Effect of high vapour pressure

The theory of §§2 and 3 has been developed on the assumption that the vapour behaves as a passive contaminant. There are two important factors limiting the validity of this assumption. One is the perturbation of the boundary-layer flow by a sufficiently large vertical velocity at the surface, even if the evaporating liquid has the same molecular weight and temperature as the air. The other is the possibility of buoyancy effects inducing changes in turbulence structure or driving convective mean flows. The buoyancy effect will be discussed in §6; an analysis of the effects of high vapour pressure follows here.

The effective vertical velocity of injection of fluid is

$$w_s = J/\rho_s, \tag{5.1}$$

where the mixture density at the surface, using the ideal-gas law, is

$$\rho_s = [M_A(P_0 - P_v) + M_v P_v]/RT, \tag{5.2}$$

where M_A is the effective molecular weight of air and P_0 the atmospheric pressure. Tennekes & Lumley (1972, §2.5) discuss the effect of mass transfer on a turbulent boundary layer, and their figure 2.9 suggests that the flow will be little affected if

$$w_s/u_* \lesssim 0.01. \tag{5.3}$$

This condition becomes

$$jc_s/\rho_s \lesssim 0.01, \tag{5.4}$$

and, since j is of the order 0.01–0.1, it will be violated as P_v/P_0 approaches unity, i.e. as the boiling point is approached.

A full analysis of this complex nonlinear interaction is beyond the scope of the solution methods of this paper, but the theory can be extended for practical use by a method standard in chemical-engineering analysis of such situations, known as 'film theory' (see e.g. Sherwood, Pigford & Wilke 1975). This is based on solving the following equations for combined vertical advection and diffusion:

$$J = \rho w = \rho\omega w - \rho D\frac{\mathrm{d}\omega}{\mathrm{d}z}, \tag{5.5}$$

where $\rho(z)$, $w(z)$ are mixture density and vertical velocity, and $\omega(z)$ the vapour mass fraction. The mass flux J is independent of z, since advection in the x-direction is ignored. Integration of (5.5) leads to the result that the mass-transfer coefficient is given by

$$j' = -j\frac{P_0}{P_v}\ln\left(1 - \frac{P_v}{P_0}\right), \tag{5.6}$$

where j is the value calculated using diffusion alone.

The result can be applied to a turbulent boundary layer if it is assumed that the major resistance to mass transfer occurs in the near-wall region where horizontal advection is unimportant and that the eddy diffusivity replacing D in (5.5) remains unaltered from its value in the unperturbed boundary layer. Although these assumptions appear rather rash, the result is very effective in predicting the variation of mass-transfer rate with P_v/P_0 observed by Reijnhart & Rose (1980) for toluene (see our figure 5). Experimental support for (5.6) in turbulent channel flows has been provided by Sherwood *et al.* (1975, pp. 175–178). In fact, O'Brien & Stutzman (1950) used the correction factor in (5.6) in processing their results reproduced in our figure 2(*b*): in their experiments P_v/P_0 was about 0.16 for benzene and 0.29 for acetone, but less than 0.1 for the other substances studied.

Reijnhart *et al.* (1980) treated high vapour pressures in their numerical model in a similar fashion by eliminating w from (5.5) to obtain

