



ESSENTIAL

COMPUTATIONAL MODELING IN CHEMISTRY

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Essential Computational Modeling in Chemistry

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General Preface

In the early eighties, when Jacques-Louis Lions and I considered the idea of a *Handbook of Numerical Analysis*, we carefully laid out specific objectives, outlined in the following excerpts from the “General Preface” which has appeared at the beginning of each of the volumes published so far:

During the past decades, giant needs for ever more sophisticated mathematical models and increasingly complex and extensive computer simulations have arisen. In this fashion, two indissociable activities, *mathematical modeling* and *computer simulation*, have gained a major status in all aspects of science, technology and industry.

In order that these two sciences be established on the safest possible grounds, mathematical rigor is indispensable. For this reason, two companion sciences, *Numerical Analysis* and *Scientific Software*, have emerged as essential steps for validating the mathematical models and the computer simulations that are based on them.

Numerical Analysis is here understood as the part of *Mathematics* that describes and analyzes all the numerical schemes that are used on computers; its objective consists in obtaining a clear, precise, and faithful, representation of all the “information” contained in a mathematical model; as such, it is the natural extension of more classical tools, such as analytic solutions, special transforms, functional analysis, as well as stability and asymptotic analysis.

The various volumes comprising the *Handbook of Numerical Analysis* will thoroughly cover all the major aspects of Numerical Analysis, by presenting accessible and in-depth surveys, which include the most recent trends.

More precisely, the Handbook will cover the *basic methods of Numerical Analysis*, gathered under the following general headings:

- Solution of Equations in \mathbb{R}^n ,
- Finite Difference Methods,
- Finite Element Methods,
- Techniques of Scientific Computing.

It will also cover the *numerical solution of actual problems of contemporary interest in Applied Mathematics*, gathered under the following general headings:

- Numerical Methods for Fluids,
- Numerical Methods for Solids.

In retrospect, it can be safely asserted that Volumes I to IX, which were edited by both of us, fulfilled most of these objectives, thanks to the eminence of the authors and the quality of their contributions.

After Jacques-Louis Lions' tragic loss in 2001, it became clear that Volume IX would be the last one of the type published so far, i.e., edited by both of us and devoted to some of the general headings defined above. It was then decided, in consultation with the publisher, that each future volume will instead be devoted to a single "*specific application*" and called for this reason a "*Special Volume*". "*Specific applications*" will include Mathematical Finance, Meteorology, Celestial Mechanics, Computational Chemistry, Living Systems, Electromagnetism, Computational Mathematics etc. It is worth noting that the inclusion of such "specific applications" in the *Handbook of Numerical Analysis* was part of our initial project.

To ensure the continuity of this enterprise, I will continue to act as Editor of each Special Volume, whose conception will be jointly coordinated and supervised by a Guest Editor.

P.G. CIARLET
July 2002

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The Modeling and Simulation of the Liquid Phase

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An overview on the theoretical and computational methodologies developed so far to study liquids and solutions is presented. The main characteristics of the different methods are outlined and the advantages and shortcomings of the computational approaches are discussed. Particular attention is focused on a specific class of methods, known as continuum solvation models, for which a more detailed description of theoretical and computational aspects is presented. For this class of methods, the concept of molecular cavity is introduced together with a description of the numerical techniques developed to mesh the corresponding surface. For selected methods representing those of larger use, an overview on their applications to the evaluation of energies and properties of liquid systems and molecules in solution is also presented.

Introduction to Liquids

For very long tradition chemistry has to deal with liquids. The chain of chemical manipulations performed in laboratories and in factories are mostly performed in a liquid medium and one of the first questions asked when a new chemical is introduced in the use is what is its solubility in solvents. There is a large number of solvents in use in the chemical practice, more than two thousand, and this number is not sufficient: often it is convenient to use solvent mixtures. Chemical reactions, the core of chemistry, are very sensitive to the solvent used to put in intimate contact the reagent species: often a delicate reaction fails if the solvent was not properly chosen. Important areas of chemical research are inherently tied to a solvent. An important example is that of biological systems. All the complex machinery of biological systems works only if the system is in water: without this solvent even the intimate structures of biological molecules collapse and lose their activity.

Chemists are so accustomed to consider many properties of liquids, from the basic physical properties to others, more specific and playing a role in specific cases in the large variety of problems that chemistry has to face. We cannot give here an overview of the properties of interest for liquids, many among which could be the object of computer modeling and we limit ourselves to indicate a few points more directly related to what will be exposed in the following of this chapter.

Liquids often occur in the chemical practice in large quantities. The effects due to the spatial limitations of the liquid sample have not great influence on the phenomena occurring at the interior, which in the current practice is called the bulk solvent. On large scale the bulk pure liquids and solutions exhibit isotropy. Liquids can be however dispersed. A typical example are the water droplets dispersed in the atmosphere, as for example in the fog. Other examples occur in liquid mixtures that present a miscibility lacuna. In all cases the ratio "surface region/bulk" can be relatively large and phenomena occurring at the interface may present properties different with respect to the same occurring in the bulk.

The region of separation between a bulk liquid and a solid body has in some cases a decisive importance. One example is the separation between a salt solution and a metal electrode. All the electrochemical phenomena are influenced by the behavior of this thin portion of the liquid. Another example are the phenomena leading to dissolution of solid bodies in the liquid phase, and to the deposition of material components of the liquid into solid particles. The surface of separation of a liquid and a solid surface presents features of different type when the liquid is in a limited amount.

