# NANOTHERMODYNAMICS

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## Contents

## Summary

Different approaches to nanothermodynamics including surface thermodynamics, non-extensive statistical mechanics, Hill's theory of nanothermodynamics, and tensorial approach to thermodynamics are given in this chapter. Starting from the first appearance of the term nanothermodynamics in the literature, its development is presented and its connection to the previous related theories on thermodynamics of

small systems has been discussed in details. Relation between nanothermodynamics and surface thermodynamics as well as non-extensive statistical thermodynamics based on Tsallis statistics is revealed through the concept of sub-division potential introduced in Hill's theory of nanothermodynamics. Extensive and intensive thermodynamic properties definitions in conventional Gibbs thermodynamics have been modified to be applicable to the small systems through the Euler's theorem of homogenous functions. Some mathematical concepts applicable in nanothermodynamics are introduced and in all topics presented, in case of the presence of experimental evidences, they have been given as well. Most important considerations of theoretical and experimental nanothermodynamics have been reviewed as the final concluding remarks to draw a comprehensive conclusion.

## 1. Introduction

Although the term nanothermodynamics has been introduced for the first time by T. L. Hill in 2000, and the same or equivalent concept has been well defined in the book written by the same scientist in 1963 and 1964 entitled "Thermodynamics of Small Systems", but the question "Small systems: when does thermodynamics apply?" was raised seven decades ago in the context of nuclear reactions and continues to be asked to this day. This question has to be asked again, because of the feasibility of creating advanced materials in "small" sizes ranging from microsystems and nanosystems to atomic clusters by the modern existing sophisticated techniques today. These materials display a variety of interesting physical properties. From theoretical point of view, it was clear right from the beginning that as the system size decreases, one has to deal with fluctuations in thermodynamic properties, but only in 1992, quantitative measurements of temperature fluctuations in a physical system using superconducting magnetometers were reported. With more recent advances in thermometry, further investigations may be forthcoming in the near future. Regarding to the definition of microphases and nanophases, thermodynamical considerations must be taken into account in addition to their sizes. In other words, it can be said that microphases can be occurred by reducing the size below one micrometer, and their properties are affected by the surface free energy. Moreover, nanophases exist in the size range of 0.5-50 nm and there is a difference between them and microphases, in case of there is no bulk phase enclosed by the surfaces. The last point can be expressed in other words: the upper limit of nanophases varies with composition and property of the phase boundaries, and the lower limit of thermodynamic description is below 0.5 nm. Therefore, as a general fact, it must be considered that the term nanophase should be applied where some justifications could be given for the existence of some changes from the microphases. In summary, nanophases must have different properties from their macrophases or microphases. Sometimes many nanophases are not only better than micro or even macro, but also they are less suited for a given task. Using thermodynamics, it can be concluded that if there is no change in the property of matter under study, it is not a nanophase. Nanothermodynamics deals with the systems consisting of finite particles or nanophases. Therefore, the study of sufficiently small systems at equilibrium requires a modification of ordinary macroscopic thermodynamics. After Gibbs, thermodynamic description of macrophases can be expressed as "the phases consist of homogeneous, macroscopic volumes of matter, separated by well-defined surfaces of negligible influence on their thermodynamic

functions". There are different approaches to deal with the sound investigation on the subject of nanothermodynamics. Surface thermodynamics, non-extensive statistical mechanics, and Hill's approach based on the concept of subdivision potential are the most common approaches, although nowadays computer simulations base on fast and powerful computers are quite active research line on this topic. Nevertheless, theoretical works and simulations have an important role in discovering the unknowns in nanothermodynamics, but the modern experimental techniques, such as superfast calorimetry, are experimental basis of the research works in nanothermodynamics.

## 2. Different Approaches to Nanothermodynamics

### 2.1. Surface Thermodynamics

Surface thermodynamics has a close relation with nanothermodynamics, or in other words it is another version of a unique concept. Due to the large ratio of surface to volume of a nanoparticle, its properties depend on the size, which is not the case for ordinary large systems. Here the influence of surface tension on chemical potential of a nanoparticle is described first, then the dependence of surface tension and surface energy on the nanoparticle size will be explained. In mathematical form, chemical potential of a liquid particle in nucleation can be given by the following equation:

$$\mu^{\alpha} = \mu_{\infty}^{\alpha} + \frac{2\sigma v^{\alpha}}{R} \tag{1}$$

where, $\mu_{\infty}^{\alpha}$ is the limiting value of $\mu^{\alpha}$ at $R \to \infty$ and $v^{\alpha}$ is molecular volume.

