An Application of Non-Extensive Statistical Mechanics to Nanosystems

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Based on the entropy formulation of Tsallis in the context of non-extensive statistical thermodynamics and the fundamental works of Hill on thermodynamics of small systems (nanothermodynamics), a connection between these two branches of thermodynamics has been made through the concept of subdivision potential in small systems. Statistical mechanical expressions for the subdivision potential, chemical potential and the partition function of small systems are derived, and the formalism for derivation of thermodynamic properties of small systems is introduced.

Keywords: Statistical mechanics, nanothermodynamics.

1. INTRODUCTION

Nano statistical thermodynamics is an extension of classical statistical thermodynamics, which deals with systems consisting of finite numbers of particles/molecules. In other words, the study of sufficiently small systems consisting of limited assembly of molecules requires a modification of classical statistical thermodynamics. For the study of small systems or nanostructures, one needs detailed information about interatomic/intermolecular forces,[1, 2] which determines the arrangement of particles as well as the geometry of these nanostructures. In this report, a mathematical concept has been introduced based on the principles of non-extensive statistical mechanics in order to derive working equations for statistical thermodynamics of small systems. Application of this mathematical concept allows us to derive analytic expressions for the partition function, the subdivision potential and the chemical potential for small systems.

It has been demonstrated that the domain of validity of classical thermodynamics and Boltzmann-Gibbs statistics, $S = k \sum_{i=1}^{W} p_i \ln p_i$ (where p_i is the probability of finding a system in a microscopic state i out of total number W of microstates), is restricted, and as a result, a good deal of attention has been put to discuss such restrictions.[3, 4] This branch of science is categorized in a special part of thermodynamics, which is named "non-extensive thermodynamics". Non-extensive thermodynamics or thermodynamics of non-extensive systems has a formalism, which is proper for the study of complex systems that do not exhibit extensivity.

To overcome difficulties of non-extensive systems, a new statistics is proposed by Tsallis,[3] which is recently modified.[4] According to Tsallis, entropy can be written by the following equation:

$$S_q = k \frac{1 - \sum_{i=1}^{W} p_i^q}{q-1} \left(\sum_{i=1}^{W} p_i = 1; q \in \Re \right) \qquad (1)$$

where k is a positive constant and W is the total number of microscopic possibilities of the system. This expression recovers the usual Boltzmann-Gibbs entropy ($S = k \sum_{i=1}^{W} p_i \ln p_i$) in the limit of $q \to 1$. The entropic index q characterizes the degree of non-extensivity reflected in the following pseudo-additivity entropy rule,

$$\begin{aligned} S_q(A + B)/k &= S_q(A)/k + S_q(B)/k \\ &\quad + (1 - q)[S_q(A)/k][S_q(B)/k] \end{aligned} \qquad (2)$$

where A and B are two independent systems. The cases $q < 1$, $q = 1$ and $q > 1$, respectively, correspond to superadditivity (superextensivity), additivity (extensivity) and subadditivity (subextensivity).

On the other hand, thermodynamics of small systems (nanothermodynamics), which has been recently become

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popular due to the fast progress in nanoscience and nano-technology,[5] has faced similar difficulties as in the case of non-extensive systems for the study of small systems.[3, 4] Nanothermodynamics, a term which was recently introduced in the literature,[6, 7] is an extension of the thermodynamics for macroscopic systems, for systems consisting of finite numbers of particles. In other words, the study of sufficiently small systems requires a modification of ordinary thermodynamics, when the thermodynamic limit is not met. Considering the fact that small systems do not generally satisfy the thermodynamic limit, they may belong to non-extensive systems.

In the present report, we propose a linkage between the nanothermodynamics and non-extensive statistical mechanics in order to develop a statistical mechanical foundation for nano/small systems. The starting point for this formulation is the presentation of the Gibbs equation for small systems.

1.1. The Gibbs Equation for Small Systems

According to Gibbs, for a one-component macroscopic system consisting of N molecules ($N \geq N_{Avogadro}$), the internal energy is a function of entropy, volume and the number of molecules in the system, i.e.: $U = U(S, V, N)$. In differential format, this equation takes the following form, which is the famous Gibbs equation:

$$dU = TdS - PdV + \mu dN \quad (3)$$

Where $\mu = (\partial U/\partial N)_{S,V}$ is defined as the chemical potential.

According to Hill,[6] for small systems ($N < N_{Avogadro}$), we must consider the detailed geometry and structure of the system and the fact that there exist surface forces, edge effects, etc. In this case, it is suggested to use the following relation for the Gibbs equation for a multi component small system:

$$dU = TdS - PdV + \Sigma_i \mu_i dN_i + \boldsymbol{E}d\boldsymbol{N} \quad (4)$$

In the above equations

$$E = (\partial U/\partial \boldsymbol{N})_{S,V,Ni} \quad (5)$$

$\boldsymbol{E}$ is named as the "subdivision potential". It is a result of contributions of surface effects, edge effects, system rotation and translation, etc., all of which are appreciable in small systems and are negligible for macroscopic systems: the term $\boldsymbol{E}d\boldsymbol{N}$ in Eq. (4) does not contribute appreciably to large systems. But the effects just mentioned are not negligible if the system under consideration consists of an assembly of a small number of molecules. $\boldsymbol{N}$ is called the number of non-interacting smaller systems inside the nano system under consideration. $\boldsymbol{N}$ is a number which is generally much smaller than the number of particles (N) in the nano system.

Eq. 4 reduces to the following format in the case of a one-component small system:

$$dU = TdS - PdV + \mu dN + \boldsymbol{E}d\boldsymbol{N} \quad (6)$$

hence

$$U = U(S, V, N, \boldsymbol{N}) \quad (7)$$

Eq. (4) can be rearranged in the following form:

$$dS = (1/T)dU + (P/T)dV - (\mu/TdN) - (\boldsymbol{E}/T)d\boldsymbol{N} \quad (8)$$

then, upon integration, we will have

$$S = (1/T)U + (P/T)V - (\mu/TN) - (\boldsymbol{E}/T)\boldsymbol{N} \quad (9)$$

Through the application of non-extensive statistical mechanics, one can find a statistical mechanical expression for the subdivision potential through which it makes it possible to formulate the details of the thermodynamics of small systems. It is also possible to solve for the partition function of small systems.

1.2. Non-Extensive Statistical Mechanics and Thermodynamics

As mentioned above, the proposed general form of entropy of non-extensive systems, given by Eq. (1) and the entropic index q (intimately related to and determined by the microscopic dynamics), characterizes the degree of non-extensivity of the system. On the other hand, the entropy in Eq. (1) reduces to the usual Boltzmann-Gibbs formula,

$$S = k\sum_{i=1}^{W} p_i \ln p_i \quad (10)$$

in the limit $q \rightarrow 1$. For $q \neq 1$, S_q is not extensive and gives rise to a host of new and interesting effects (which would be relevant for the description of thermodynamically anomalous systems). The difference between extensive and non-extensive systems in Eq. (9) is the term $-(\boldsymbol{E}/T)\boldsymbol{N}$. This term should be calculated from the difference between extensive entropy and non-extensive entropy:

$$-(\boldsymbol{E}/T)\boldsymbol{N} = k\{-[1/(1-q)]\cdot[1 - \Sigma_i p_i^q] + \Sigma_i p_i \ln p_i\}, \quad i = 1 \rightarrow W \quad (11)$$

When parameter $q = 1$, the subdivision potential disappears as it should for macroscopic systems. It can also be shown that

$$-\partial[(\boldsymbol{E}/T)\boldsymbol{N}]/\partial q = -k[1/(1-q)^2]\cdot[1 + (1-q) \Sigma_i p_i^q(-1 + \ln p_i)], \quad i = 1 \rightarrow W \quad (12)$$

Equations (11) and (12) constitute the statistical mechanical definitions of subdivision potential. Through the application of canonical ensemble theory of statistical mechanics, one may be able to develop computational techniques for subdivision potential and other properties of nanosystems.

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Recently, Wang and co-workers[4] have formulated the grand canonical partition function of a non-extensive system in the following form:

$$Z_q = \left\{ \sum_i^v \exp[-q\beta(E_i - \mu N_i)] \right\}^{1/q} \qquad (13)$$

For an ideal gas, by considering Eq. (13), the partition function will reduce to the following form:

$$Z_q = \left\{ \frac{V}{h^3} \left(\frac{2\pi mkT}{q} \right)^{3N/2} \right\}^{1/q} \qquad (14)$$

Now, let us introduce the configurational integral as,

$$Z_q = Z_q^{ig} \left[\int \dots \int e^{-\beta \phi q} dr_1 \dots dr_N \right]^{1/q} / V^N \qquad (15)$$

Based on the well-known equation,

$$U_q = -\left(\frac{\partial \ln Z}{\partial \beta} \right)_{N,V} \qquad (16)$$

we can write the chemical potential in the following form,

$$\mu = G_q/N = [U_q + PV - TS_q]/N \qquad (17)$$

Therefore, we are at the position that we can develop an equation for subdivision potential by using Eqs. (6), (8), (10) and (13)–(16) as follows,

$$\mu_{\text{new}} = \mu(\beta q) + \boldsymbol{E}N/N \qquad (18)$$

It is seen that for conventional (extensive) systems in which $q = 1$, we have $\boldsymbol{E} = 0$, and this is quite in agreement with the basic arguments in non-extensive thermodynamics.

With the availability of analytic expressions for the chemical potential and subdivision potential of nanosytems, it is now possible to attempt to predict phase transitions in nanosystems,[8, 9] which are a basic science behind molecular self replication.[10, 11]

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