The liquid phase can be present under the form of separate drops, or of a thin liquid film on the solid surface: both occurrences have a great importance in some chemical problems.

Surfaces of bulk liquids can be covered by a thin layer of an immiscible liquid. This is a phenomenon frequently observed in everyday life. Such thin layers can be organized into a structure that maintains some aspects of normal liquids but presents a high local order. With an appropriate selection of the chemical composition of this second phase, it is easy to form ordered layers of well-defined molecular thickness and membranes. Membranes, on their part, preserves fluid-like properties at their interior which can be exploited, for example, in the machinery of biological systems. A liquid can contain small solid particles within the bulk. Many phenomena and many practical applications are based on this particular type of liquid systems. A well-known phenomenon that has played an important role in the development of science is the Brownian motion. The solvent eases the dispersion in the bulk of such small particles, that are however subjected to gravity forces leading to sedimentation. Gravity, one of the basic forces in the universe, plays a little role in the microscopic approach to the study of material systems, but this example shows that there are reasons to forecast that in the future also gravity will be included into some computational models. A liquid can also contain at its interior portion of a second phase organized with specific shapes. This is the domain of micelles, vesicles and other similar structures, all subject of intense research both of basic type and addressing practical applications.

The ordering of specific chemical systems into layers and vesicles has a counterpart in bulk liquids. A special category of liquids are called liquid crystals. They combine macroscopic properties shared by all liquids, in particular the properties of assuming the shape of the vessel in which they are put and the capability of dissolving other chemicals, with a long range order making them similar to crystals. This long range order may assume different forms, to which corresponds specific names for the liquid crystal phase, smectic, nematic, cholesteric. In general the liquid crystal are specific phases of a liquid that can also have an isotropic phase without long range order. For many substances the changes in physical parameters temperature and pressure (T , P) rule the transformation from a solid, to a liquid and then to a gaseous phase (in the order on increasing T and decreasing P), while in the substances giving origin to liquid crystals there are some additional phases between solid and isotropic liquid. The liquid crystals are a subject of intensive study, because of their quite peculiar optical and electric properties.

1. Physical approaches to the study of liquids

The distinction we introduce here between physical and chemical approaches to the study of liquid systems is mainly justified by exposition reasons. The basic principles are the same in both approaches and there is a mutual interchange of methods and procedures: both approaches grow up in harmony. Actually there is a basic difference in the motivations of the two approaches: chemistry is directly interested to the details due to differences in the chemical composition of the fluid (the study of pure liquids

could be viewed in this context as an extreme case of solutions), physics arrives to consider effects due to chemical composition (and of specific solutions in particular) at the end of a longer route. The physical approaches we shall consider here do not play much attention to the chemical composition of the system (but some aspects have still to be considered).

1.1. Macroscopic approaches

Historically, and also logically, the first contribution of the physical understanding of liquids was obtained with macroscopic approaches. We shall not consider here the mechanical studies that come first in the physical enquiry about fluids, but we directly shift to the thermodynamic approach elaborated in the nineteenth century. The science of heat, thermodynamics, regards all the matter in general, and considers liquids as a specific state of aggregation of the matter, to be treated on the same footing as the others. This emphasis on the uniformity of thermodynamic laws actually is at the basis of our understanding of the phenomena of phase transformation we have quoted above, and of the transfer of models (that we shall quote in the following) elaborated for the gas phase, being simpler to study, to liquids.

Thermodynamics is a rigorous discipline, and the definition of thermodynamic functions (at the equilibrium and out of the equilibrium) must be always reminded in performing studies on liquids with theoretical tools. Even when the model is reduced to a molecular model with attention paid to the details of quantum mechanical (QM) calculations on a reduced portion of the liquid, it is wise (often necessary) to keep in mind what is the thermodynamic status of the system, and to what selection of fixed macroscopic variables (pressure, volume, temperature, energy, chemical potential) is made in assessing the models.

A second macroscopic approach of interest for us regards the electric properties of the liquid. Here again we have to go back to the nineteenth century to find the elaboration of the macroscopic theory. A large portion of liquids are poor conductors of electricity (while there are notable exceptions, the whole electrochemistry is based on the conducting properties of ionic solutions), and for this reason the dielectric behavior plays the prominent role. It is convenient to give a short summary because we shall need it later. An external electric field induces a polarization of continuum dielectric media. In the standard version of the Maxwell elaboration, the attention is focused on the dipole polarization with respect to a homogeneous electric field. A vector field, \mathbf{P} , is defined giving the value of the dipole density; this vector is related to the two other vector fields defined by Maxwell to satisfy the two basic constitutive relations for electrostatic fields in vacuo: the electric field \mathbf{E} and the displacement vector \mathbf{D} (by definition $\mathbf{E} - \mathbf{D} = 4\pi\mathbf{P}$).

In the simplest case (homogeneous linear dielectrics, constant electric field) the relationship $\mathbf{P} = \chi\mathbf{E}$ with $\chi = (1 - \epsilon)/4\pi$ holds. The macroscopic dielectric description of the liquids is not limited to the basic homogeneous and isotropic description we have here recalled. For anisotropic fluids (as liquid crystals) a tensorial definition of χ and of the dielectric constant ϵ must be introduced. There are cases in which the linear regime is not sufficient and the polarization must be described with the aid of