PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Introduction: significance of capillary driven flows in materials processing

The Royal Society

Phil. Trans. R. Soc. Lond. A 1998 **356**, 815-818
doi: 10.1098/rsta.1998.0188

The Royal Society

Introduction: significance of capillary driven flows in materials processing

By E. D. Hondros

Department of Materials, Imperial College of Science, Technology and Medicine, London SW7 2BZ, UK

In this introductory paper to the Royal Society Discussion Meeting, Marangoni and Interfacial Phenomena in Materials Processing, we present first the historical background to the general phenomenon of capillary gradient-driven flows, or 'Marangoni' flows. The many early observations in organic and inorganic liquids reflect the intense scientific curiosity surrounding this and other capillarity-induced phenomena. However, only in recent decades has the significance of this effect in various industrial technologies been appreciated. In this volume, we have deliberately focused on Marangoni observations relevant to the procedures and technologies involved in the production and processing of materials. The papers collected here demonstrate a clear significance of Marangoni flows in a variety of processes.

Keywords: Marangoni flow; high temperature materials; materials processing; capillary action; surface tension gradients

'... numerous motions of extremely curious and wonderful characters in fluids undergoing evaporation.'

James Thomson 1855

The broad theme of this volume relates closely to the science of capillary action in fluids and, in particular, how one somewhat neglected aspect of this science is seen today to bear on important phenomena associated with the processing of modern materials. Since capillarity has been one of the important classical branches of study in the natural sciences, it is no surprise that nearly all the famous names of science of the 18th and 19th centuries were attracted to this field, including, among many others, Gauss, Young, Franklin, Laplace and Raleigh. Thus much of the basic understanding of this theme had become established by the turn of the 20th century; see, for example, the seminal article, 'Capillary action', by Maxwell (1878), who also describes the historical development of the subject up to that time.

Specifically, we are concerned here with phenomena induced by surface tension gradients which derive from temperature or surface concentration variations. During the middle of the last century, James Thomson (1855), the elder brother of Lord Kelvin, experimented with the spreading of alcohol drops on the surface of water and was probably the first to invoke the idea of surface tension-driven flows to explain this and many other intriguing manifestations of capillary gradients, such as the 'tears of strong wine' in liquids containing alcohol, or the bizarre 'camphor dance'. The extraordinary spread of interest in such surface phenomena in the past century and the resulting comprehensive literature on the subject (Tomlinson (1873) cites 37 references in his paper on the motions of camphor) surely reflects the easy accessibility of such study, requiring only elementary chemical substances and equipment, accurate observations and an enquiring intellect; in the absence of a bewildering armoury of the sophisticated equipment of our time, anyone could dabble in the intricacies of soap bubbles.

Without entering into details of the numerous fascinating studies involving movements on liquid surfaces, and the heatedly contested claims on the priority of discovery, it suffices for our purposes to mention the publication by Marangoni (1878), who provided a wealth of detailed information on the effects of variations of the potential energy of liquid surfaces arising from variations in temperature and composition. These effects have now come to be conveniently associated with his name, noting incidentally that Thomson's (1855) short but illuminating paper was curiously forgotten during these debates on priority.

Among the more important general phenomena involving Marangoni flows, we note that associated with the name of Bénard (1901), which refers to the formation of a polygonal cellular structure in a thin liquid layer heated from below, an effect discovered recently in thin semiconductor films, and a subject of continual interest and theoretical analysis, as reported in this volume.

Yet for decades, the earlier numerous observations lay in the realm of interesting scientific curiosities, useful for illustrating the wonders of surface tension. The role of the basic effect in technology was probably first demonstrated by chemical engineers in the field of liquid–liquid extraction: there is a natural progression from classical observations of the twitching of air bubbles in alcohol containing water, to the spontaneous agitation of interfaces between unequilibrated fluids, leading to the contemporary extensive knowledge in the field of interfacial turbulence.

This Discussion Meeting is firmly in the field of materials processing, encompassing all the procedures whereby raw products are transformed into useful engineering materials: arguably the study of materials processing is one of the high priority R&D pursuits in most materials research centres today.

We focus here on a variety of observations in materials processing, particularly in metallic systems which have been suspected to demonstrate Marangoni flows: e.g. in pyrometallurgy, in which interest lies in interfacial mass transfer; in the complex mixing hydrodynamics of furnaces containing melts; in the erosion of the walls of ceramic crucibles containing liquid metals. These instances reflect both a scientific and industrial interest. In fact, phenomena attributable to Marangoni flows have been reported in innumerable instances relevant to modern technologies, such as in hot salt corrosion in aero-turbine blades; the drying of solvent-containing paints; the drying of silicon wafers used in electronics; even the modelling of the role of Marangoni flows in the micro-pools produced by plasma disruptions on the first wall of a prospective thermonuclear fusion reactor.

