# Preface: Network of Science

**Science of Emergence**

**Physical Chemistry**



Figure 1: The Science Network (Tree)

The past half century has seen a rapid expansion of the body of knowledge acquired in many different scientific disciplines. This is not only obvious from the proliferation and growth of scientific journals, it has also transformed traditional textbooks into impressive, voluminous dictionaries with *1000* pages or more. As a result, individual semester courses can only sample any broad subject area such as Physical Chemistry. Altogether however, the news is dominantly positive: The flood of new scientific results has not led to more philosophical confusion and uncertainty about the internal workings of Nature. On the contrary, it has become increasingly obvious that the sciences and the objects of their study share many similar underlying concepts and driving forces. The new research area Science of Emergence has recognized and benefits from this fact. The (physical) sciences and their applications, applied mathematics, life and social sciences form an interacting information network (see Fig.1). Very approximately, different disciplines can be thought of as representing distinct branches of a tree, depending on and sustaining each other and the whole. Developments and growth in one part benefit the whole. Natural Philosophy, of course, provides the basis for interpretation of all observation.

The existence of such interrelations is obvious for Biology, Chemistry, Physics, and Mathematics. A similar connection between Chemistry, Biology, Astronomy, and Social Sciences does perhaps not spring immediately to mind. Nevertheless, cooperative self-assembly, replication, and aggregation phenomena, on the one hand, and diffusion and other transport processes, on the other, are found in both, the small laboratory chemical experiment and processes occurring simultaneously in the enormous intergalactic clouds. Modern Cosmology even invokes Darwinian-type laws of natural evolution, replication, and selection for the evolution of the entire Universe. Furthermore, transport mechanisms discussed in physics and chemistry have also entered considerations in the field of Quantitative Sociology. For example, the spread of public opinion is thought to reflect the principles of transport of matter. One has every reason to suspect that algorithms controlling data flows through modern “social networks” sustained by the electronic Internet employ similar devices. The long-standing question as to the origin of life in our universe may be difficult, even impossible, to answer definitively, since it is impossible to revisit the site and time of the emergence of life on Earth. However, the emergence of life can perhaps be understood as a consequence of the *adaptive behavior of complex systems*, topics of similar interest are pursued in the Life Sciences, Medicine, Engineering, and in Computer Science. These are the topics addressed by the science of emergence.

It is philosophically satisfying that the shared fundamental principles governing the dynamics of emerging complex systems seem to be representable by increasingly simpler general principles. ***In spite of their simplicity, these “laws” may drive systems to exhibit a broad range of processes and behavior, ranging from very simple, deterministic and orderly behavior, to very complex, chaotic, and finally random phenomena. The latter occurs in the extreme “thermodynamic limit,” where systems lose all information on their history***. Which phenomena are realized depends on the type and the strength of interactions between the constituents of a system as well as on its initial conditions.

Following these ideas, the present course begins with attempts to illustrate different types of system dynamics that can lead to very complex, possibly unpredictable behavior observed in nature and/or in the lab. Non-linear dynamics can produce asymptotic behavior in which a simple system can assume various distinct states in an unlimited series, behave erratically, or become randomized in its motion degrees of freedom. Examples are systems consisting of coupled harmonic oscillators, autocatalytic chemical reactions, possibly the climate system on Earth. The interactions of different populations or species on Earth and their important competition for finite resources appear to follow dynamics that can, in a similar fashion, also be observed in the chemical kinetics of autocatalytic chemical reactions. Such reactions are finally responsible for the phenomena of replication, self-assembly, and growth of organic matter. Here, a few fundamental properties of an existing environment spawn stochastically replication processes that can lead to intricate self-similar (fractal) structures that are so obvious in nature. The mathematical model of cellular automata gives intellectual access to the effect of prevalent conditions in a given neighborhood on the replication, growth, or demise, of a simple cellular structure, from one generation to the next.

In the limit of highly complex or multiple interactions between system components, its matter can evolve into a state of ***maximum randomization and*** ***minimum structure.*** Strictly, Statistical (Equilibrium-) Thermodynamics describes the ***macroscopic*** ***state of matter in equilibrium***. Thermodynamics addresses properties of this equilibrium and indications for it existence, and makes predictions as to the direction of change between equivalent configurations of a system that are compatible with its environment. In order to understand meaning and effect of equilibrium conditions, it is useful to consider also the behavior of thermodynamic systems not exactly at, but close to equilibrium. Such systems approach their final equilibrium state in transport processes such as diffusion in gases and solutions.

The ***macroscopic thermodynamic approach*** is a ***phenomenological*** one, based on observation and a description of matter in terms of the smallest number of variables (***observables***) possible, the ***laws connecting them,*** and an experimental determination of the important parameters and constants entering such a phenomenological description. For example, the ***volume V, pressure p, and temperature T constitute a minimal set of observables*** describing the properties of an ***amount n***of a substance. The major equation governing the relation between the observables is the ***equation of state (EOS)***. Phenomenologically, one characterizes the main states of matter as ***solid***, ***liquid***, and ***gas.*** Sometimes, a ***plasma***, a condition where the constituents of matter have disintegrated or "melted",is referred to as the "***fourth state of matter***".

 ***Microscopic Statistical Mechanics*** or ***Statistical Thermodynamics*** attempts to derive an understanding of the above macroscopic behavior of matter from the ***specific microscopic structure and the more or less random interactions of its constituents***, the atoms or molecules. Because of its focus on microscopic phenomena, statistical mechanics is basically a quantal theory. For example, statistical mechanics answers questions regarding the influence of the ***quantized vibrational modes*** of a molecule on the ***specific heat*** of a gas composed of such particles. It addresses the question of how the molecular ***van der Waals forces*** determine the short-and long-range ***correlations*** between the particles leading to ***different macroscopic phases of matter***. Both, macroscopic and microscopic statistical approaches will be discussed in the following.

After Quantum Chemistry and Statistical Thermodynamics, ***Chemical Kinetics*** is the third major branch of Physical Chemistry. It is concerned with the direction of chemical reactions and their rates. This branch of physical chemistry explores the dependence of the dynamics of chemical reactions on both macroscopic and microscopic properties of matter. It studies the influence of ***velocities and scattering probabilities between individual molecules*** on the reaction rates, as well as the dependence of these rates on ***temperature***, ***potential energies*** and ***dynamically induced forces*** such as ***viscosity***. These topics are closely related to ***transport phenomena*** such as ***Brownian motion and diffusion***. It is not obvious, how exactly to draw a separation between Kinetics and Statistical Mechanics. Some of the topics of Chemical Kinetics are discussed here in the context of the gas laws and equilibration phenomena.

As for all scientific theory (model of the world), it is important to be aware of the range of applicability of ***Statistical Thermodynamics***. In science, as far as one knows, there are ***no absolute truths***, every model of the world is based on a limited number of observations and has, therefore, a ***limited domain of validity***. The following gives a brief description of the subject of thermodynamics and its relation to other theories of natural processes.

 A particular goal of *Physical Chemistry* is to understand the physical basis of the microscopic and macroscopic ***structure*** of the substances of interest to chemists and of the underlying ***dynamics*** of physio-chemical processes. Microscopic structure of atoms and molecules is the subject of ***Quantum Chemistry***. The present course material is meant to present a framework for the processes that may, or may not, lead to the special complex systems in random equilibrium that are the focus of conventional ***Thermodynamics, Statistical Mechanics***, and ***Chemical Kinetics***.

The understanding of matter and processes to be gained in a study of physical chemistry goes much beyond a qualitative elucidation of the basic principles and concepts and aims at a ***quantitative description***. Therefore, ***mathematics is the language of physical chemistry***, just like that of theoretical physics.