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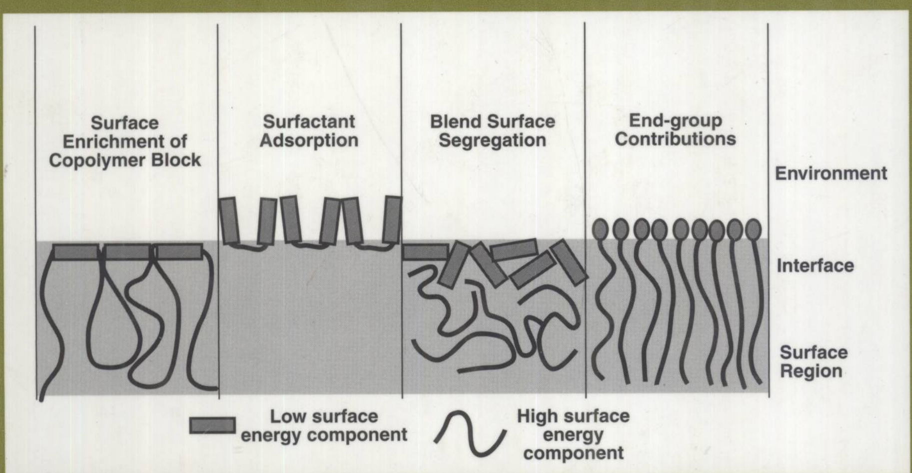
SURFACE CHARACTERIZATION METHODS

Principles, Techniques, and Applications



edited by

Andrew J. Milling

SURFACE CHARACTERIZATION METHODS

Principles, Techniques, and Applications

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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.

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Contents

1

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

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*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."

one molecule increases. Elastic deformations are described by the surface stress Υ_{ij}.* The surface stress can be defined as the reversible work needed to form a unit area of new surface by stretching a solid surface at constant temperature, electric field, and chemical potential with a linear stress. Since the response of a solid surface may depend on the direction the stress is applied, the surface stress is, in general, a tensorial quantity. For an isotropic material the directional dependence of the surface stress disappears, and it becomes a scalar quantity Υ. The surface stress is a surface excess property. However one should note that, in a real experiment, the measured mechanical work embodies terms that depend on the strain state of both bulk and surface [13]. The surface stress is mainly determined in mechanical experiments.

The change in the surface area of a solid is often described in terms of the surface strain. The total surface strain ε_{tot} is given by $d\Omega/\Omega = d\varepsilon_{\text{tot}}$, where Ω is the total area. The total strain may be divided into the plastic strain $d\varepsilon_{\text{p}}$ and the elastic strain $d\varepsilon_{\text{e}}$ so that $d\varepsilon_{\text{tot}} = d\varepsilon_{\text{p}} + d\varepsilon_{\text{e}}$.

In general the work required to form new surface area of a solid (plastic and elastic) is given by the expression [14]

$$\gamma^{\text{S}} = \frac{d\varepsilon_{\text{p}}}{d\varepsilon_{\text{tot}}} \cdot \gamma + \frac{d\varepsilon_{\text{e}}}{d\varepsilon_{\text{tot}}} \cdot \Upsilon \tag{1}$$

γ^{S} is called the ''generalized surface intensive parameter'' or ''surface energy'' [15,16]. The generalized surface intensive parameter depends on the path a certain state is reached while the surface tension and the surface stress are independent of the specific process. Therefore only γ and Υ are properties characterizing a solid surface, while γ^{S} is not a state function in a thermodynamic sense.

From a more fundamental point of view the difference between γ and Υ in an elastic solid arises from the inequality for immobile components of chemical potentials. In principle, for real solids such equalization is possible, but it proceeds very slowly so that always $\gamma \neq \Upsilon$ in practice.

Whether elastic or plastic behavior is observed depends not only on the process but also on the temperature. At very low temperature, real solids display mainly elastic properties. The higher the temperature, the larger the plasticity of the solid is. At temperatures close to the melting point, often methods developed for liquids can be employed to measure surface tension.

A determination of γ and Υ is often complicated in that solid surfaces are usually not in thermodynamic equilibrium. Even ideally pure solids have dislocations or vacancies that disturb the normal structure of the crystalline lattice.

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*Most authors use the term ''surface stress.'' Rusanov and Prokhorov [21] prefer the expression ''mechanical surface tension γ.'' The symbol Υ was also used by Linford [16], and we do not see a reason to choose another symbol.