

Some Mathematical Concepts Applicable in Nanothermodynamics

G.A. Mansoori¹, G.R. Vakili-Nezhad^{2,*} and A.R. Ashrafi³

¹University of Illinois at Chicago, (M/C 063) Chicago, IL 60607-7052, USA,
mansoori@uic.edu

²Department of Chemical Engineering, Faculty of Engineering, University of
Kashan, Kashan, Iran, vakili@kashanu.ac.ir

³Department of Mathematics, Faculty of Science,
University of Kashan, Kashan, Iran, ashrafi@kashanu.ac.ir

Abstract

Nanothermodynamics is an extension of usual thermodynamics, which deals with the systems consisting of finite particles. In other words, the study of sufficiently small systems at equilibrium requires a modification of ordinary macroscopic thermodynamics. In this note, we solve two mathematical problems related to this area of nanotechnology.

Keywords: Nanothermodynamics, lattices point.

1. Introduction

Nanothermodynamics, a term, which has been recently introduced in the literature, is an extension of usual thermodynamics, which deals with the systems consisting of finite particles. In other words, the study of sufficiently small systems at equilibrium requires a modification of ordinary macroscopic thermodynamics. This new subject has been investigated and the most fundamental results have been published as the thermodynamics of small systems. For the study of small systems or nanostructures, one needs some detailed information about the geometry and arrangement of the particles in these nanostructures. In this letter, two mathematical concepts have been considered. One of them belongs to the geometrical number theory which has been known as the Gauss's circle problem, and the other one relates to the Euler theory of homogeneous functions. Both of these mathematical concepts could be applied in nanothermodynamics.

(*). Corresponding author

2. Physical Significance

Following McQuarrie [5], the degeneracy of the translational energy of a particle could be estimated as 1/8 volume of a sphere with the radius R . This approximation is fair for sufficient high temperatures and for the cases which R is not large enough fails. On the other hand, in conventional statistical mechanics the number of particles is large enough. In the first part of this work, we present a new formulation suitable for the latter case, and in the second part the Euler's theorem is applied for the small systems. The physical significance of this theorem could be directly applied to the non-extensive systems. These systems could be considered as small systems.

3. Problem Statement

Here is a theorem which has been proved applicable for the case in which the above mentioned approximation could not be used for the calculation of degeneracy. We recall that, a point with integer coordinates called a geometric point, which could be considered as lattice points in a nanostructure.

Theorem. Suppose B is a sphere with radius of R , which its center is in the origin of the coordinates. The number of geometric points of B is expressed by the following equation:

$$1 + 4[R] + 4 \sum_{k=-[R]}^{[R]} \left\{ [\sqrt{R^2 - k^2}] + 2 \sum_{t=1}^{\sqrt{\frac{R^2 - k^2}{2}}} [\sqrt{R^2 - k^2 - t^2}] - \left[\sqrt{\frac{R^2 - k^2}{2}} \right]^2 \right\},$$

where $[x]$ denotes the greatest integer $\leq x$.

Proof. We first compute the number of geometric points of a circle of radius r with the origin as its center. To do this, we first assume that:

$$\begin{aligned} A &= \{ (0, y) \mid 0 < y \leq r \} \\ B &= \{ (x, y) \mid 0 < x \leq \frac{r}{\sqrt{2}} ; 0 < y \leq \sqrt{r^2 - x^2} \} \\ C &= \{ (x, y) \mid 0 < y \leq \frac{r}{\sqrt{2}} ; 0 < x \leq \sqrt{r^2 - y^2} \} \\ D &= \{ (x, y) \mid 0 < x, y \leq \frac{r}{\sqrt{2}} \}. \end{aligned}$$

Then, we can see that $|A| = [r]$, $|B| = |C|$ and $|D| = 4[\frac{r}{\sqrt{2}}]^2$. On the other hand, we have eight similar regions with the same number of geometric points, in the three dimensional space. These regions are out of the square constructed

by the vertices $(\frac{\pm r}{\sqrt{2}}, \frac{\pm r}{\sqrt{2}})$. Therefore, it is enough to compute the number of geometric points of a region and multiply it by 8. But, the number of geometric points in a region is equal to $\sum_{k=1}^{\frac{r}{\sqrt{2}}} (\sqrt{r^2 - k^2} - \frac{r}{\sqrt{2}})$. This shows that the number of geometric points in the sphere of radius R is as follows:

$$1 + 4[R] + 4 \sum_{k=-[R]}^{[R]} \left\{ [\sqrt{R^2 - k^2}] + 2 \sum_{t=1}^{\sqrt{\frac{R^2 - k^2}{2}}} [\sqrt{R^2 - k^2 - t^2}] - [\sqrt{\frac{R^2 - k^2}{2}}]^2 \right\}.$$

The second problem that has been considered in this note is related to the Euler's homogeneous functions. We know from usual macroscopic thermodynamics that two categories of thermodynamic properties known as extensive and intensive properties exist that mathematically speaking are Euler's homogeneous functions in the first and zero degrees in mole numbers, or

$$f(nX_1, nX_2, nX_3, \dots) = n^\lambda f(X_1, X_2, X_3, \dots); \lambda \neq 1,$$

where, $\lambda = 0$ for intensive, $\lambda = 1$ for extensive properties, f is a thermodynamic property and λ is an exponent. In nanothermodynamics these thermodynamic functions lost their properties and there is no longer a linear relationship between the number of moles of the system and its extensive properties (such as internal energies, entropy, etc.). Here we propose a similar relation as the above equation for extensive properties but with $\lambda \neq 1$ for the non-extensive thermodynamic properties of the small systems. Since, in the small systems we are faced to the new class of thermodynamic properties which have not usual mathematical and physical interpretations of the extensive properties of the macroscopic systems. Therefore,

$$F(NX_1, NX_2, NX_3, \dots) = N^\lambda f(X_1, X_2, X_3, \dots); \lambda \neq 1.$$

For determining λ some experimental data or reliable calculations on the relevant properties of small system must be carried out.

References

- [1] G.E. Andrews, Number Theory, Hindustan Publishing Corporation, 1984, 3th ed., 1992.
- [2] T.L. Hill, A different approach to nanothermodynamics, Nano Lett., 1(5)(2001), 273-275.
- [3] T.L. Hill, NanoSeconds Perspective: Nanothermodynamic, Nano Lett., 1(3)(2001), 111-112.

- [4] T.L. Hill, Extension of Nanothermodynamic to Include a One-Dimensional Surface Excess, *Nano Lett.*, **1**(3)(2001), 159-160.
- [5] D. McQuarrie, *Statistical Thermodynamics*, Harper and Row, 1977.