For a long time, dependency of surface tension to the surface curvature has been an important problem in the theory of capillary. For fluid interfaces classical Gibbs-Tolman equation can be written in the following form:

$$\frac{d \ln \sigma}{d \ln R_s} = \frac{\left(\dfrac{2\delta}{R_s}\right)\left[1 + \dfrac{\delta}{R_s} + \dfrac{\left(\dfrac{\delta}{R_s}\right)^2}{3}\right]}{1 + \left(\dfrac{2\delta}{R_s}\right)\left[1 + \dfrac{\delta}{R_s} + \dfrac{\left(\dfrac{\delta}{R_s}\right)^2}{3}\right]} \tag{2}$$

Where $\delta$ is the Tolman parameter, $R_s$ belongs to the surface tension, and $R$ is the

radius of the equimolecular surface. In case of a flat interface, the following equation can be derived from Eq. (2) :

$$\frac{\sigma}{\sigma_\infty} = 1 - \frac{2\sigma}{R} + \cdots \tag{3}$$

Moreover, molecular dynamics simulations have shown the dependence of the surface tension of argon cluster on the cluster radius. For nanoparticles, dependency of surface tension to size is really important. According to Gibbs, $\sigma$ is the work required for formation of unit area of a new surface. Using the molecular pair potential, and doing the calculations, some interesting results could be obtained. For example, it has been demonstrated that the extraction of a molecule from bulk is more difficult than to transfer the molecule to the surface. Another fact is that cohesion energy belongs equally to the concave and convex touching surfaces, and the surface energies of both phases are the same, and independent of the curvature sign.

### 2.1.1. Phase Transitions in Nanoparticles

Because of the small size of nanoparticles, instantaneous phase changes exist in these systems, and it is hard to assume or define equilibrium state between two phases inside a particle. Therefore, in the new approach of surface thermodynamics, Gibbs energy values are compared for the whole nanoparticle, before and after phase transition. In this case, due to the constant amount of matter in the particle, the following equation can be applied to the equilibrium condition of a nanoparticle comprising a uniform bulk phase $\alpha$, and a piecewise smooth surface:

$$d\Phi = -SdT + V_0 \sum_{s,t} e_{st}^\alpha dE_{st}^\beta \tag{4}$$

where, $V_0$ is the particle volume in a strainless state, $e$ is strain tensor, and $E$ is stress tensors. This equation refers to any complex particle including its surface layer. Considering the polymorphous transformation of a particle, the following equation can be written:

$$\frac{dT}{dP^\beta} = \frac{\Delta V}{\Delta S} \tag{5}$$

which is the Clapeyron-Clausius equation with a little difference of external pressure of $P^\beta$ instead of real pressure $P^\alpha$ whose action causes phase transition. External pressure affects the phase transition process in a particle. For a mechanically isotrope system, we have $\Delta SdT = \Delta(V - V_0)dP^\alpha$, which can be written as:

$$\frac{dT}{dP^\alpha} = \frac{\Delta V}{\Delta S} \tag{6}$$

By the following example, the tendency of the comminution process could be explained by the Clapeyron-Clausius equation. If the derivative $dT/dP^{\alpha}$ is negative, internal pressure of particles increases, and phase transition temperature decreases with decreasing the particle size in the comminution process. The derivative $dT/dP^{\alpha}$ in the Clapeyron-Clausius equation can have any sign, because molar volume decreases with increasing pressure under isothermal conditions, and increasing temperature under isobaric conditions increases molar entropy. There are two distinct cases of normal and abnormal, due to the positive or negative slope of the line of a polymorphous transformation in the state diagram $T - P^{\alpha}$. In the normal case, matter changes to more dense modification, and to less modification in the abnormal case. Various real phase transitions such as $CaCO_3$ phases (vaterite, calcite and aragonite) or massicot and litharge phases of PbO can be explained using the above discussions. For second order phase transitions, change of entropy and change of volume are zero, and the Clapeyron-Clausius equation becomes indeterminate. In this situation, thermodynamic potentials of phases as well as any other quantities could be equated.

### 2.1.2. Quasi-Chemical Description of Solid Nanoparticles

The new approach of quasi-chemical to nanoparticles has been discussed by Rusanov in 2005. The heart of this approach is assuming a nanoparticle as a single large and complex molecule or an ion of multiple charge, rather than a piece of a phase. Here the term supramolecule has been chosen instead of nanoparticle. If $\{n\}$ gives the composition of the supramolecule, its chemical potential could be written in the following form:

$$\mu_{\{n\}} = G^0_{\{n\}} + k_B T \ln\left(C_{\{n\}} \Lambda^3_{\{n\}} f_{\{n\}}\right) \tag{7}$$

Where, $G^0_{\{n\}}$ is the Gibbs energy of a supramolecule of sort $\{n\}$ in a dispersion containing other supramolecules, $k_B$ is the Boltzmann constant, $\Lambda_{\{n\}}$ is the de Broglie wavelength, and $f_{\{n\}}$ is the activity coefficient of supramolecules. From this equation, two physiochemical processes have been explained theoretically. The first process has been a polymorphous transformation, and the second one dissolution or evaporation of nanoparticles.

