

Chapter 1

Introduction

The atomistic point of view was first formulated by Demokritos of Abdera, pupil of Leukippos of Milet, about twenty-four centuries ago. Demokritos explained the well known phenomenon of diffusion in air by assuming that both air and fragrance are composed of tiny structureless particles called *the atoms*, the ultimate result of division of any material object into its smallest parts. The very word “a-tomos” means something that can not be cut into smaller parts, and it was not clear in Demokritos’ times whether such a concept is realized in nature. The fact that it is still unclear to us if all observable matter can be produced with elementary (and thus indivisible) particles proves that the Ancient Greeks knew how to ask very fundamental questions indeed.

Since then, the atomistic theory has had its ups and downs. After a long medieval period when European science was in a dormant state, most of the theories in physics and chemistry started with the Aristotelean treasure of knowledge, conserved in Arabic translation. The approach putting forward four basic elements, fire, air, water and earth, conceived as continuous media, prevailed. Nevertheless the atomistic point of view was shared by such giants of science as Kepler and Newton who believed that even light was nothing other than a beam of tiny elastic particles.

For about two centuries after Kepler and Newton the atomistic point of view coexisted with theories in which continuous fluids were supposed to play the role of carriers of basic physical properties like electricity, magnetism, heat (for which two types of fluids were responsible, a “hot” and a “cold” one); and since Huygens optical waves were supposed to propagate in a continuous medium called *the aether*.

The atomistic point of view was revived in the nineteenth century by spectacular advances in chemistry. An impressive number of new elements

was discovered, and the quantitative rules of chemical reactions became clear. Since Dalton, the atomistic point of view prevailed in chemistry, and due to theoretical advances made by Einstein and Smoluchowski, and thanks to subtle experimental techniques introduced by Jean Perrin, Avogadro's number could be estimated very precisely. Nowadays atoms, and the patterns they form in solids, can be visualized with special devices using ultra-high resolution electronic microscopy. These observations confirm how intricate and rich geometrical structures can result from atomic interactions. And quite recently, the time resolution of modern instruments has become so acute, reaching the picosecond (10^{-12} sec.) limit, so that for the first time direct observation of chemical reactions between atoms and molecules becomes possible.

Here we come close to the main subject of this book. Statistical physics developed in the works of Boltzmann, Maxwell and Gibbs confirmed and enriched the beautiful edifice of classical thermodynamics, including the problems related to the coexistence between different phases of matter and various phase transitions. The elegant treatment of phase transitions by Ehrenfest and Landau remains among the best examples of efficient and simple theoretical models in physics. However, the classical treatment of phase transitions is still a part of equilibrium thermodynamics, and it describes the initial and final equilibrium states of matter before and after the phase transitions occur; non-equilibrium, and often violent, processes like boiling are not considered.

This also concerns the processes resulting in the formation of solid matter, be it from the liquid or from the gaseous state. Only recently have the models known as Molecular Dynamics (MD), using powerful computer techniques, been able to simulate such condensation processes by following the evolution of hundreds or thousands of atoms interacting via more or less realistic forces e.g. given by the Lennard-Jones potentials.

In numerous successful simulations and *ab initio* computations, there is still no unique and efficient theoretical approach available unifying the description of formation and solidification of atomic and molecular structures. The aim of this book is to provide theoretical tools that can fill this gap, at least partially.

The last quarter of the twentieth century brought two discoveries in condensed matter physics whose impact on that domain can be compared to that of the revolutionary theories of general physics. These two discoveries deeply modified our perception of the differences between ordered and disordered states of matter, showing that the previous clear distinction

between crystalline and non-crystalline configurations was very crude and did not take into account many intermediate situations.

The two experimental facts we are referring to are the existence of quasicrystals and fullerenes. Both were discovered at about the same time, in the early eighties, and both came as a great surprise. The quasicrystalline lattices displayed five- and ten-fold symmetries, formally forbidden by classical crystallography; the giant fullerene C_{60} molecules made of 60 carbon atoms generated a revolution in carbon chemistry.

These experimental discoveries also boosted the theoretical research in condensed matter physics and in physical chemistry.

The models of agglomeration and growth of local structures representing various degrees of order can be applied to many materials. Most of the time the crystalline state of matter results from processes in which the growth of local structures leads progressively to global lattice buildup, often with a given symmetry. Under optimal conditions the slow agglomeration and growth may lead to almost perfect crystalline lattices; under less favorable conditions many defects may appear, and in certain situations the resulting solid state is partly or totally disordered.

There are many intriguing growth processes in nature leading to amorphous solids, to quasi-crystals and other aperiodic structures. The fullerenes and other carbon nanostructures are among the most fascinating examples. Biology also provides many examples of self-organized growth, and certain viruses presenting icosahedral structure can be analyzed using similar mathematical models of agglomeration. Finally, glasses are perhaps the most important field of application of models of agglomeration and growth.

The main goal of this book is to present a unifying and coherent point of view explaining common physical and mathematical features whose understanding can help us to produce simple models of agglomeration and growth. When applied to atomic and molecular networks including nanoscale structures, they can explain the interplay between the geometrical and physical properties of dominant local structures and the final properties of the resulting state of condensed matter with various degrees of local and global order.

The originality of the approach to modeling of various structures proposed in this book consists in using mathematical methods inspired by other branches of physics, mostly dynamical systems and mechanics, as well as geometry and field theory. The mathematical models presented here are inspired by the theoretical work on amorphous solids and quasicrystals de-

veloped by A. Janner in Holland, M. Kléman, J.-F. Sadoc and R. Mosseri in France, P. Kramer and H.-R. Trebin in Germany, P. Steinhardt in the United States, N. Rivier in England and France, Venkataraman and Sahoo in India, A. Volovik, V. Dzyaloshinsky and M. Monastyrski in Russia. They take into account forces acting between atoms and molecules which determine local geometrical configurations, which in turn modify the interactions and define the closest neighbors.

