

## SHORTER COMMUNICATIONS

### SURFACE RENEWAL PHENOMENA IN LIQUID-LIQUID DROPLET SYSTEMS WITH AND WITHOUT MASS TRANSFER

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The numerous theoretical descriptions of mass transfer across fluid interfaces can be divided into two basic groups. The first of these is the well known film theory [1, 2], which postulates a laminar layer on each side of the interface. The supposition that solute concentrations within both these layers are at steady-state implies that there is no exchange of fluid with the bulk phases, which may be turbulent. By contrast, the various surface renewal theories all assume that this exchange does occur and a number of mechanisms have been proposed for this process. These include the Higbie model [3] which, when applied to a droplet for example, suggests that fresh surface is continuously created in the region of the front stagnation point and convected to the rear as a result of the no-slip condition with the continuous phase. Thus, this model envisages complete replacement of the laminar film at regular intervals. An alternative mechanism, based on the random intrusion of turbulent eddies into the interface, has been proposed by Danckwerts [4, 5]. A further variation due to Kishinevski and Pamfilov [6] also argues in favour of turbulent renewal but maintains that solute transfer near the interface proceeds by turbulent convection as opposed to the assumption of molecular diffusion common to all the earlier models. Despite their differences, however, these three basic renewal theories all have the one aspect in common namely that the surface renewal mechanism is linked to the hydrodynamics of the system.

In a recent experimental study, we have measured the frequency of disturbances at a predetermined position on the surface of a growing pendant droplet immersed in a second immiscible liquid phase. Such a situation is representative of conditions at the dispersed phase inlet of a liquid extraction column and is very relevant to column design procedures, particularly since an appreciable fraction of the total mass transfer occurring within the unit is known to take place during the droplet formation period. Furthermore information on surface renewal rates as a function of surface position and droplet size is a prerequisite to modelling the transfer process for growing pendant droplets.

The experimental technique made use of a finely focused u.v. laser pulse to induce a local colour change in a suitable photochromic chemical tracer dissolved in the droplet, thereby "labelling" a small element of the droplet surface. The subsequent history of this spot was then recorded by high speed cinematography and the time intervals between successive perturbations of the coloured spot measured directly from the film record. Although the use of photochromic tracers for flow visualisation purposes had been proposed earlier by [7, 8], they apparently failed to find a tracer suitable for use in the region of liquid-liquid interfaces [9]. In this case it is essential to use tracers whose coloured complexes do not disturb the fluid interface. This difficulty was overcome in the present work by using the photochemical reduction of an aqueous solution of potassium ferric oxalate in the presence of potassium ferricyanide as the tracer. Irradiation of this

solution resulted in a deep blue colouration due to the formation of ferrous ferricyanide. The colour change took place in less than 4 ms and was quite satisfactory for the present purposes. The depth of penetration of the laser was estimated to be 50 nm.

Throughout this work, the dispersed phase was a dilute aqueous solution of the inorganic tracer and the continuous phase was toluene. Each phase was initially saturated with the other before any measurements were made. Aqueous droplets were allowed to form at a single nozzle and a small element of surface was labelled by triggering the laser early on during the droplet formation period. Measurements were made labelling the droplet surface at three principal positions; near the apex, at the major diameter and adjacent to the nozzle.

The measurements were then repeated with an undistributed solute present in the continuous toluene phase so that diffusion took place into the aqueous droplet. Three solutes were investigated viz. 2v/v% propionic acid, 3v/v% diacetone alcohol and 4v/v% acetone. A limited amount of work was also carried out with the "two component" system aqueous tracer solution/ethyl acetate so that ethyl acetate diffused into the aqueous droplet. All these systems behaved similarly from a phenomenological point of view.

Our findings may be summarised as follows:

(1) In the absence of mass transfer, there were no indications of any disturbance to the tracer spot and this was verified for nozzle Reynolds numbers as high as 300. These results indicate that surface renewal due to hydrodynamic turbulence as proposed by Danckwerts [4] did not occur in these systems in the absence of mass transfer.