$$J = -\frac{\rho D}{1-\omega}\frac{\mathrm{d}\omega}{\mathrm{d}z}, \tag{5.7}$$

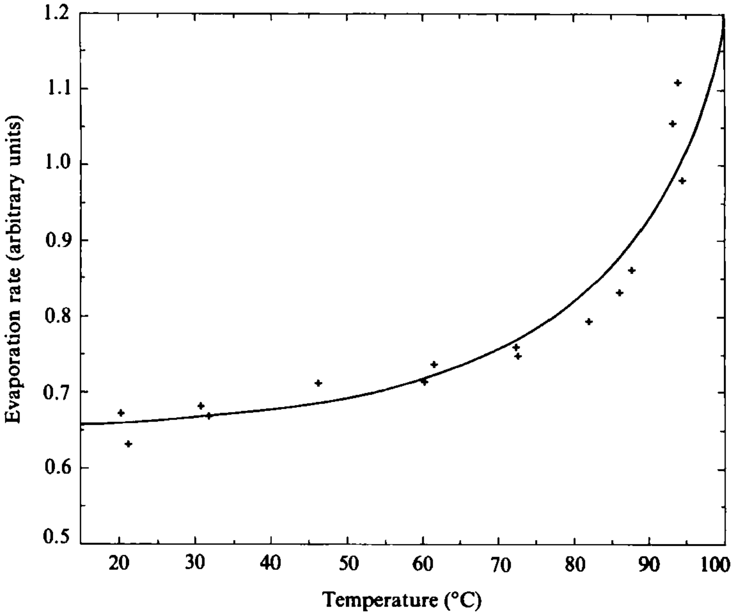

FIGURE 5. Comparison of data of Reijnhart & Rose (1980) for dependence of evaporation rate of toluene on temperature with variation predicted by film theory (5.6). The passive contaminant evaporation rate is taken as 0.65 (arbitrary units). +, data from figure 4 of Reijnhart & Rose.

again neglecting the effects of horizontal advection. They then used a diffusivity enhanced by the factor $(1-\omega)^{-1}$ in their numerical scheme. They introduced a further approximation to remove the nonlinearity by evaluating the diffusivity by linear interpolation between its enhanced value at the boundary and the original value at the top of the viscous sublayer.

Note that (5.6) tends to infinity as the boiling point is approached. This is physically reasonable, since in a boiling pool the vaporization rate is controlled by the rate at which heat enters the pool, not by the rate at which vapour is removed by the wind. In fact the mean pool temperature can never quite reach the boiling point, as temperature gradients must exist to cause heat transfer at the nucleation sites.

6. Estimates of buoyancy effects

The density difference ratio between the saturated vapour and the air at the same temperature is

$$\Delta' = \frac{\rho_S - \rho_A}{\rho_A} = \left(\frac{M_V}{M_A} - 1\right)\frac{P_V}{P_0}, \tag{6.1}$$

where ρ_S is given by (5.2) and $\rho_A = P_0 M_A / RT$. A dense vapour layer of thickness z_1 will tend to spread with a speed of order $(g\Delta' z_1)^{\frac{1}{2}}$, as observed in experiments on heavy-gas dispersion (see e.g. Brighton, Prince & Webber 1985), and so for this mean convective motion to be negligible we require the Richardson number

$$Ri = g\Delta' z_1 / U_1^2 \tag{6.2}$$

to be much less than unity. Using (3.7) and (6.1), this condition becomes

$$Ri = 0.02\frac{ngd}{U_1^2}\left(\frac{M_V}{M_A}-1\right)\frac{P_V}{P_0} \ll 1. \tag{6.3}$$

Secondly, we can also gauge the dynamic effects of the density change due to the vapour by evaluating the Monin–Obukhov lengthscale corresponding to a mass flux J of vapour from the surface. Monin & Yaglom (1971, §7.1) explain how this parameter measures the gravitational influence of a temperature gradient on the structure of a turbulent boundary layer. To apply their analysis to the effect of vapour, we note that the contribution of density fluctuations to the buoyancy forces in the turbulent kinetic-energy balance is, to adapt Monin & Yaglom's equations (7.1) and (7.2),

$$B = -g\overline{\rho' w'} = -g\Delta'\rho_0\overline{\chi' w'}, \tag{6.4}$$

and the vertical flux of the scalar quantity χ is given by

$$\overline{\chi' w'} = \frac{J}{c_S} = u_* j \tag{6.5}$$

(cf. (2.25)). The Monin–Obukhov lengthscale is defined by

$$L = \rho_0 u_*^3/\kappa B \tag{6.6}$$

(Monin & Yaglom 1971, equations (7.2) and (7.12)). The meaning of this lengthscale is that stratification influences the boundary-layer structure significantly only at heights z of order $|L|$. In our case, we require $|z_1/L| \ll 1$ to ensure that the vapour acts as a passive contaminant. In fact this requirement probably need not be interpreted too stringently if we base L on the surface mass flux, since the flux will decrease with height in our developing internal boundary layer. From (2.12), (6.2), (6.4) and (6.5) we have

$$\frac{z_1}{L} = \frac{j}{n^2\kappa}Ri, \tag{6.7}$$

and the factor multiplying Ri is of order unity in the range of practical interest, so that this criterion is equivalent to (6.3).