In this sense, mathematical models of agglomeration and growth of structures are facing an intrinsic non-linearity problem encountered in General Relativity, where the constitutive equations describing the matter and material fields and forces must be formulated in a curved space-time whose geometry is determined by the distribution of matter itself.

The description of non-equilibrium processes like glass transition must go beyond traditional equilibrium thermodynamics. This is achieved by replacing the *space of states* by the space of all *agglomeration paths* i.e. all possible processes leading to a given cluster size. This approach is inspired by Feynman's ideas contained in his "space-time approach" to relativistic quantum mechanics.

The mathematical models presented in this book do not use any sophisticated mathematics and do not require any particular knowledge beyond the standard algebra and calculus delivered in graduate courses. Certain particular properties of stochastic matrices and non-linear differential equations are recalled in the Appendix.

The knowledge of physics required does not go beyond the regular graduate curriculum.

The book is organized as follows:

- Chapters 2 and 3 contain an introduction to the geometrical and topological problems encountered in the construction of lattices and networks. Incidentally, the first stochastic agglomeration model in one dimension is introduced;
- Chapter 4 gives necessary information about bonds and interatomic forces in various atomic networks;
- Chapter 5 presents mathematical models of agglomeration and growth of different structures;
- Chapters 6, 7 and 8 are devoted, respectively, to mathematical models of quasicrystals, nucleation and growth of fullerenes and of icosahedral viral capsids;
- Chapters 9 and 10 serve as a short introduction to glass physics and chemistry, with particular attention paid to the thermodynamical behavior;

- Chapter 11 presents various mathematical models of glass transition;
- Chapter 12 generalizes the results to multi-component glasses, including the immiscibility problem;
- Chapter 13 contains the model of glass transition including rapid cooling effects;
- Chapter 14 discusses problems of connectivity and rigidity in glasses, including the most recent results.

Several chapters begin with “Preambles” giving a short historical introduction to the subject: quasicrystals, fullerenes and nanotubes, capsid viruses and glasses.

Many chapters of this book present the results obtained by my former Ph.D students and collaborators. Although published in numerous journal articles cited in the bibliography, there is also a lot of previously unpublished material. In particular:

- Much of the original material of Chapter 4 is provided by the Ph.D thesis (1987) of Dina-Maria dos Santos-Loff, currently Professor in the Mathematics Department of the University of Coimbra (Portugal).

- The first agglomeration model of Chapter 5 was developed with D.M. dos Santos-Loff. The stochastic matrix model presented in the same chapter was developed with R. A. Barrio, G.G. Naumis and R. Aldrovandi; more details can be found in R. Aldrovandi’s excellent book on matrices in mathematical physics. [Aldrovandi (2001)]

- Many results on quasi-crystalline growth described in Chapter 6 were obtained in collaboration with D.M. dos Santos-Loff and in several papers by R.A. Barrio and R.A. Paredes.

- Certain results on fullerenes were obtained with K.H. Bennemann and K.A. Penson.

- The model of icosahedral virus growth owes a lot to fruitful discussions with R. Twarock and N. Stonehouse.

- The glass transition models described in Chapter 11 were worked out with M. Micoulaut, R.A. Barrio, G.G. Naumis, D.M. dos Santos-Loff and R. Aldrovandi.

- Most of the results of Chapter 12 are due to M. Micoulaut (ternary glasses) and O. Mares (immiscibility model)

- Part of the numerical results of Chapter 13 are due to M. Micoulaut.

- The analysis of vibrational modes in glasses is due to G.G. Naumis; the results on the reversibility window are due to P. Boolchand, M. Micoulaut and collaborators; the results on window glass composition were obtained in collaboration with J.C. Phillips and P. Boolchand.

To read one book is good; to read many books is even better. The following list provides useful reading on subjects treated in this monograph:

- Mathematical Tools:

M.C.M. Coxeter [Coxeter (1948)], R. Aldrovandi [Aldrovandi (2001)], F.R. Gantmacher [Gantmacher (1990)], D.K. Faddeev and V.N. Faddeeva [Faddeev and Faddeeva (1963)];

- Statistical Physics:

W. Kauzmann [Kauzmann (1966)], R. Kubo [Kubo (1965)], M. Fisher [Fisher (1965)], J. Zinn-Justin [Zinn-Justin (1997)];

- Solid State Physics:

C. Kittel, [Kittel (1966)], N. Ashcroft and D. Mermin, [Ashcroft and Mermin (1980)];

- Defects in Condensed Matter Physics:

J.-F. Sadoc and R. Mosseri [Sadoc and R. Mosseri (1999)], M. Kléman: [M. Kléman (1983)], M. Monastyrski [Monastyrski (1999)];

- Amorphous Solids:

J.M. Ziman [Ziman (1979)], R. Zallen [Zallen (1983)], S.R. Elliott [Elliott (1990)];

- Fractals:

B. Mandelbrot, [Mandelbrot (1982)];

- Quasicrystals:

M. S en echal, [M. S en echal (1995)];

- Fullerenes:

D. Tomanek and R.J. Enbody [Tomanek and Enbody eds. (2000)];

- Glasses:

J. Zarzycki [Zarzycki (1982)], P. Boolchand (ed.) [Boolchand (2001)], Z.U. Borisova [Borisova (1981)], S.R. Elliott [Elliott (1990)];

- Models of Growth in Biology:

A. Carbone *et al.*, [Carbone *et al.*, (2000)]