The data did however indicate surface circulation towards the nozzle, although the labelled element of surface remained unperturbed. This circulation trend is consistent with published work which indicates that recirculation within the droplet commences in the Reynolds number range 10-35 [10].

(2) Cine films obtained with an undistributed solute were striking in that the laser-induced spot experienced a series of violent, sporadic disturbances which led progressively to the disintegration of the spot. Furthermore these perturbations persisted for a measurable period of time, although this interval was difficult to determine since the disturbances tended to decay only slowly. Interfacial disturbances of this type are loosely classed as Marangoni effects and a basic theoretical analysis, due to Sternling and Scriven [11], argues that the phenomenon is due to spatial variations in interfacial solute concentrations which arise spontaneously during mass transfer. Under favourable conditions, the consequent interfacial tension gradients induce a flow in the plane of the interface which must be supplied by the movement of fresh fluid from the interior of the droplet.

It is therefore apparent that, so far as the present systems are concerned, there was a complete absence of any interfacial disturbances attributable solely to hydrodynamic turbulence.

On the other hand, in the presence of an undistributed solute, Marangoni effects are very possibly the mechanism by which the observed interfacial disturbances are induced and therefore the mechanism by which mass transfer rates are increased beyond the level predicted by molecular diffusional theory alone. A full account of this work will be published in due course.

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## NONSIMILAR LAMINAR NATURAL CONVECTION IN A THERMALLY STRATIFIED FLUID

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## NOMENCLATURE

$a$ ,	ambient temperature gradient, $dT_\infty/dx$ ;
$C_f$ ,	local skin-friction coefficient;
$F$ ,	dimensionless stream function;
$F_{wp}$ ,	mass transfer parameter;
$F''(\xi, 0)$ ,	surface skin-friction parameter;
$g$ ,	gravitational acceleration;
$G$ ,	dimensionless temperature;
$G'(\xi, 0)$ ,	surface heat-transfer parameter;
$Gr_{x^*}$ ,	local Grashof number;
$k$ ,	thermal conductivity;
$Nu$ ,	local Nusselt number;
$Pr$ ,	Prandtl number;
$q$ ,	local heat-transfer rate per unit area;
$T$ ,	temperature;
$T_\infty$ ,	ambient temperature;
$T_\infty(0)$ ,	ambient temperature at $x = 0$ ;
$x, y$ ,	distances along and perpendicular to the surface.

## Greek symbols

$\beta$ ,	bulk coefficient of thermal expansion;
$\eta, \zeta$ ,	transformed co-ordinates;
$\nu$ ,	kinematic viscosity;
$\rho$ ,	density;
$\tau$ ,	shear stress at the surface;
$\psi$ ,	dimensional stream function.

## Superscript

' differentiation with respect to  $\eta$ .

## Subscripts

w, condition at the surface;  
 $\zeta$ , derivative with respect to  $\zeta$ .

## 1. INTRODUCTION

THE PROBLEMS of natural convection heat transfer from bodies immersed in fluids do not always admit similarity solutions. The nonsimilarity in this case arises either due to thermally stratified fluid (in which the body is immersed) or due to non-uniform surface temperature of the body. Stratified fluid occurs quite frequently in nature (for example in the atmosphere and ocean) as well as in a number of engineering devices. Although the effect of stratification on the heat removal processes is important, only a few studies have been reported in the literature. Eichhorn [1] studied the effect of linear thermal stratification on the heat transfer of a vertical plate and obtained solutions for three terms in the series expansions of the partial differential equations. Subsequently, Fujii *et al.* [2] considered the effect of non-linear thermal stratification on the foregoing problem and obtained solutions for four terms of the series. Recently, Chen and Eichhorn [3] re-studied the problem of [1] and obtained the solution using the local nonsimilarity method developed by