### 2.1.3. Size Dependent Interface Energy

Extension of thermodynamic methods to very small objects such as nanoparticles faces many principal difficulties. Here we are going to present various formulas which have been given for different interfaces including solid-liquid, solid-solid, solid-vapor, and liquid-vapor interfaces. For each case the bulk interface energy will be introduced, then their dependency to the size will be presented too. "The bulk solid-liquid interface free energy ($\gamma_{\text{slo}}$) is defined as the reversible work required to form or to extend a unit area

of interface between a crystal and its coexisting fluid plastically". Many important physical processes and phenomena like crystal growth from the melt, homogenous nucleation, surface melting and roughening can be explained through this property. Therefore, models representing the bulk solid-liquid interface are really necessary. Turnbull equation based on the nucleation experiments and the classical nucleation theory (CNT) can be written in the following form:

$$\gamma_{\mathrm{CNT}} = \frac{\tau H_{\mathrm{m}}}{\left(V_{\mathrm{s}}^2 N_{\mathrm{a}}\right)^{\frac{1}{3}}} \tag{8}$$

where, $\tau$ is Turnbull coefficient, and its value for metals is 0.45, while for nonmetallic elements equals to 0.34. $H_{\mathrm{m}}$ is melting enthalpy and $N_{\mathrm{a}}$ is Avogadro constant. The calculated values for $\gamma$ are lower than the real ones for metals. Another equation which is formulated by Ewing is given by:

$$\gamma_{\mathrm{sl}} = hH_{\mathrm{m}} \big/ (4V_{\mathrm{s}}) + \left(\frac{N_{\mathrm{a}}b'k}{V_1}\right)\int_0^{b'} g_1(r)\ln g(r)dr \tag{9}$$

where, $h$ is the atomic diameter in crystals, and $V_{\mathrm{s}}$ and $V_1$ are the g-atom volumes of the solid and liquid phases, respectively. $b'$ is the cut-off distance beyond which $g_1(r)$ shows no significant deviation from unity and $k$ is Boltzmann's constant. Other equations given by some researchers are:

$$\gamma_{\mathrm{sl}} = 0.21H_{\mathrm{m}} \big/ \left(V_{\mathrm{s}}^2 N_{\mathrm{a}}\right)^{1/3} + 0.52\times10^{-7}T\big/V_{\mathrm{s}}^{2/3} \tag{10}$$

and

$$\gamma_{\mathrm{sl}} = \Phi\left(H_{\mathrm{m}} + TS_{\mathrm{m}}\right) \bigg/ \left[2\left(\frac{V_{\mathrm{s}}^2}{N_{\mathrm{a}}}\right)^{1/3}\right] \tag{11}$$

In the later equation, $\Phi$ is a geometric factor (depending on the interface orientation) between 0.29 and 0.63 for cubic or *hcp* structures, and $S_{\mathrm{m}}$ is melting entropy. But the most powerful theoretical method for $\gamma_{\mathrm{sl}}$ is the Gibbs-Thomson (also known as Kelvin) equation which can be written as,

$$\gamma_{\mathrm{sl}} = D_{\mathrm{n}}H_{\mathrm{m}}\left(T_{\mathrm{n}}\right)\left(1 - \frac{T_{\mathrm{n}}}{T_{\mathrm{m}}}\right)\bigg/\left(4V_{\mathrm{s}}\right) \tag{12}$$

This equation describes the equilibrium between a small spherical solid nucleus and the infinite amount of its liquid. In Eq. (12) $D_n$ is the critical diameter of the solid nucleus and $T_n$ is the nucleation temperature. Eq. (12) is valid when the temperature is less than melting temperature or equivalently,"where the equilibrium size of the solid phase has a finite positive value". Physical interpretation of Eq. (12) can be expressed in the following form: from thermodynamic point of view, growth of the solid phase is more favorable than its dissolution for solid nucleus with size $D$ greater than $D_n$ at $T_n$. Therefore, $\gamma_{sl}$ can be determined, provided $D_n$ at $T_n$ is known. By introducing size dependent $\gamma_{sl}$, the classical nucleation theory has been re-examined to present the Gibbs free energy change, $\Delta G(D,T)$, of the metallic systems consisting of the nucleus and the rest fluid:

$$\frac{\Delta G(D,T)}{\dfrac{\pi h^3}{3V_s}} = \left[ \frac{1 - \dfrac{3h}{D}}{\dfrac{D}{2h}} \frac{7T}{T_m + 6T} \frac{S_{vib}}{R} - \frac{T_m - T}{2T_m} \right] \frac{7T}{T_m + 6T} \left( \frac{D}{h} \right)^2 \tag{13}$$

where, $S_{vib}$ is the vibrational part of the overall melting entropy. It is clear that critical diameter of nucleation ($D_n$) can be obtained from the following equation:

$$\frac{\partial \Delta G(D,T)}{\partial D} = 0 \tag{14}$$

The bulk solid-liquid interface free energy for 62 metallic crystals and 38 organic crystals have been reported. These values can be used in the equations proposed for the size dependent solid-liquid interface energy [$\gamma_{sl}(D)$]. The following equation includes effect of size on the solid- liquid interface energy:

$$\frac{\gamma_{sl}(D)}{\gamma_{slo}} = \frac{\left[ 1 - \dfrac{8\kappa f^2}{3\gamma_{slo}D} \right]}{1 - \dfrac{8\kappa f}{3D}} \tag{15}$$

where, $f = \partial(\gamma_{sl}A)/\partial A$ is the interface stress, and $\kappa$ is compressibility $\kappa = -\Delta V / (VP)$. Moreover, the integrated size and temperature dependent interface energy can be determined as:

$$\frac{\gamma_{sl}(D,T)}{\gamma_{slo}(T_m)} = \left(1 - \frac{3h}{D}\right)\left(\frac{7T}{T_m + 6T}\right)^2 \tag{16}$$

Where, $h$ is given by the following equations:

$$h \cong \frac{D_0}{3} \tag{17}$$

$$h = \frac{D_0}{2} \tag{18}$$

where $D_0$ is critical diameter between solid and liquid. Equation (17) is for particles or wires and Eq. (18) for films.

By the assumption that the bulk solid-solid interface energy $\gamma_{sso}$ at $T_m$ is approximately twice of $\gamma_{sl0}$ we can write,

$$\gamma_{sso}(T_m) \approx 2\gamma_{slo}(T_m) \approx \frac{4hS_{vib}H_m}{3V_sR} \tag{19}$$

Equation (19) can be used for calculation of the $\gamma_{sso}$ values, at least for metals and organic crystals. Similar to the deduction of $\gamma_{sl}(D)$, the size dependent solid-solid interface energy, $\gamma_{ss}(D)$, can be expressed in the following form:

$$\frac{\gamma_{ss}(D)}{\gamma_{sso}} = \frac{1 - \dfrac{D_0}{4D}}{1 - \dfrac{\gamma_{sso}D_0}{4fD}} \tag{20}$$

Good agreement has been seen between the predictions of Eq. (20) and computer simulation results for copper.

The bulk solid-vapor interface energy can be defined as the difference of free energy between surface atoms and interior ones. Experimental determination of this property is quite difficult and that is why the models for predicting this property are needed for research works in this area. There have been several attempts to calculate $\gamma_{svo}$ values for metals using *ab initio* techniques or semi-empirical methods. The following equation has been presented for calculating $\gamma_{svo}$:

$$\gamma_{\text{svo}} = \frac{\left(2 - k_1 - k_1^{1/2}\right)E_{\text{b}}}{2N_{\text{a}}A_{\text{s}}} \tag{21}$$

where, $k_1 = Z_{\text{s}}/Z_{\text{B}}$, the ratio between coordination numbers of surface atoms and interior ones, $E_{\text{b}}$ is bulk cohesive energy, and $A_{\text{s}}$ denotes the area of the two-dimensional unit cell of solid. Comparison of surface energies of *fcc* metals with the predicted values of Eq. (21) has been made and good results have been observed. If nanocrystals have the same structure of the corresponding bulk, then the size dependent solid-vapor interface energy can be written as:

$$\frac{\gamma_{\text{sv}}(D)}{\gamma_{\text{sv}}} = \left[1 - \frac{1}{\frac{2D}{h} - 1}\right]\exp\left(-\frac{2S_{\text{b}}}{3R}\frac{1}{\frac{2D}{h} - 1}\right) \tag{22}$$

Predictions of this equation have been compared with the experimental results for Be and Mg, and good agreement has been observed. There is an interesting relation between $\gamma_{\text{sv}}$ of different facets to their corresponding bulk values. This relation can be expressed in the following form:

$$\frac{\gamma_{\text{sv}}^1(D)}{\gamma_{\text{sv}}^2(D)} = \frac{\gamma_{\text{svo}}^1}{\gamma_{\text{svo}}^2} \tag{23}$$

This equation shows that, in spite of size-dependency of $\gamma_{\text{sv}}(D)$, the solid-vapor interface energy ratio between different facets is size-dependent, and simply this ratio equals to the corresponding bulk ratio. This fact has been justified for Au nanoparticles with different sizes and structures.

The bulk liquid-vapor interface energy $\gamma_{\text{lvo}}$ of pure substances has been given by the Eotvos or Guggenheim empirical equations:

$$\gamma_{\text{lvo}}(T)V_1^{2/3} = Q\left(1 - \frac{T}{T_{\text{c}}}\right) \tag{24}$$

or

$$\frac{\gamma_{\text{lvo}}(T)}{\gamma_{\text{lvo}}(T_{\text{m}})} = \left(1 - \frac{T}{T_{\text{c}}}\right)^w$$

where $Q$ and $w$ are system-dependent parameters. For example $w = 0.8$ for strongly hydrogen bonded substances, and $w = 11/9$ for $H_2$, $N_2$ and CO. The size dependency of liquid-vapor interface energy $\gamma_{lv}(D)$ can be expressed by the following equation:

$$\frac{\gamma_{lv}(D)}{\gamma_{lvo}}\left[1 - \frac{1}{\frac{2D}{h} - 1}\right]\exp\left(-\frac{2S_b}{3R}\frac{1}{\frac{2D}{h} - 1}\right) \tag{25}$$

The parameters involved in this equation have been reported for Na, Al and H₂O. Simulation results and predictions of Eq. (26) have been compared with good agreement. There are some applications for size dependent interface energy. The followings are just some examples: thermodynamic phase stabilities of nanocarbon, static hysteresis of solid transition of CdSe nanocrystals, the critical layer number of epitaxially grown films, critical misfit of epitaxial growth metallic thin films, reconstruction possibility of *fcc* metallic surfaces at room temperature, and temperature-dependent self-diffusion coefficient in liquid elements. As a final result of this section it can be said that due to the rapid developments of nanomaterials and nanotechnology, size dependent models of interface energy provide clue to explore the novel properties of nanomaterials.

## 2.1.4. Thermodynamics of Confined Fluids in Nanopores

Recently, it has been shown that thermodynamic equations for confined fluids in the nanometric scale may be different from their counterparts in macrothermodynamics. For the study of pressure-volume-temperature (*PVT*) behavior of the confined fluids in a small pore (nanopore), the van der Waals equation of state has been modified by considering the tensorial nature of pressure in nanopores. Here using the modified form of the van der Waals equation of state, some thermodynamic properties have been obtained to interpret the complex phenomenon of phase change or fragmentation of the confined fluids in nanopores.

Following the pioneering work of Landau and Lifshitz, on the assumption of pressure as a diagonal tensor, the following equations of state have been proposed for a confined fluid in a long nanotube with nanosized diameter,

$$p_{xx} = p_{yy} = \frac{NkT}{v - Nb} - \frac{N^2}{V^2}\left[a - \varepsilon\sigma^3\left(3\frac{c_1}{\sqrt{A}} + 4\frac{c_2}{A}\right)\right] \tag{27}$$

$$p_{zz} = \frac{NkT}{v - Nb} - \frac{N^2}{V^2}\left[a - 2\varepsilon\sigma^3\left(\frac{c_1}{\sqrt{A}} + \frac{c_2}{A}\right)\right] \tag{28}$$

where $c_1 = 4.6571, c_2 = -2.1185$, and $a$ and $b$ are the van der Waals equation of

state bulk parameters. $\varepsilon$ and $\sigma$ are energy and size parameters of the Lennard-Jones potential parameters, respectively, and $A$ is the cross sectional area of the nanopore. These equations recover the conventional van der Waals equation of state (in bulk), when the cross sectional area approaches to infinity,

$$p_{xx} = p_{yy} = p_{zz} \tag{29}$$

General definition of fugacity is given by the following equation,

$$f = p \exp\left( \int_0^p (Z-1) \frac{dp}{p} \right) \tag{30}$$

Therefore, considering the various components of the pressure tensor in different directions as well as the general definition of fugacity, the following direction dependent equations are obtained for the fugacity of a confined fluid in a nanopore in different directions,

$$f_{xx} = f_{yy} = p_{xx} \exp\left( \int_0^{p_{xx}} (Z_{xx}-1) \frac{dp_{xx}}{p_{xx}} \right) = p_{yy} \exp\left( \int_0^{p_{yy}} (Z_{yy}-1) \frac{dp_{yy}}{p_{yy}} \right) \tag{31}$$

and,

$$f_{zz} = p_{zz} \exp\left( \int_0^{p_{zz}} (Z_{zz}-1) \frac{dp_{zz}}{p_{zz}} \right) \tag{32}$$

where, $Z_{xx}$, $Z_{yy}$ and $Z_{zz}$ are compressibility factors in $x, y$ and $z$ directions, respectively. They could be obtained by multiplication of V/RT to the both sides of Eqs. (27) and (28). After obtaining the relevant equations for the compressibility factors, we can use Eqs. (31) and (32) to derive the fugacity of a confined fluid in a nanopore for each direction. The results can be written as follows:

$$\ln f_{xx} = \frac{\ln(V-Nb)}{V} - \frac{N}{kTV}\left[ a - \varepsilon\sigma^3\left( 3\frac{c_1}{\sqrt{A}} + 4\frac{c_2}{A} \right) \right] + Z_{xx} - 1 + \frac{\ln NkT}{V} \tag{33}$$

$$\ln f_{yy} = \frac{\ln(V-Nb)}{V} - \frac{N}{kTV}\left[ a - \varepsilon\sigma^3\left( 3\frac{c_1}{\sqrt{A}} + 4\frac{c_2}{A} \right) \right] + Z_{yy} - 1 + \frac{\ln NkT}{V} \tag{34}$$

$$\ln f_{zz} = \frac{\ln(V-Nb)}{V} - \frac{N}{kTV}\left[ a - 2\varepsilon\sigma^3\left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right) \right] + Z_{zz} - 1 + \frac{\ln NkT}{V} \tag{35}$$

In the above equations $Z_{xx}$, $Z_{yy}$ and $Z_{xx}$ can be expressed by the following equations,

$$Z_{xx} = Z_{yy} = \frac{V}{V - Nb} - \frac{N}{kTV}\left[ a - \varepsilon\sigma^3\left( 3\frac{c_1}{\sqrt{A}} + 4\frac{c_2}{A} \right) \right] \qquad (36)$$

$$Z_{zz} = \frac{V}{V - Nb} - \frac{N}{kTV}\left[ a - 2\varepsilon\sigma^3\left( \frac{c_1}{\sqrt{A}} + \frac{c_2}{A} \right) \right] \qquad (37)$$

According to Eqs. (33) to (35), the fugacity of a confined fluid in a nanopore is an anisotrope property, dependent to the geometrical direction. On the other hand, fugacity can be applied as a criterion for expressing the equilibrium conditions in fluid phase equilibria. Therefore, it can be said that there are different phases in the $x$-$y$ directions than the $z$ direction in a long nanosized tube like carbon nanotube. This fact has been confirmed in the experimental observations of the fragmentation phenomenon of the confined water in long nanotubes.

## 2.1.5. Thermodynamic Properties of Some Nanostructures

Here we will concentrate on two important classes of carbon nanostructures which have many applications to nanoscience and nanotechnology. These are diamondoids and fullerenes. Diamondoid hydrocarbons are ringed compounds that have a diamond like structure consisting of a number of six-member carbon rings fused together. They have high melting points and low strain energy, which highlights their relative stability. Recently, interest in higher diamondoids has been renewed by molecular simulation studies suggesting possible applications in nanotechnology. Due to the application of diamondoids to nanotechnology, here some thermodynamic properties of two important members of these nanostructures (adamantane and diamantane) are presented.

Phase boundary experiments of adamantane have been carried out, and the following equation has been presented for the vapor pressure curve,

$$\ln P\left(\text{kPa}\right) = -\frac{6570}{T} + 188.18 \qquad 483 < T < 543\text{K} \qquad (38)$$

Similarly, the equation representing the liquid-vapor curve of diamantane can be expressed in the following form,

$$\ln P\left(\text{kPa}\right) = -\frac{5680}{T} + 14.858 \qquad 516 < T < 716\text{K} \qquad (39)$$

Further information about the phase behavior of diamondoids has been reviewed by Vakili-Nezhaad (2007).

Buckminsterfullerene (or fullerene, $C_{60}$) is a new allotrope of carbon (after graphite and diamond) which was discovered by Kroto and co-workers by the method of laser evaporation of graphite. Since the time of discovery of fullerenes, investigations have

been carried out to find out more about these nanostructures due to their applications in nanotechnology. Thermodynamic properties of these nanostructures have a vital role in proper application of these molecules. Among thermodynamic properties, heat capacities are very important for almost all operations related to the fullerenes. For calculation of heat capacities, frequencies of $C_{60}$ are required. Recently, heat capacities of solid phase fullerene have been calculated based on the calculated vibrational frequencies of $C_{60}$ using efficient quantum mechanical methods. These methods have been used through *ab initio* GAUSSIAN98 program with the STO-3 basis set and HYPER7 program with PM3 and AM1. The results of these calculations have been used in the following equation for calculating heat capacity of $C_{60}$ at constant volume,

$$C_V = R \sum_{i=1}^{46} g_i \left( \frac{\theta_i}{T} \right)^2 \frac{\exp(\theta_i/T)}{\left[ \exp(\theta_i/T) - 1 \right]^2} \tag{40}$$

where, $R$ is gas constant, $T$ is temperature, and $\theta_i = h v_i / k$ is characteristic frequency. To obtain heat capacity at constant pressure, $C_P$, the Nernst-Lindemann equation can be used as follows,

$$C_P - C_V = \frac{3 R A^0 C_P T}{T_m^0} \tag{41}$$

where $A^0$ is an experimental coefficient equals to $3.9 \times 10^{-3}$ kmol/J, and $T_m^0$ denotes the equilibrium melting temperature which is estimated to be 1000 $K$.

## 2.1.6. Structural Properties of Nanoclusters

First, we must know phase transitions in small systems are gradual, not sharp. As a result of this fact, it must be said that there are bonds of temperature and pressure within which two or more cluster structures may coexist dynamically, like that of coexisting chemical isomers. Second, thermodynamic properties are strongly size dependent. Hill has presented the following equation for the Gibbs free energy $G$ of a small system including bulk and surface effects:

$$G = N g(p,T) + b(p,T) N^{2/3} + c(p,T) N^{1/3} + d(p,T) \tag{42}$$

where, $g(p,T)$ is the specific Gibbs potential. The term including $N^{2/3}$ is a surface free energy, the term including $N^{1/3}$ is due to edge contributions and the last one goes back to other things like rotation of the cluster. Although in case of small systems all terms are important, but in the limit $N \to \infty$, $G \to N g$, and macroscopic relation will be obtained. In what follows the role of entropic contributions to the free energy at high temperatures will be considered, then melting of clusters will be discussed from experimental and theoretical (simulation) points of view. Later, size dependence of the

melting phenomenon will be given, and finally some systems of particular interest will be reviewed. By increasing the temperature, structural transitions can be taken place because of entropic effects. Here the theoretical foundations of the existence of entropy-driven solid-solid transitions will be reviewed, considering both classical harmonic approximation and anharmonic and quantum corrections.

For considering structural transitions in the harmonic approximation, in case of neglecting the coupling of rotational and vibrational motions, $Z_s$ can be written as:

$$Z_s = Z_s^{tr} Z_s^{rot} Z_s^{vib} \tag{43}$$

where, $Z_s^{tr}$ and $Z_s^{rot}$ are related to the center of mass translation and to rigid rotational motions, respectively, and $Z_s^{vib}$ is vibrational motion around $S$. The related functions can be written as follows:

$$Z_s^{vib} = e^{-\beta E_s^0} \prod \left( \frac{k_B T}{\hbar \omega_{s,j}} \right) \tag{44}$$

$$Z_s^{tr} = v \left( \frac{M k_B T}{2\pi \hbar^2} \right)^{3/2} \tag{45}$$

$$Z_s^{rot} = \left( \frac{2\pi k_B T \overline{I}_s}{\hbar^2} \right)^{3/2} \tag{46}$$

where, $E_s^0$ is the minimum energy, $\kappa = 3N - 6$ ($N$ is cluster size) is the upper limit of multiplication operator, $\omega_{s,j}$ is the normal mode frequency, $v$ is the volume of the box in which the cluster is contained, $M$ is the cluster mass, and $I_s$ is the average internal moment in s, $\overline{I}_s = \left[ I_s^{xx} I_s^{yy} I_s^{zz} \right]^{1/3}$, with $I_s^{xx}$, $I_s^{yy}$ and $I_s^{zz}$ as the principal moments of inertia. Although the harmonic superposition approximation is often accurate for cluster thermodynamics up to temperatures close to the melting point range, however, anharmonic effects must be included in some cases. For example solid-solid transitions can be close to the melting temperature, and anharmonic effects are not negligible. Also quantum corrections must be considered for the corrections to $Z_s^{vib}$. In this case, we have the quantum partition function of a set of oscillators as follows:

$$Z_s^{vib} = e^{-\beta E_s^0} \prod_{i=0}^{k} \left[ 2\sinh\left(\beta \hbar \omega_{i,s}/2\right) \right]^{-1} \tag{47}$$

Quantum corrections are needed when the temperature is less that 70% of Debye

temperature.

