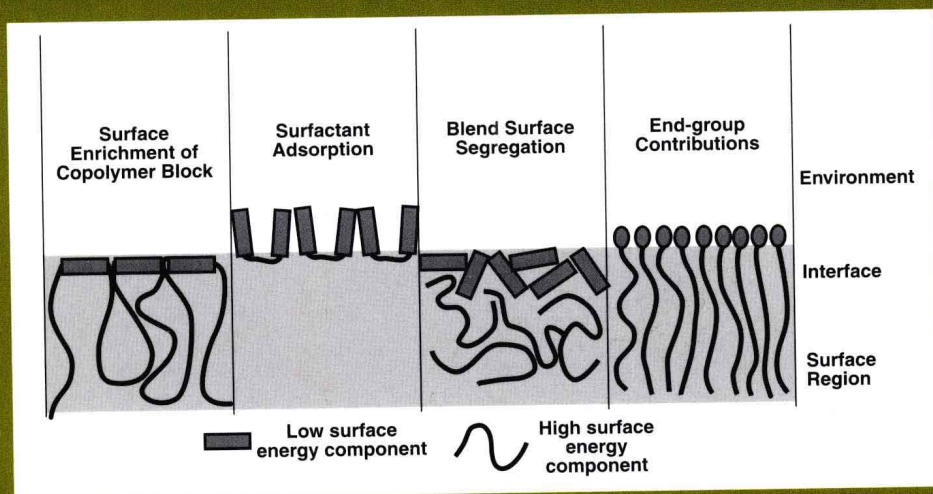


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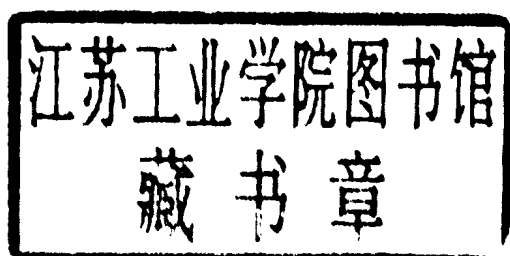
SURFACE CHARACTERIZATION METHODS

Principles, Techniques, and Applications



edited by
Andrew J. Milling

SURFACE CHARACTERIZATION METHODS



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**Principles, Techniques,
and Applications**

edited by
Andrew J. Milling

*University of Durham
Durham, England*



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Preface

During my career in chemistry, I have become increasingly aware that a multidisciplinary approach is required to carry out research in the field of surface characterization, and that this field is certainly not the sole reserve of the physical chemist. A host of experimental methodologies are available to researchers interested in surface analysis per se, or as an adjunct to other applications. The current literature is on the whole highly specialized, dealing with specific topics in great detail. While such books are of use to the specialist, it is felt that there is certainly a need for a reference text that provides a more general appreciation of the surface characterization methods currently in use or being developed in modern laboratories. The ubiquity of surfaces entails that many fields, ranging from the processing of particulate materials (such as colloids) to molecular recognition processes, require a deeper understanding of surface and interfacial properties. Indeed, this is exemplified in the burgeoning interest in surface chemistry within the life sciences, and this is an important feature of the text.

The book, comprising a series of monographs by contemporary experts, outlines the underlying scientific principles and experimental techniques for a broad sample of discrete surface analysis techniques. The assembled material draws heavily from cornerstones of physical and analytical chemistry. Specific themes such as surface energies, electrokinetic characterization, van der Waals interactions, wetting behavior, self-assembly, adsorption behavior, mass spectroscopy, and scattering methodologies are described within the general context of surface analysis.

The book is intended to serve as a resource text and also to aid the active researcher in solving surface analysis problems that may arise in a variety of

circumstances. The “techniques” aspect illustrates that there are often various approaches to characterizing a particular aspect of surface behavior, using in many cases equipment that either is commercially available or can be readily assembled. The scope of the material will appeal to researchers from final-year undergraduate students through senior researchers.

I would like to collectively thank several colleagues for their kind assistance in proofreading at various stages, for which I am extremely grateful. I would like to especially thank all the contributing authors, Professor A. Hubbard, for his great help in the genesis of this project, and Anita Lekhwani and Joseph Stubenrauch at Marcel Dekker, Inc., for their significant contribution and enthusiasm in the production of this text.

Andrew J. Milling

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Measurement of the Surface Tension and Surface Stress of Solids

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I. INTRODUCTION

The surface tension is a fundamental parameter of a solid since it depends directly on the binding forces of the material [1,2]. It is also of great practical interest. The adsorption of substances onto solids is determined by the surface tension, and it is of fundamental importance in biocompatibility [3]. The behavior of colloidal dispersions, adhesion, and friction are influenced by the surface tension. Since the surface tension enters the Young equation, it is important for contact angle phenomena such as detergency, wetting, water repellency, and flotation. When making micro- or nanoscopic structures, a knowledge of the surface tension is essential since, owing to the large surface-to-volume ratio, surface phenomena dominate the fabrication process [4]. The reconstruction of silicon and germanium surfaces [5,6] and the shape and structure of small particles [7,8,9] depends on the surface tension. In addition, it influences crystal growth [10,11].

The surface tension is equal to the reversible work per unit area needed to create a surface. For liquids this definition is sufficient. If a liquid (effects due to a possible curvature of the surface are ignored) is distorted, there is no barrier to prevent molecules from entering or leaving the surface. In the new equilibrium state each molecule covers the same area as in the original undistorted state. The number of molecules in the surface has changed, but the area per molecule remains the same. Such a deformation is called plastic.

The main difference between a solid and a liquid is that the molecules in a solid are not mobile. Therefore, as Gibbs already noted, the work required to create new surface area depends on the way the new solid surface is formed [12]. Plastic deformations are possible for solids too. An example is the cleavage of a crystal. Plastic deformations are described by the surface tension γ also called superficial work.* The surface tension may be defined as the reversible work at constant elastic strain, temperature, electric field, and chemical potential required to form a unit area of new surface. It is a scalar quantity. The surface tension is usually measured in adhesion and adsorption experiments.

New surface area of a solid can also be created elastically by stretching pre-existing surface. In this case molecules cannot migrate to the surface and therefore the number of molecules remains constant but the area occupied by

*Different authors use different symbols and different expressions for the surface tension. The term "superficial work" with the symbol σ was proposed by Linford [16]. The IUPAC recommends the symbol γ_π [15]. To avoid confusion with the surface charge density and for practical reasons we follow Lyklema (J. Lyklema, *Fundamentals of Interface and Colloid Science*, Vol. 1, Academic Press, London, 1991, p. 2.100) and Moy and Neumann (E. Moy and A. W. Neumann, in A. W. Neumann and J. K. Spelt (eds.), *Surfactant Science Series* 63, *Applied Surface Thermodynamics*, Marcel Dekker, New York, 1996, pp. 333–378), who used the symbol γ . Rusanov and Prokhorov [21] use "thermodynamic surface tension σ ."