We note the disparate nature of the above observations, the only link between them being the suspected or demonstrated presence of Marangoni flows. Each of the subjects has been explored separately by workers pursuing problems in their own field, whether this be weld penetration or crucible erosion; and in each subject area, those concerned have arrived, often with some hesitation, at an explanation based on capillary-driven flows. Hence, one of our objectives in this meeting has been to stimulate interactions between theoreticians and specialists engaged in the various subject areas. Indeed, in order to understand the various phenomena in the materials processing field, the simple classical treatment has in general been sufficient. The urgent requirement has been for reliable high temperature physicochemical data,

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

such as surface tension, viscosity and thermal conductivity in alloy systems, a matter which is now beginning to be seriously addressed and is reported in this volume. Again, the recent theoretical studies of more complex convectional patterns, such as those reported here in Bénard cellular systems, should be valuable in future studies of high temperature multiphase metallic melts.

There is one contemporary area in which Marangoni phenomena have been studied in a coordinated manner, namely in melt and crystal processes in microgravity conditions, associated with space research programmes. Here, a whole literature has now emerged, following the considerable experimental and theoretical research carried out which is reported in regular conferences devoted to the broader field of materials and fluidic processes in microgravity. We note that leading workers from this field have contributed to this Meeting and also in a one-day associated event sponsored by the CIBA Foundation. Their experience will stimulate these Discussions on materials processes important to industry. One of the prime needs of our theme is cross-fertilization.

In this Meeting, which started off as a tentative exploration of past speculative reports, we have been rewarded by several papers which, through dedicated experimentation and the application of new data on physicochemical properties combined with computer modelling, not only confirm earlier speculations, but also reveal original insights and unexpected Marangoni-related phenomena, in particular, in materials technologies.

As examples, we mention the following:

(1) The confirmation that the problem of 'flux line erosion', which has for years bedeviled the glass-making and pyrometallurgical industries, is clearly related to Marangoni flows which wash the refractory wall with a thin film of corrosive slag from the bulk. Here we are tempted to quote the final remarks of Professor Makai in his paper: 'The trivial phenomenon of "tears of wine" that was caught by the piercing eyes of the scientist Thomson, holds the key to the solution of the industrially serious problem of corrosion of refractories.'

(2) Again, by applying newly acquired data on the surface tension of alloys at high temperatures in combination with modelling of localized melting, there is a clear demonstration of how surface active solutes in steel can switch the temperature coefficient of surface tension to positive values; in turn, this reverses the direction of the Marangoni flows in the molten pool during arc or laser welding, giving rise to deeper penetration of molten metal.

(3) In another elegant example of computerized modelling, a team from the NPL and Imperial College has demonstrated that in the rapidly growing technology of producing clean industrial alloys for advanced applications using electron beam melting, Marangoni flows driven by surface active additives can be used to control the distribution and removal of inclusions.

(4) In a more theoretical description backed up by experimental data, a team from Grenoble shows that in the reactive spreading of liquid alloy droplets over a ceramic substrate (which bears on the modern technology of multi-material processing by liquid metal infiltration), Marangoni convection governs the process kinetics through the transport of reactive species to the spreading front.

(5) Some of the problems of growth of both organic and inorganic crystals in microgravity relate to perturbations arising from Marangoni flows, problems that are being tackled by the microgravity research community. Of more general interest, a Japanese team reports that in the growth of silicon crystals from the melt in micro-

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

gravity conditions, Marangoni instabilities abound, through temperature differences at the solid–liquid interfaces and also through the extreme sensitivity of the surface tension of silicon to oxygen in the ambient atmosphere.

Finally, it is hoped that this volume will help to extend to a wider audience the subject of Marangoni hydrodynamics and an appreciation of their relevance to materials phenomena; and furthermore, as in other analytical approaches used in modern materials research, the knowledge of capillary action and capillary-induced flow might form part of the common scientific equipment of students and workers engaged in this growing and commercially rewarding field of materials processing.

References

Bénard, H. 1901 Les tourbillons cellulaires dans une nappe liquide transportant de la chaleur par convection on régime permanent. *Ann. Chim. Phys.* Ser. 7, **23**, 62–144.

Marangoni, C. 1878 Difesa della teoria dell'elasticità superficiace dei liquidi. *Nuovo Cim.* Ser. 3, **3**, 97–115.

Maxwell, G. J. C. 1878 Capillary action. *Encyclopaedia Brittanica*, 9th edn. New York.

Thomson, J. 1855 On certain curious motions observable at the surfaces of wine and other alcoholic liquors. *Phil. Mag.* Ser. 4, **10**, 330–333.

Tomlinson, C. 1873 On the motion of camphor and of certain liquids on the surface of water. *Phil. Mag.* **46**, 376–388.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES