

## Chapter 3

# Thermodynamics and Statistical Mechanics of Small Systems

*“I am of the opinion that the task of theory consists in constructing a picture of the external world that exists purely internally and must be our guiding star in all thought and experiment; that is in completing, as it were, the thinking process and carrying out globally what on a small scale occurs within us whenever we form an idea.”*

*The immediate elaboration and constant perfection of this picture is then the chief task of theory. Imagination is always its cradle, and observant understanding its tutor. How childlike were the first theories of the universe, from Pythagoras and Plato until Hegel and Schelling. The imagination at that time was over-productive, the text by experiment was lacking. No wonder that these theories became the laughing stock of empiricists and practical men, and yet they already contained the seeds of all the great theories of later times: those of Copernicus, atomism, the mechanical theory of weightless media, Darwinism and so on.”* **Ludwig Boltzmann** (in “*On the Significance of Theories*” 1890).

### Introduction

This chapter is concerned with one of the important subjects of computational nanotechnology, namely thermodynamics and statistical mechanics and their applications in molecular systems to predict the properties and performances involving nanoscale structures. A scientific and technological revolution has begun in our ability to systematically organize and manipulate matter on a bottom-up fashion starting from atomic level as well as design tools, machinery and energy conversion devices in nanoscale towards the development of nanotechnology. There is also a parallel miniaturization activity to scale down large tools, machinery and energy conversion systems to micro and nanoscales

towards the same goals [1-4]. The science of miniaturization is being developed and the limitations in scaling down large systems to nanoscale are under investigation. Advancement and knowledge about the thermodynamics of small systems is essential to help achieve these goals.

Principles of thermodynamics and statistical mechanics for macroscopic systems are well defined and mathematical relations between thermodynamic properties and molecular characteristics are derived. The objective here is to introduce the basics of the thermodynamics of small systems and introduce statistical mechanical techniques, which are applicable to small systems. This will help to link the foundation of molecular based study of matter and the basis for nano science and technology. Development of predictive computational and modeling options for the behavior of nano systems will depend on advancements in their thermodynamics.

The subject of thermodynamics of small systems was first introduced by T.L. Hill in two volumes in 1963 and 1964 [5] to deal with chemical thermodynamics of mixtures, colloidal particles, polymers and macromolecules. Nanothermodynamics, a term which is recently introduced in the literature by T.L. Hill [6-8], is a revisitation of the original work of T.L. Hill mentioned above on thermodynamics of small systems.

Significant accomplishments in performance and changes of manufacturing paradigms are only possible with the advancement of principles of science of small systems including thermodynamics. The answer to the question of how soon will this next industrial revolution arrive depends, a great deal, on the intensity of such scientific activities.

Thermodynamics, in general, is concerned with those physical and chemical phenomena, which involve heat and temperature. From the practical definition, thermodynamics is the phenomenological theory of converting heat to work and understanding the role of energy and other properties of matter in this conversion process. Equilibrium thermodynamics is confined to the equilibrium states of matter. Change of one equilibrium state to another is infinitely slow and as a result it is independent of time. Concepts of heat, work, energy, and properties of matter exist in public vocabulary of every language. Thermodynamic laws, which govern the relations between these concepts, originate from

ordinary experiences in our daily lives. Statistical thermodynamics, in general, is concerned with the atomic or molecular structure of matter and the relationship between microscopic structure and the macroscopic thermodynamic behavior of substances.

Historically, thermodynamics took its name from the study of efficiency of heat engines by Carnot. In his 1824 thesis, Carnot stated that the efficiency of a heat engine depended only on the temperature difference between its heat source and heat sink and not on the working substance. A decade was passed when Clapeyron developed the relationship between vapor pressure and an unknown function of empirical temperature scale. Clausius later identified this unknown function as the absolute temperature scale. The equation relating the vapor pressure to the absolute temperature is known as the Clausius-Calpeyron equation [9]. It was in 1850 when Clausius published his thesis on the Second Law of thermodynamics, which is known as "the Clausius statement." It was this statement that marked the beginning of thermodynamics as a science as it was stated by Gibbs in the late nineteenth century. A year after publication of this thesis, Thomson formulated explicitly the First and Second Laws of thermodynamics. Thomson had already defined an absolute temperature scale in 1848 and was aware of the 1845 publication by Joule in which Joule had demonstrated the equivalence of heat and work.

It was 1865 when Clausius introduced the term "entropy" and stated "The energy of universe is constant. The entropy of universe tends towards a maximum". Introduction of the term entropy resulted in a new formulation of the Second Law by Clausius.

Since the findings of Clausius, many other investigators have contributed to the science of thermodynamics. The thesis by Gibbs published in 1875 entitled "On the equilibrium of heterogeneous substances" and his other publications have a special place in thermodynamics of mixtures and phase equilibrium. Gibbs extended the science of thermodynamics in a general form to heterogeneous systems with and without chemical reactions. He is also credited for derivation and formulation of completely general equilibrium conditions for various cases. Other early contributors to this branch of thermodynamics are the following: (i) Helmholtz, who in 1882 independent of Gibbs, introduced

the concept of free energy and derived the relationship now known as the Gibbs-Helmholtz equation, (ii) Duhem, who in 1886, derived the Gibbs-Duhem equation, Planck, who in 1887, divided the changes of state into two classes of thermodynamic processes, namely reversible and irreversible processes, (iii) Nerst, who in 1906, published his heat theorem, and Carathe'odory, who in 1909, developed a new axiomatic basis of thermodynamics.

In the present chapter, we also introduce the basics of thermodynamics for small systems, which is of interest in the field of nanotechnology, miniaturization and the science of conversion of thermal to mechanical energy in small systems including the laws of thermodynamics of nano systems. It must be emphasized that what is generally known as thermodynamics in the literature deals with systems in equilibrium. However, the materials presented in this chapter are general and are not limited to systems in equilibrium.

### **Thermodynamic Systems in Nanoscale**

The definition of a thermodynamic system in nanoscale is quite similar to that of macroscopic systems. In thermodynamics, a system is any region completely enclosed within a well-defined boundary. Everything outside the system is then defined as the surroundings. The boundary may be either rigid or movable. It can be impermeable or it can allow heat, work or mass to be transported through it. In any given situation a system may be defined in several ways.

Although it is possible to speak of the subject matter of thermodynamics in a general sense, the establishment of any relationships among thermodynamic properties of a system requires that they be related to a particular system. The known macroscopic thermodynamic property relations apply to systems, which contain a very large number of atoms or molecules. The validity of such relations to nano systems is open to question.

The state of a system is an important concept in thermodynamics and is defined as the complete set of all its properties, which can change during various specified processes. The properties, which comprise this set, depend on the kinds of interactions, which can take place both within

the system and between the system and its surroundings. Any two systems, subject to the same group of processes, which have the same values of all properties in this set, are then indistinguishable and we describe them as being in identical states.

A process in thermodynamics is defined as a method of operation in which specific quantities of heat and various types of mass and work are transferred to or from the system to alter its state. One of the objectives of thermodynamics is to relate these state changes in a system to the quantity of energy in the form of heat and work transferred across its boundaries.

The simplest system in nanoscale may be chosen as a single particle, like an atom or molecule, in a closed space with rigid boundaries. In the absence of chemical reactions, the only processes in which it can participate are transfers of kinetic or potential energy to or from the particle, from or to the walls. The state for this one-particle system is a set of coordinates in a multi-dimensional space indicating its position and its momentum in various vector directions. For example, a simple rigid spherical monatomic molecule would require six such coordinates, three for its position and three for its momentum in order to completely define its state. For a system containing  $N$  rigid spherical monatomic molecules the state of the system is defined by the  $6N$  set of all position and momentum values for all the particles. They can thus determine all the thermodynamic properties of the group. For systems consisting of very large number of such particles in equilibrium, the thermodynamic property relations are already established (see for example MCSL theory [10]). For systems containing limited number of rigid sphere particles, the thermodynamic property relationships need to be established.

The set of all the thermodynamic properties of a multi-particle system including its temperature, pressure, volume, internal energy, etc is defined as the thermodynamic state of this system. An important aspect of the relationships between thermodynamic properties in a large, macroscopic and also known as extensive system, is the question of how many different thermodynamic properties of a given system are independently variable. The number of these represents the smallest number of properties, which must be specified in order to completely determine the entire thermodynamic state of the system. All other

thermodynamic properties of this system are then fixed and can be calculated from these specified values. The number of these values, which must be specified, is called the variance or the degrees of freedom of the system. Small or nano systems, on the other hand, could be looked at from the point of view of nonextensivity or thermodynamics of nonextensive systems. This subject will be discussed in this chapter as well.

The systems of interest to nanoscience and nanotechnology are the isolated individual nanostructures and their assemblies, small droplets and bubbles, clusters, and fluids and solids confined in small spaces, like inside nanotubes and fullerene, and going through phase changes. Nano systems are made of countable (limited) number of atoms or molecules. Their sizes are larger than individual molecules and smaller than micro systems. One of the characteristic features of nano systems is their high surface-to-volume ratio. Their electronic and magnetic properties are often distinguished by quantum mechanical behavior. Their mechanical and thermal properties can be formulated within the framework of classical statistical mechanics of small systems as presented by Hill [5-8], and through the newly developed nonextensive statistical mechanics as presented in this Chapter.

Small systems of interest in nanotechnology are generally made up of condensed (liquid or solid) matter. Nano systems can contain all forms of condensed matter, be it soft or hard, organic or inorganic and/or biological components. A deep understanding of the interactions between individual atoms and molecules composing the nano systems and their statistical mechanical modeling is essential for nanotechnology.

### **Energy, Heat and Work in Nanosystems**

Energy is a quantity which measures a combination of effort expended and results produced. For macroscopic systems energy is often defined as "the ability to perform work" by a system under consideration. At the macroscopic level, the idea expressed is probably sufficient in most cases, but for nano systems this definition is not sufficient enough because the term "work" requires a more precise definition than it's

generally well understood macroscopic definition. A useful definition of energy from the viewpoint of thermodynamics of small systems could be "the capacity to induce a change which would be visible in nanoscale". This is to distinguish work from heat, which is a change in the energy of the system with no visible change in nanoscale. It must be pointed out that this definition is also subject to error as the size of a nano system decreases to a level that its fluctuations are of larger scale and closer to molecular motions.

Work is generally defined as the product of a driving force and its associated displacement, which represents a means of transfer of energy between a system and its surroundings. A driving force causes and controls the direction of change in energy, which is a property of the system. The quantitative value of this change is called a "displacement". In thermodynamics, this quantity has meaning only in relation to a specifically defined system. Relative to a particular system there are generally two ways of locating a driving force and the displacement it produces.

In one way both the driving force and the displacement are properties of the system and are located entirely within it, so that the energy calculated from their product represents a change in the internal energy of the system.

In another way, however, the displacement could occur within the system but the driving force producing it is a property of the surroundings and is applied externally at the system. Similarly, both the driving force and its displacement could be located entirely within the surroundings. In both of these cases the calculated energy is then a change in the total energy of the system. The total energy of a system is the sum of its internal, kinetic and potential energies.

Heat is another means of exchange of energy between the system and its surroundings through the system boundary. The distinction between heat and work is the fact that heat is a means of energy with no visible change in nanoscale but in random atomic and molecular translation, rotation and vibrations on the boundary of the system.

By definition, the boundary of a system is a region of zero thickness containing no matter at all. In any quantitative application of thermodynamics, it is always important to make a careful distinction

between energy changes within a system and the concepts of work and heat, which are means of exchange of energy between the system and its surroundings.

In what follows we introduce the specificities of the thermodynamics of nano systems, which includes an examination of laws of thermodynamics and the concept of nonextensivity of nano systems.

### Laws of Thermodynamics

Classical thermodynamics is a typical example of an axiomatic science. The rigorous deduction of thermodynamic concepts from its basic axioms is an intricate logical problem [11-13]. In an axiomatic science certain aspects of nature are explained and predicted by deduction from a few basic axioms which are assumed to be always true. The axioms themselves need not be proved but they should be sufficiently self-evident to be readily acceptable and certainly without known contradictions. The application of thermodynamics of large systems to the prediction of changes in given properties of matter in relation to energy transfers across its boundaries is based on four fundamental axioms, the Zero<sup>th</sup>, First, Second, and Third Laws of thermodynamics. The question whether these four axioms are necessary and sufficient for all systems whether small or large, including nano systems, is something to be investigated in the future. In the present discussion, we examine the format of these four axioms for nano systems.

Thermodynamics and statistical mechanics of large systems consisting of many particles beyond the thermodynamic limit ( $V$  and  $N$  go to infinity,  $N/V=\rho_N$  is finite) is well-developed [14-16]. Normally the science of thermodynamics describes the *most likely macroscopic behavior* of large systems (consisting of  $10^{23}$  particles  $\sim 1$  ccm in volume or more) under slow changes of a few macroscopic properties. The really large systems (like astrophysical objects) as well as small systems (like those of interest in nanotechnology) are excluded.

Recent developments in nanoscience and nanotechnology have brought about a great deal of interest into the extension of thermodynamics and statistical mechanics to small systems consisting of

countable particles below the thermodynamic limit. Hence, if we like to extend thermodynamics and statistical mechanics to small systems in order to remain on a firm basis we must go back to its founders and, like them establish new formalism of thermodynamics and statistical mechanics of small systems starting from the safe grounds of mechanics. One should point out difficulties with and possibly the changes that we have to introduce in thermodynamics and statistical mechanics to make them applicable to small systems.

Structural characteristics in nanoscale systems are dynamic, not the static equilibrium of macroscopic phases. Coexistence of phases is expected to occur over bands of temperature and pressure, rather than along just sharp points. The pressure in a nano system cannot be considered isotropic any more and must be generally treated as a tensor. The Gibbs phase rule loses its meaning, and many phase-like forms may occur for nanoscale systems that are unobservable in the macroscopic counterparts of those systems [5,17].

Such questions as property relations and phase transitions in small (nano) systems are subjects to be investigated and formulated provided the formulation of working equations of thermodynamics and statistical mechanics of small systems are developed. The principles of phase transitions in small systems are presented in Chapter 7 of this book. One distinction between macroscopic and small systems is the fact that while the thermodynamic property relations (equations of state) of macroscopic systems are independent of the environment, they are environment-dependent in small systems [5].

It is worth mentioning that the molecular self-assembly (bottom-up technology) which is originally proposed by Feynman [18] has its roots in phase transitions. As Hill has pointed out [5] small system effects will be particularly noticeable at phase transitions and in the critical region. A comprehensive understanding of thermodynamics and statistical mechanics of small systems will help bring about the possibility of formulation of alternative self-assemblies of various atomic and molecular assemblies. The subjects of phase transitions and self-assemblies in small systems will be discussed in Chapters 7 and 9, respectively.

To formulate the thermodynamics of small systems, one has to start evaluating thermodynamics from the first principles reviewing the concepts, laws, definitions and formulations and draw a set of guidelines for their applications to small systems. Historically thermodynamics was developed for understanding the phenomena of converting thermal energy to mechanical energy. With the advent of technology thermodynamics assumed a universal aspect applicable for all kinds of systems, whether open or closed, and under variations of temperature, pressure, volume and composition. The concept of irreversible thermodynamics [19,20] is an extension of thermodynamics to dynamic systems under various external forces generating varieties of fluxes in the system. It is quite appropriate to examine the laws of thermodynamics for a small (nano) system, which does not satisfy the “thermodynamic limit”.

### **The Zero<sup>th</sup> Law**

The Zero<sup>th</sup> Law of thermodynamics consists of the establishment of an absolute temperature scale. Temperature of a macroscopic system is a well-defined property, its fluctuations are quite negligible, and it is a measure of its thermal equilibrium (or lack of it). While the temperature of a small system is also a well-defined thermodynamic property as is in macroscopic systems, it generally has larger fluctuations with respect to time and space which would magnify as the size of the system reduces.

In nano systems, as it is well explained in the following statement by the US National Initiative on Nanotechnology [2] fluctuations play an important role: *“There are also many different types of time scales, ranging from  $10^{-15}$  s to several seconds, so consideration must be given to the fact that the particles are actually undergoing fluctuations in time and to the fact that there are uneven size distributions. To provide reliable results, researchers must also consider the relative accuracy appropriate for the space and time scales that are required; however, the cost of accuracy can be high. The temporal scale goes linearly in the number of particles  $N$ , the spatial scale goes as  $O(N \cdot \log N)$ , yet the accuracy scale can go as high as  $N^7$  to  $N!$  with a significant prefactor.”* While fluctuations in small systems are recognized to be generally appreciable in magnitude, they are not yet quantitatively correlated to

their properties. If we are going to extend applications of thermodynamics and statistical mechanics to small systems, accurate calculation of fluctuations are quite necessary.

It must be pointed out that, in addition to temperature fluctuations, appreciable fluctuations may also exist in pressure and energies (internal energy, Gibbs free energy and Helmholtz free energy) of small systems. Equilibrium is defined as the condition when there is no visible change in the temperature, pressure and energies of a system with respect to time. Due to the appreciable fluctuations in small systems, there will be difficulties in defining the concepts of thermal, mechanical and chemical equilibrium.

Another important concept in thermodynamics is reversibility and irreversibility. A reversible system is one that when the direction of a driving force (like heat or work) is changed, the system goes back to its original condition. Thermodynamic reversibility in macroscopic systems has become synonymous with thermodynamic equilibrium. A nano system, on the other hand, may be reversible, but it may not be at equilibrium. Similar to macro systems a small system can be defined as isolated, closed (also known as control mass), open (also known as control volume), adiabatic, isothermal, isometric (or isochoric, also known as constant volume) and isobaric (constant pressure).

It is customary in statistical mechanics to express fluctuations in thermodynamic properties in terms of distribution functions and, thus, as derivatives of other properties [5,16]. Recent advances in the fluctuation theory of statistical mechanics of macroscopic systems has been quite successful to quantify and predict the behavior of complex mixtures [16] for which intermolecular potential energy functions are not accurately available.

### **The First Law**

The First Law of thermodynamics as defined for macroscopic systems in which no nuclear reactions is taking place is simply the law of conservation of energy and conservation of mass. When, due to nuclear reactions, mass and energy are mutually interchangeable, conservation of mass and conservation of energy should be combined into a single conservation law which, as far as we know, is universal.

The intuitive acceptability of this law for all systems, whether in nano or macroscopic scales, is apparent. The concepts of conservation of mass and energy in various forms have existed from antiquity, long before any precise demonstration of them could be made. The verse in Galatians 7, of the Book of Judges "whatever a man sows, this he will also reap." is, in a sense, the biblical affirmation of the law of conservation of mass. The Greek philosopher Empedocles developed a theory of physical elements. He believed that everything was made up of four elements: earth, fire, air, water. He considered matter indestructible, although its forms--earth, fire, air, or water-- could be interchanged. The situation was confused in the middle Ages by a feeling that fire actually "destroyed" the matter, which burned. This was set right in 1774 when the French chemist, Antoine Laurent Lavoisier, conclusively demonstrated the conservation of mass in chemical reactions.

An intuitive feeling for energy conservation is also deep-rooted even though its demonstration is experimentally more difficult than that for mass conservation. The earliest demonstration of energy conservation made in 1797 is credited to Count Rumford, known primarily for the work he did on the nature of heat and for whom the Rumford fireplace is named. Fortunately, he made his observations in a cannon factory where the mechanical work of boring cannon was converted into heat and transferred to a large amount of cooling water. If this heat transfer had not been very large relative to the heat losses, the correct conclusion could easily have escaped him. The first accurate measurement and indisputable demonstration of the precise equivalence of mechanical work and the total thermal energy obtainable from it did not occur until the experiment of Joule in 1843.

In 1843 Joule developed an experiment to convert the mechanical energy to thermal energy through fluid motion and mixing of water, known as the Joule's water friction experiment. A well-insulated calorimeter was equipped with baffles to increase the frictional drag on the paddles. A weight falling a measured distance performs a known amount of work. By measuring the temperature increase in the water in the calorimeter as the weight falls, the amount of heat generated by the work can be calculated. Through the Joule's experiment, we learned about the equivalence and relationship of thermal energy and the

mechanical energy spent to generate it. Later, the metric unit of energy was named in honor of Joule (1 Calorie = 4.186 Joule).

In another experiment, Joule measured the heat produced by compression of air and by electrical currents. In 1840, he stated a law, now called Joule's Law, that heat is produced in an electrical conductor. Together with W. Thomson (Lord Kelvin) he discovered in 1853 the effect known as Joule-Thomson effect. Discovery of the principle of magnetostriction is also credited to Joule. He did not claim, however, to have formulated a general Law of Conservation of Energy. Nevertheless, his experiments were certainly fundamental in bringing that formulation about [21].

The First Law of thermodynamics, which is the same as the principle of conservation of mass and energy, provides us with the relation between heat, work and energy content of a system. The equation for the First Law of thermodynamics for a closed (controlled mass) macro system takes the following form,

$$dE = \delta Q_{in} + \delta W_{in} \quad (1)$$

where  $dE$  stands for the exact differential energy increase in the system due to addition of inexact differential amounts of heat and work,  $\delta Q_{in}$  and

$$\delta W_{in} = -\sum_i P_{ii}^{ext} d\epsilon_{ii} V,$$

respectively, to the system,  $P_{ii}^{ext}$  ( $i=x,y,z$ ) are the components of the external diagonal pressure tensor  $\vec{P}^{ext}$  and  $d\epsilon_{ii}$  is the specific deformation of volume  $V$  due to the external pressure tensor [22]. This equation is valid for small systems as well as large systems. However, clear distinction / separation between the terms heat and work may be a bit foggy for certain small systems and especially when the size of the nano system decreases.

As we mentioned before a useful definition of energy from the viewpoint of thermodynamics of small systems could be "the capacity to induce a change, which would be visible in nanoscale". There are three kinds of energy important in thermodynamics: Kinetic energy, potential energy, and internal energy due to intermolecular interactions in a

system. Work and heat are means of energy exchanges between a system and its surroundings or another system. Transfer of energy through work mode is a visible phenomenon in macroscopic systems. However, it is invisible in a nano system, but it occurs as a result of the collective motion of an assembly of particles of the nano system resulting in changes in energy levels of its constituting particles. Transfer of energy through heat mode is also an invisible phenomenon, which occurs in atomic and molecular level. It is caused by a change not of the energy levels but of the population of these levels.

While the First Law, which is actually the conservation of energy, is one of the fundamental laws of physics, it alone cannot explain everything related to conversion of thermal to mechanical energy. Another law is required to understand that the thermal energy can change form to mechanical energy. For instance, how the energy in a barrel of oil can move an automobile and for what maximum distance. This is the realm of the Second Law providing the inequality expression for the entropy production as is discussed below.

### **The Second Law**

Lord Kelvin originally proposed the Second Law of thermodynamics in the nineteenth century. He stated that heat always flows from hot to cold. Rudolph Clausius later stated that it was impossible to convert all the energy content of a system completely to work since some heat is always released to the surroundings. Kelvin and Clausius had macro systems in mind where fluctuations from average values are insignificant in large time scales. According to the Second Law of thermodynamics for a closed (controlled mass) system we have [20],

$$dP_S = dS - \delta Q_{in}/T_{ext} \geq 0. \quad (2)$$

This definition of the differential entropy production in a closed (controlled mass) system,  $dP_S$ , which is originally developed for macro systems is still valid for nano / small systems. As it will be demonstrated later, for small systems the term entropy,  $S$ , may assume a new statistical form due to nonextensivity of nano systems.

Now, by joining the First and the second Law equations for a closed system and with the consideration of the definition of work,

$$\delta W_{in} = -\sum_i P_{ii}^{ext} d\epsilon_{ii} V,$$

the following inequality can be derived for the differential total entropy of a system:

$$dS \geq \frac{dE}{T_{ext}} + \frac{1}{T_{ext}} \sum_i P_{ii}^{ext} d\epsilon_{ii} V \quad (3)$$

This is a general inequality, which seems to be valid for large as well as small systems. Of course, for a system in equilibrium the inequality sign will be removed and the resulting equation is the well-known Gibbs equation. However, due to appreciable fluctuations in properties of small systems, definition of the static equilibrium, as we know it for large systems, will be difficult, if not impossible to make. In nano systems and in very short periods of time such fluctuations are observed to be significant, violating the Second Law [23]. However, for longer times nano systems are expected to be closer to reversibility than macroscopic systems.

### **The Third Law**

The Third Law of thermodynamics for large systems, also known as “the Nernst heat theorem”, states that the absolute zero temperature is unattainable. Although one can approach absolute zero, one cannot actually reach this limit. The third law of thermodynamics states that if one could reach absolute zero, all bodies would have the same entropy. In another words, a body at absolute zero could exist in only one possible state, which would possess a definite energy, called the zero-point energy. This state is defined as having zero entropy.

It is impossible to reach absolute zero because properties of all systems are in dynamic equilibrium and their atomic and molecular properties fluctuate about their average values. Likewise, the energy per particle of a macroscopic system is an average value, and individual particle energies of the system will fluctuate around this value. As a result, temperature cannot reach absolute zero due to energy fluctuation.

The Third Law for a macroscopic system also states that the limit of the entropy of a substance is zero as its temperature approaches zero, a concept necessary in making absolute entropy calculations and in establishing the relationship between entropy as obtained from the statistical behavior of a multi-particle system.

The non-attainability of absolute zero temperature seems also to be valid for nano systems due also to fluctuations. However, it may be possible to devise a confined nano system whose fluctuations are more damped. As a result, such a system is more likely to approach closer to absolute zero temperature than macro systems. One could make it to have even negative temperature such as for paramagnetic spins, which are cooled off by applying a magnetic field so that entropy decreases with energy and leads to negative temperatures [24].

Currently, the third law of thermodynamics is stated as a definition: the entropy of a perfect crystal of an element at the absolute zero of temperature is zero. This definition seems to be valid for small systems as well as large systems.

### **Statistical Mechanics of Small Systems**

The objective of statistical mechanics is generally to develop predictive tools for computation of properties and local structure of fluids, solids and phase transitions from the knowledge of the nature of molecules comprising the systems as well as intra- and intermolecular interactions. The accuracy of the predictive tools developed through statistical mechanics will depend on two factors. The accuracy of molecular and intermolecular properties and parameters available for the material in mind and the accuracy of the statistical mechanical theory used for such calculations.

Statistical mechanical prediction of the behavior of matter in macroscopic scale, in the thermodynamic limit ( $V$  &  $N \rightarrow \infty$  and  $N/V = \rho_N$  finite), is well developed and a variety of molecular-based theories and models are available for prediction of the behavior of macroscopic systems. There is also a wealth of data available for thermodynamic and transport properties of matter in macroscopic scale, which can be used

for testing and comparison of molecular based theories of matter in macroscopic scale. In the case of nano (small) scale there is little or no such data available and the molecular theories of matter in nanoscale are in their infancy. With the recent advent of tools to observe, study and measure the behavior of matter in nanoscale it is expected that in a near future experimental nanoscale data will become available. In the present section we introduce an analytic statistical mechanical technique which has potential for application in nano systems. In the next chapter, we will introduce the computer simulation techniques, which have been proposed and used for molecular based study of matter in nanoscale.

Statistical mechanics of small systems is not a new subject. Many investigators have studied small systems consisting of one or more macromolecule, droplets, bubbles, clusters, etc. utilizing the techniques of statistical mechanics [4-8,25,26]. Computer simulation approaches, like Monte Carlo and molecular dynamics techniques, have been used extensively for such studies and they will be presented and reviewed in the next few chapters. However, a general analytic formalism for dealing with small systems and developing working equations for thermodynamic properties, without regard to their nature, through statistical mechanics is still lacking.

Recent nanotechnology advances, both bottom-up and top-down approaches, have made it possible to envision complex and advanced systems, processes, reactors, storage tanks, machines and other moving systems which include matter in all possible phases and phase transitions. There is a need to understand and develop analytic predictive models, for example, for the behavior of a matter confined in a fullerene, or flowing in a nanotube at various state conditions of pressures, temperatures and compositions. For such diverse circumstances and for application of such components in the design of nanomachinery, the development of analytic predictive approaches of properties of matter in nanoscale is necessary to build accurate computational techniques to model such nanomachinery.

It is a well-known fact that the behavior of matter confined in nano systems (inside a fullerene, in a nanotube, etc.) is a function of the environmental geometry, size and wall effects that are surrounding it. This has not been the case with macroscopic scale of matter where we

have been able to develop universal correlations and equations of state to be applied in all possible applications regardless of the geometry of the confinement systems. For example the property-relations of water (its equation of state), is universally needed for many applications. Such applications include in the use of water as working fluid in thermal to mechanical energy conversion devices, in the use of water as the reagent or solvent in many chemical processes and in oceanographic, meteorological and geothermal studies. However, the same equations of state of water may not be applicable in small systems. Even if one develops such database for a particular nanosystem, the results may not be applicable in other nano system. This demonstrates the need for a methodology for the development of universal analytic techniques of thermodynamic property relations in nanoscale. One of the prime candidates for this endeavor seems to be the newly developed thermodynamics and statistical mechanics of nonextensive systems. In what follows we present the principle of thermodynamics and statistical mechanics of nonextensive systems and discuss its validity for small systems due to their nonextensive nature.

### **Thermodynamics and Statistical Mechanics of Nonextensive Systems**

Statistical mechanical treatment of macroscopic systems consisting of an assembly of molecules starts with the Boltzmann formula along with the use of a statistical ensemble averaging techniques for the probability distribution of molecules / particles in the system. There exist various ensemble-averaging techniques in statistical mechanics including microcanonical, canonical, grand canonical and Gibbs ensembles.

It should be pointed out that the use of thermodynamic limit and of extensivity are closely interwoven with the development of classical statistical mechanics as are reported in many books published on this topic [14,15, 25-30]. Hence, to extend the use of statistical mechanics to small systems we must go back to its foundations and establish the new formalism starting from the appropriate grounds of *mechanics* and *statistics*. One such appropriate approach is the thermodynamics and

statistical mechanics of nonextensive systems originally developed in 1988 by Tsallis [31].

In order to explain the nature of nonextensivity of nanoscale systems the following discussion is presented.

In thermodynamics, properties (variables) are classified as being either extensive or intensive. When properties of a system are independent of the number of particles present in the system, they are called "intensive properties (variables)". Otherwise, those properties (variables) are called extensive properties (variables). The test for an intensive property is to observe how it is affected when a given system is combined with some fraction of an exact replica of itself to create a new system differing only in size. Intensive properties are those, which are unchanged by this process. Those properties whose values are increased or decreased in direct proportion to the enlargement or reduction of the system are called "extensive properties". For example, if we exactly double the size of a large or macroscopic system in thermodynamic limit by combining it with an exact replica of itself, all the extensive properties are then exactly double and all intensive properties are unchanged. For nano systems, these rules in defining intensive and extensive thermodynamic properties don't seem, in general, to be satisfied. Accordingly, nano systems are in the category of nonextensive systems.

### **Euler's Theorem of Homogenous Functions**

Euler's theorem of homogeneous functions is used to distinguish the extensive and intensive thermodynamic properties. According to the Euler's theorem of homogeneous functions, a function  $f(x_1, x_2, \dots, x_r)$  that satisfies the following condition is called a homogeneous function of degree  $\lambda$ :

$$f(tx_1, tx_2, \dots, tx_r) = t^\lambda f(x_1, x_2, \dots, x_r) \quad (4)$$

For a homogeneous function of degree  $\lambda$  it can be readily shown that the following condition also holds

$$x_1 \frac{\partial f}{\partial x_1} + x_2 \frac{\partial f}{\partial x_2} + \dots + x_r \frac{\partial f}{\partial x_r} = \lambda f . \quad (5)$$

When the Euler's theorem is used for thermodynamic property relations of macroscopic systems, the value of exponent  $\lambda$  defines the nature of thermodynamic variable. When exponent  $\lambda = 0$  the thermodynamic variable is intensive and when  $\lambda = 1$  the variable will be extensive.

In nano systems distinction of intensive and extensive thermodynamic variables (properties) from one another loses its significance. The definitions of such inherent intensive properties as temperature and pressure also lose their firmness due to fluctuations. Accordingly in small systems we may need to propose a similar relation as the above equation for intensive and extensive properties but with  $\lambda \neq 0$  or  $1$ . Actually the numerical value of  $\lambda$  may be non-integer and it may vary for systems of varying sizes and natures. This is because; in small systems, we are faced with a new class of thermodynamic properties which do not possess the usual mathematical and physical interpretations of the extensive properties of the macroscopic systems. For determining  $\lambda$  some experimental data or reliable calculations on the relevant properties of the small system under consideration need to be carried out.

Any extensive thermodynamic property is a summation of the same property of the particles of the system, which are related to the energetics and space occupied by the particles. Any intensive thermodynamic property is, in the other hand, the result of an average of the particles' position and momentum coordinates with respect to an external frame of reference.

Consequently, if we alter the number of particles by changing only the size of the system, we should then alter the extensive properties proportionately and retain the intensive properties for large systems in thermodynamic limit. For small / nano systems, this may not be the case, i.e. extensive thermodynamic properties would alter inproportionately and intensive properties may not be retained.

### **Boltzmann and Boltzmann–Gibbs Formulae of Entropy**

In the nineteenth century, Ludwig Boltzmann derived the Second Law by assuming that matter was composed of particulate bodies (atoms, molecules, etc.) by applying Newtonian mechanics along with principles of statistics. According to Boltzmann, the Second Law of thermodynamics is probabilistic in nature. He worked on statistical mechanics using probability to describe how the properties of atoms determine the properties of matter. In particular, he demonstrated the Second Law of thermodynamics in a statistical statement form. According to Boltzmann:

$$S = k_B \ln(W), \quad (6)$$

where  $S$  is the entropy of a system,  $k_B = 1.38054 \times 10^{-23}$  [Joule/Kelvin] is the thermodynamic unit of measurement of entropy, now known as the Boltzmann constant,  $W$  is the "probability" of the system in its mathematical sense, that is the number of distinct ways of arranging the particles consistent with the overall properties of the system.

Two important characteristics of Boltzmann entropy are [30]:

- (i) its nondecrease: if no heat enters or leaves a system, its entropy cannot decrease;
- (ii) its additivity: the entropy of two systems, taken together, is the sum of their separate entropies.

However, in statistical mechanics of finite (nano) systems, it is impossible to completely satisfy both of the above-mentioned characteristics [32].

Boltzmann entropy,  $S$ , as defined by Eq.(6), is for a macroscopic (large) state over a statistical ensemble in equiprobability. It is considered the entropy of a coarse-grained distribution and Gibbs later expressed it when the probabilities are not all the same. In terms of the probability distribution of the observational states of the system resulting in the well-known Boltzmann-Gibbs formula:

$$S = -k_B \sum_{i=1}^W p_i \ln p_i. \quad (7)$$

Gibbs from Eq. (6) derived the Boltzmann-Gibbs expression for entropy in 1870s by considering a system consisting of a large number,  $N$ , elements (molecules, organisms, etc.) classified into  $W$  classes (energy-states, species, etc.).  $W$  is the total number of such microscopic possibilities. In this equation  $p_i$  is probability of distribution of a set of particles  $i$  in the system. In the case of equiprobability (i.e.,  $p_i=1/W$ ) Eq. (7) reduces to Eq. (6), the original Boltzmann formula.

For over a century, engineers, physicists and chemists have used this formula for entropy to describe various macroscopic physical systems. It is the starting point of the science of statistical mechanics and thermodynamics through the formulation of ensemble theories [27-30].

### **Tsallis Formula of Entropy**

Boltzmann and Boltzmann-Gibbs entropy formulas have limitations since they are based on the assumption of additivity of entropy [31]. The very notions of extensivity (additivity) and intensivity in thermodynamics are essentially based on the requirement that the system is homogeneous, which is provided for big systems with weak interactions or, more precisely, in the thermodynamic limit,  $(N,V)\rightarrow\infty$ ,  $N/V=\text{finite}$ . These notions make no strict sense for inhomogeneous systems such as the small (nano) systems or systems characterized by the size of the order of correlation length [33]. This is indicative of the fact that small / nano systems are truly nonextensive and statistical mechanics of nonextensive systems may be applied for these cases.

It has been demonstrated that the domain of validity of classical thermodynamics and Boltzmann-Gibbs statistics, Eq. (7) is restricted, and as a result, a good deal of attention have been put to discuss such restrictions [31, 33-35]. This branch of science is categorized in a special part of thermodynamics, which is named “nonextensive thermodynamics”. Nonextensive thermodynamics or thermodynamics of nonextensive systems has a formalism, which is proper for the study of small as well as other systems that do not exhibit extensivity.

To overcome difficulties of nonextensive systems a new statistics was proposed by Tsallis [31], which has recently been modified [34]. According to Tsallis the entropy can be expressed by the following formula:

$$S_q = k \frac{1 - \sum_{i=1}^W p_i^q}{q-1} \quad \left( \sum_{i=1}^W p_i = 1; q \in \mathfrak{R} \right), \quad (8)$$

where  $k$  is a positive constant and  $W$  is the total number of microscopic possibilities of the system. The parameter  $q$  appearing in this equation is known as the “entropic index”.

Equation 6 can be analyzed further depending on the value and sign of entropic index  $q$ :

- (1) For all positive values of  $q$  ( $q > 0$ ) since

$$\sum_{i=1}^W p_i = 1 \quad \text{and} \quad 0 \leq p_i < 1, \quad \text{then} \quad \sum_{i=1}^W p_i^q \leq 1.$$

As a result, it is obvious that  $S_q$  as given by Eq. (8) is always positive.

- (2) In the case of equiprobability (i.e.,  $p_i = 1/W$ ) Eq. 6 reduces to

$$S_q = k \frac{1 - W^{1-q}}{q-1}.$$

Then for  $q=1$  this equation reduces to  $S_1 = k \cdot \ln W$ , which is the same as Eq. (6), the original Boltzmann formula.

- (3) In the limit when  $q \rightarrow 1$  we can write  $p_i^{q-1} = e^{(q-1) \ln p_i} \sim 1 + (q-1) \ln p_i$ . By replacing this expression in Eq. (8) and in the limit  $q \rightarrow 1$  we obtain

$$S_1 = -k \sum_{i=1}^W p_i \ln p_i,$$

which is the usual Boltzmann-Gibbs formula as given by Eq. (7).

- (4) In the case of certainty, when all the probabilities vanish but one which will be equal to unity ( $p_1=1$ ;  $p_i=0$  for  $i > 1$ ), the entropy,  $S_q$ , will be equals to zero ( $S_q=0$ ). In this case the value of  $q$  will be immaterial. This is consistent with the results from Boltzmann-Gibbs formula, Eq. (7).

- (5) Generally when two independent systems  $A$  and  $B$  join, the probabilities in the joined system will have the following relation with the probabilities of each system before joining:

$$p_{ij}^{A+B} = p_i^A \cdot p_j^B$$

Considering this expression in the entropy of the mixture  $S(A+B)$ , we will get:

$$\frac{S_q(A+B)}{k} = \frac{1 - \sum_{i=1}^W (p_i^A \cdot p_j^B)^q}{q-1} = \frac{S_q(A)}{k} + \frac{S_q(B)}{k} + (1-q) \frac{S_q(A)}{k} \cdot \frac{S_q(B)}{k}. \quad (9)$$

This equation is indicative of the fact that the entropy is non-additive, which is a result of nonextensivity of the systems.

- (6) Another important property of the nonextensive systems is the following [36]. Suppose that the set of  $W$  possibilities is arbitrarily separated into two subsets having respectively  $W_L$  and  $W_M$  possibilities ( $W_L + W_M = W$ ). We define

$$p_L = \sum_{i=1}^{W_L} p_i \quad \text{and} \quad p_M = \sum_{i=W_L+1}^W p_i,$$

hence  $p_L + p_M = 1$ . In this case we can define conditional probabilities

$$p_{Li} = \frac{p_i}{p_L} \quad \text{and} \quad p_{Mi} = \frac{p_i}{p_M}.$$

Then for these conditional probabilities and using Eq. 8, for entropy of nonextensive systems we can straightforwardly derive the following equation [36,37]

$$S_q(\{p_i\}) = S_q(p_L, p_M) + p_L^q S_q\left(\left\{\frac{p_i}{p_L}\right\}\right) + p_M^q S_q\left(\left\{\frac{p_i}{p_M}\right\}\right). \quad (10)$$

This equation plays a central role in the whole generalization of the statistical mechanics of nonextensive systems. Indeed, since the probabilities  $\{p_i\}$  are generically numbers between zero and unity then we can conclude that,  $\{p_i\}^q > p_i$  for  $q < 1$  and  $\{p_i\}^q < p_i$  for  $q > 1$ . Henceforth the entropic index  $q < 1$  and  $q > 1$  will, respectively, would represent the rare and the frequent events. This simple property lies at the heart of the whole formulation of statistical mechanics of nonextensive systems [36,37].

- (7) Another interesting property of the Tsallis entropy, Eq. (8), is the following. The Boltzmann-Gibbs formula for entropy as given by Eq. (7) satisfies the following relation:

$$S = -k \sum_{i=1}^w p_i \ln p_i = -k \left[ \frac{d}{d\alpha} \sum_{i=1}^w p_i^\alpha \right]_{\alpha=1}. \quad (11)$$

In 1909 Jackson [36,38] introduced the following generalized differential operator for an arbitrary function  $f(x)$ :

$$D_\lambda f(x) \equiv \frac{f(\lambda x) - f(x)}{\lambda x - x}. \quad (12)$$

This generalized differential operator satisfies the following limiting condition

$$D_1 \equiv \lim_{\lambda \rightarrow 1} D_\lambda = \frac{d}{dx}. \quad (13)$$

By considering Eq.s (12) and (13), Abe [39] has concluded the following expression for Tsallis entropy as given by Eq. (8)

$$-k [D_q \sum_{i=1}^w p_i^\alpha]_{\alpha=1} = k \frac{1 - \sum_{i=1}^w p_i^q}{q-1} = S_q. \quad (14)$$

This interesting property provides additional insight into the characteristics of the Tsallis generalized entropic form of nonextensive systems,  $S_q$ , as given by Eq. (8). Therefore, its connection with Jackson's differential operator appears to be a kind of natural. Indeed, this operator "tests" the function  $f(x)$  under dilatation of  $x$ , in contrast to the usual derivative, which "tests"  $f(x)$  under translation of  $x$ .

- (8) Finally, let us close the present set of properties reminding that  $S_q$  has, with regard to  $\{p_i\}$ , a definite concavity for all values of  $q$  ( $S_q$  is always concave for  $q > 0$  and always convex for  $q < 0$ ). In this sense, it contrasts with Rényi's entropy,

$$\left( \sum_{i=1}^w p_i^q \right) / (1-q) = \{ \ln [1 + (1-q) S_q] \} / (1-q),$$

which does not have this property for all values of  $q$ . Hungarian mathematician Alfréd Rényi constructed the proper entropy for fractal geometries [40].

The entropic index  $q$  characterizes the degree of non-extensivity reflected in the above, so called, pseudo-additivity entropy rule [31,34]. The cases  $q < 1$ ,  $q = 1$  and  $q > 1$  respectively, are named the cases of superadditivity (superextensivity), and subadditivity (subextensivity), respectively. Parameter  $q$  is also called the “nonextensive index”.

The above expression for entropy, Eq.(8), is applied in many systems including cosmic and nano systems. Eq.s (8) and (9) for entropy can adapt to suit the physical characteristics of many nonextensive systems while preserving the fundamental property of entropy in the Second Law of thermodynamics. Namely, that the entropy production of a system is positive with time in all processes [35]. Although Eq. (8) for entropy reduces to the Boltzmann-Gibbs formula in the case of extensivity as given by Eq. (7), i.e. when the entropy of a system is merely the sum of the entropies of its subsystems. This entropy expression is considered to be much broader than the Boltzmann-Gibbs expression since it describes many nonextensive phenomena including small systems, which are of interest here. As mentioned above the proposed general form of entropy for non-extensive systems, given by Eq. (8) and the entropic index  $q$  (intimately related to and determined by the microscopic dynamics), characterizes the degree of nonextensivity of the system.

### **Microcanonical Ensemble for Nonextensive Systems**

The canonical ensemble is characterized by its fixed volume  $V$ , fixed number of particles (atoms or molecules)  $N$  and fixed absolute temperature  $T$ . In other words,  $V$ ,  $N$  and  $T$  are the independent variables chosen in the system. The objective here is to calculate the ensemble average values for such mechanical properties of the system as pressure, internal energy, etc. provided the entropy of the system is given by the Tsallis formula, Eq.(8):

Let us now present the connection between the microscopic states of a system and the thermodynamic quantities. We start by assuming that we have a quantum system with discrete energy levels in small systems as we have in large systems. We take as our starting point the Tsallis formula of the entropy as given by Eq. (8),

$$S_q = k \left( 1 - \sum_{i=1}^W p_i^q \right) / (q-1),$$

in which  $p_i$  stands for the probability for the system to exist in the quantum state ( $i$ ). The constant  $k$  is still the Boltzmann's constant ( $k_B = 1.38054 \times 10^{-23}$  [Joule/Kelvin]) which has units of energy divided by temperature. The guiding principle is to maximize the entropy under the constraints as will be presented below.

At first, let us consider maximization of the entropy for an isolated system. If we maximize the entropy, Eq. (8), with respect to the probabilities, we will find that the maximum entropy occurs when all  $p_i$ 's are the same and they are constant. Let us imagine that there are exactly  $\Omega = \Omega(\varepsilon)$  states at equal energy levels of  $\varepsilon$  (or this many states in a small range of energies centered about  $\varepsilon$ ). The sum of all probabilities must be equal to unity, which is the constraint on the system, so  $p_i = 1/\Omega$ . This will result in the following maximum entropy expression for the isolated system with respect to its degeneracy  $\Omega$ :

$$S_q = k \frac{1 - \Omega^{-q+1}}{q-1} \quad \text{and} \quad dS_q = k \Omega^q d\Omega \quad (15)$$

This formula connects the microscopic degeneracy to the thermodynamic variable  $S_q$ . By joining Eq's (1)-(3) when the system is in equilibrium we arrive at the Gibbs equation,

$$dU = TdS - PdV \quad (16)$$

From Eq. (16) we conclude that

$$\left( \frac{\partial S}{\partial U} \right)_V = \frac{1}{T} \quad (17)$$

and from Eq.s (15) and (17) we derive,

$$\Omega^q \left( \frac{\partial \Omega}{\partial U} \right)_V = \frac{1}{kT} \quad (18)$$

This is a fundamental equation of statistical mechanics of nonextensive systems, which relates the temperature to the change in the degeneracy with respect to energy. Since the degeneracy must increase with energy, the temperature is a positive quantity. Note that the combination

$kT(\text{change in})\Omega^q\partial\Omega$  is thermodynamically related to an energy change  $\partial U$ . The discussion so far relates to the *microcanonical* partition function: the case where the system is completely isolated from the environment. In the following section, we discuss the case of canonical ensemble for nonextensive systems.

### **Canonical Ensemble for Nonextensive Systems**

Let us now allow the nonextensive system under consideration exchange energy across a boundary wall, which separates it from its surroundings. We maximize the entropy under the constraint that the average energy of the system is a constant. For nonextensive systems, the internal energy constraint is postulated to be

$$U_q = -k \sum_{i=1}^W p_i^q \varepsilon_i. \quad (19)$$

To perform this optimization with constraints, we employ the method of Lagrange multipliers. We consider the entropy expression modified by two constraints: one for the average energy

$$U_q = -k \sum_{i=1}^W p_i^q \varepsilon_i,$$

and one for the normalization of probabilities

$$\sum_{i=1}^W p_i = 1.$$

This means we minimize the following function  $S'_q$ ,

$$S'_q = k \frac{1 - \sum_{i=1}^W p_i^q}{q-1} - \beta \sum_{i=1}^W p_i^q \varepsilon_i - \theta \sum_{i=1}^W p_i.$$

It should be noted that  $\beta$  has units of inverse temperature while  $\theta$  is dimensionless. In order to perform the minimization the following equation must be solved for the probability,

$$dS'_q / dp_i = k \frac{-qp_i^{q-1}}{q-1} - \beta qp_i^{q-1} \varepsilon_i - \theta = 0.$$

Then, the following expression for the probability is derived [36]

$$p_i = c[kq/(q-1) + \beta q \epsilon_i]^{1/(q-1)}.$$

This equation can be written as

$$p_i = [1 - (1-q)\beta \epsilon_i]^{1/(q-1)} / Z_q,$$

where,

$$Z_q(\beta) = \sum_{j=1}^W [1 - (1-q)\beta \epsilon_j]^{1/(q-1)},$$

is the generalized nonextensive canonical ensemble partition function. With the availability of partition function one can derive the expressions for thermodynamic properties and their relationships with one another. Similar approach as mentioned above can be used to solve for other ensemble theories of statistical mechanics.

### **Conclusions and Discussion**

The historical development of classical thermodynamics of large / macroscopic systems and its applications to a wide range of practical problems took place without any reference at all to the particles comprising the system. It was based only on human experiences with the macroscopic behavior of matter as it relates to conversion of thermal to mechanical energy. This development is entirely rigorous and has the merit of establishing the validity of general thermodynamic principles to all types of matter regardless of its molecular character, but in the thermodynamic limit. However, we need to re-examine classical thermodynamics and its application to small systems before we can apply it to such systems. In this chapter, we have introduced this subject and many more things need to be done to complete it.

It should be pointed out that the problem of predicting and correlating thermodynamic properties of small systems, whether empirically or from molecular properties, is an open and unexplored field of research, while this subject for macroscopic system is in its maturity.

Further research into statistical mechanics for nanoscale systems would lead to possibilities to study the evolution of physical, chemical and biophysical systems on significantly reduced length, time and energy scales. The analytic statistical mechanical modelling and its application to nano systems could be achieved through mathematical modeling employing concepts from statistical mechanics of large systems as well as quantum mechanical many-body theories. It can provide insight into the formation, evolution and properties of nanostructures, self-assemblies and their relation with macroscopic behavior of matter.

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