In the wind-tunnel experiments discussed in §4.1 the largest values of z_1/L (generally slightly greater than Ri) were all considerably less than 1: 0.08 (Gray 1974), 0.06 (O'Brien & Strutzman 1950), and less than 0.02 for the others. Thus it appears that buoyancy can be ruled out as a major factor contributing to the inconsistencies seen in figure 2(*b*).

In §4.3 we noted that there were greater discrepancies in the results for evaporation from open-air pans (see table 1). Evaluating z_1/L for Jones & McGugan's (1978) isopropanol test gives only 0.04, but in Jeulink's (1983) *n*-hexane tests with $U_1 = 0.8$ m/s this parameter reaches about 0.25. Of the factors in (6.3), it is in fact variations in P_V/P_0 that give the greatest differences between experiments. Taking the correlation for lakes given in figure 4 with $d = 228$ m, $U_1 = 5$ m/s and temperature 10 °C gives z_1/L as only 0.024.

7. Conclusions

In this paper we have presented a new analytical method of calculating the mean evaporation rate, or mass-transfer coefficient, from a plane liquid surface into a turbulent boundary layer. The theory is based on a combination of recent analysis of diffusion from a line source with relations for the near-wall equilibrium profiles of vapour concentration. The solution involves no new empirical constants, and should be valid for a large range of pool sizes for both smooth and rough surfaces. Over this large range a simple power-law dependence on pool size is not valid.

There are great inconsistencies between experimental results for nominally similar parameter ranges, so it is not possible to assess the accuracy of our results, but it does appear that the more careful experiments give a good match. The most serious limit on the validity of the theory for passive vapours is the requirement $n \ll 1$. For some of the experimental data in figure 2(*b*), d/z_0 is around 10^3, with n greater than $\frac{1}{3}$. In the region where the theory matches the more reliable data, $d/z_0 \approx 10^4$ and $n \approx \frac{1}{4}$, so this condition does not seem too limiting in practice.

Since the data are so scattered, particularly for larger-scale, outdoor experiments, it would be desirable for new carefully controlled experiments to be carried out. These are needed to investigate the doubts about the dependence on Schmidt number discussed in §4.2 and to study the effects of roughness change, high vapour pressure and of buoyancy, which are liable to become important for actual accidental spills of hazardous substances. We have suggested simple practical ways of extending the theory to cover the first two factors, but to include buoyancy will require application of results from current research on heavy-gas dispersion.

This work was done for the UK Health and Safety Executive. However, all views and opinions expressed are those of the author alone; they do not necessarily reflect either the views or the policy of the Health and Safety Executive.

Appendix A. Inversion of the Laplace transform of the mass flux

The Laplace transform (3.1*a*) is to be inverted to yield $j(X)$ with $\tilde{\chi}_0 = p^{-1}$ using the standard Bromwich contour integral:

$$j(X) = \frac{1}{2\pi \mathrm{i}} \int_C \mathrm{e}^{pX} \tilde{j}(p)\, \mathrm{d}p, \qquad \text{(A 1)}$$

where C is a contour parallel to the imaginary axis and passing to the right of the singularities of $\tilde{j}(p)$ (Carslaw & Jaeger 1963, chap. IV). The integrand has a branch point at $p = 0$ and a simple pole at $p_0 = \mathrm{e}^A$. To cast (A 1) in a more manageable form, it is desirable to deform C into a contour C' wrapped around a branch cut along the negative real axis as shown in figure 6. However, the pole apparently gives a contribution to $j(X)$ that grows exponentially, whereas one expects this evaporation problem to have a decreasing solution for j. In fact this contribution may be ignored because it represents the effect of an eigensolution for the diffusion equation with values of χ prescribed on the boundary: the expression

$$\chi(X, Z) \propto \mathrm{e}^{p_0 X} K_0 \left[\frac{p_0^{\frac{1}{2}} Z^{\frac{1}{2}(n+1)}}{\frac{1}{2}(n+1)} \right] \qquad \text{(A 2)}$$

satisfies (2.20) and condition (2.29*a*) with $\chi_0 = 0$ along the whole x-axis. The appearance of this unwanted solution is a consequence of letting the logarithmic profile exist arbitrarily close to the surface, whereas in fact it merges into the diffusive sublayer: it can be ruled out because it violates the physical condition $(\chi_0 - \chi)/j > 0$. Returning to figure 6 and making the contour deformation $C \rightarrow C'$ now yields the result (3.2).

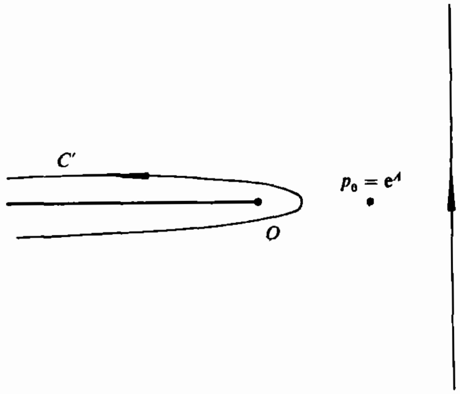

FIGURE 6. Deformation of the contour used in Appendix A. O is the origin in the p-plane.

Appendix B. Evaluation of integrals (3.2*b*) and (3.5*b*)

Integrating (3.2*b*) by parts and substituting $s = p\xi$, we obtain

$$G(\xi) = \frac{1}{2} - \int_0^\infty \pi^{-1} \tan^{-1}\left[\frac{\ln\xi - \ln s}{\pi}\right] e^{-s}\, ds. \tag{B 1}$$

A formal expansion of this integral can be obtained by expanding the inverse tangent as a Taylor series in $\ln s$ to give

$$G(\xi) = \frac{1}{2} - \frac{g_0}{\pi}\tan^{-1}\frac{\ln\xi}{\pi} + \frac{g_1}{\ln^2\xi + \pi^2} + \frac{g_2 \ln\xi}{(\ln^2\xi+\pi^2)^2} + \frac{g_3(\ln^2\xi - \frac{1}{3}\pi^2)}{(\ln^2\xi+\pi^2)^3} + \ldots, \tag{B 2a}$$

where

$$g_j = \int_0^\infty e^{-s}(\ln s)^j\, ds. \tag{B 2b}$$

These integrals can be evaluated by observing that

$$\sum_{j=0}^{\infty} \frac{g_j x^j}{j!} = \int_0^\infty e^{-s} e^{x \ln s}\, ds = \Gamma(1+x)$$

$$= 1 - \gamma x + \tfrac{1}{2}(\gamma^2 + \tfrac{1}{6}\pi^2)x^2 - \tfrac{1}{6}(\gamma^3 + \tfrac{1}{2}\pi^2\gamma + 2\zeta(3))x^3 + \ldots. \tag{B 3}$$

Here we have used Abramowitz & Stegun's (1972) formulae (6.4.1), (6.4.2), (3.6.23) and (23.2.24), ζ being the Riemann zeta function. Hence $g_0 = 1$, $g_1 = -0.5772$, $g_2 = 1.978$ and $g_3 = -5.445$.

Integration by parts of the terms of (B 2*a*) leads to a similar series for $\bar{G}$:

$$\bar{G}(\xi) = \frac{1}{2} - \frac{\bar{g}_0}{\pi}\tan^{-1}\frac{\ln\xi}{\pi} + \frac{\bar{g}_1}{\ln^2\xi + \pi^2} + \frac{\bar{g}_2 \ln\xi}{(\ln^2\xi+\pi^2)^2} + \frac{\bar{g}_3(\ln^2\xi - \frac{1}{3}\pi^2)}{(\ln^2\xi+\pi^2)^3} + \ldots, \tag{B 4a}$$

where

$$\left.\begin{aligned} \bar{g}_0 &= 1, \\ \bar{g}_1 &= 1 - \gamma = 0.4228, \\ \bar{g}_2 &= 1 + (1-\gamma)^2 + \tfrac{1}{6}\pi^2 = 2.824, \\ \bar{g}_3 &= (1-\gamma)^3 + (3 + \tfrac{1}{2}\pi^2)(1-\gamma) - 2\zeta(3) = 1.025. \end{aligned}\right\} \tag{B 4b}$$

The convergence properties of the series (B 2) and (B 4) are not obvious, but they do provide a valid asymptotic expansion for large ξ. Moreover $\bar{G}(\xi)$ has been computed numerically over the range $|\ln \xi| \leqslant 50$ and found to agree with the sum of terms in (B 4*a*) to within about $\frac{1}{2}\%$. Hence these series are the most convenient way for obtaining numerical values, and have been so used to calculate the results of §4.

I am very grateful to Dr D. M. Webber for supplying all the results in this Appendix.

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