Regarding to the melting of nanoclusters, there are several differences between the solid-solid transition of clusters, and that of its bulk counterpart as follows:

- The melting point is reduced with a complex dependence on size.
- The latent heat is smaller.
- The transition takes place smoothly over a finite range of temperature.
- The microcanonical average kinetic energy may be nonmonotically increasing function of the total energy in the range of the transition. It means that the heat capacity can become negative in microcanonical environments.
- The melting transition depends on cluster structure and chemical ordering.

Two classes of experiments for studying cluster melting can be mentioned as follows:

- Measurement of the caloric curve, i.e. the cluster's internal energy as a function of temperature.
- Study of physical properties change, across the melting point.

In addition to experimental methods, there are computational methods for the study of nanoclusters melting. The most common method for study the melting transition, is the calculation of caloric curve. This goes back to a smooth jump in the melting region corresponding to the heat capacity peak. But this method does not work always, because the jump may be small, difficult to find, or even absent. A good criterion for distinguishing solid like and liquid like phases is the Landau free energy which is defined as $F_1(Q) = k_B T \ln P(Q) + Const.$ where $P(Q)$ is the probability of the observing value of $Q$ of the order parameter for the transition in the simulation run. Now the practical problem is finding the proper order parameters. Possible order parameters may be listed as the total potential energy $E_p$, the difference between the configurational energy and the global minimum energy, the orientational and order parameters $Q_L$, the signatures of the common neighbor analysis, the radial distribution function, and surface disordering phenomena. Although Lindemann criterion could be used for distinguishing between solid like and liquid like phases, but a better idea is to introduce the distance fluctuation measure $\Delta_{DF}$ as follows:

$$\Delta_{DF} = \frac{2}{N(N-1)} \sum_{i<j} \frac{\sqrt{\langle \Delta r_{ij}^2 \rangle}}{\langle r_{ij} \rangle} \tag{48}$$

where, $r_{ij}$ is the distance between $i$ and $j$ atoms, and $\langle \Delta r_{ij}^2 \rangle = \left\langle \left( r_{ij} - \langle r_{ij} \rangle \right)^2 \right\rangle$. Both criteria of Lindemann and distance fluctuation are the representative of the mobility of a phase, but the main difference between these two is that the latter is based on the fluctuation of the distance between pairs of atoms, while the former is based on the

fluctuation of individual atoms relative to their average position. The critical value of $\Delta_{DF}$ has been suggested by Zhou and coworkers to be in the range of 0.03 to 0.05. Standard simulation methods such as molecular dynamics and Monte-Carlo have been used for the study of melting of nanoclusters. Monte Carlo method is based on a fictitious dynamics, while molecular dynamics provides a realistic simulation of melting and freezing processes. On the other hand, Monte Carlo is suitable for static quantities due to its speed in sampling the configuration space. Quasiergodicity is a major problem in calculating thermodynamic properties. This problem goes back to the incomplete sampling of the configurational space in the phase change region. Also, quasiergodicity can produce overestimation of transition temperatures in molecular dynamic caloric curves when the heating rate is too fast. To overcome the systematic errors resulting from quasiergodicity, several methods have been employed. These methods include the histogram, jump walking, smart walking, and parallel tempering methods. Many of these methods are based on the coupling of configurations of ergodic higher temperature simulations to the quasi-ergodic lower temperature simulation.

For a given material, the cluster melting point usually decreases monotonically with decreasing size with some irregular variations. The first attempt was made in 1909 by Pawlow using classical calculation to present the following equation:

$$1 - \frac{T_m(N)}{T_m(\infty)} = \frac{2}{\rho_s r_s L}\left[\gamma_{sv} - \gamma_{lv}\left(\frac{\rho_s}{\rho_l}\right)^{2/3}\right] \tag{49}$$

Some developments have been made on this equation. One of the most recent works done by Chushak and Bartell leads to the following equation:

$$1 - \frac{T_m(N)}{T_m(\infty)} = \frac{2}{\rho_l L}\left\{\frac{\gamma_{sl}}{r-\delta} + \frac{\gamma_{lv}}{r}\left[1 - \gamma_{lv}\left(\frac{\rho_s}{\rho_l}\right)^{2/3}\right]\right\} \tag{50}$$

where, $\delta$ is a liquid shell thickness. Comparison between the results taken from theoretical models and experimental data as well as the simulations has been carried out, and some models like Eq. (50) has shown good agreements. There are some relevant studies of selected systems which are going to be reviewed shortly here. Experiments have shown a complex dependency of $T_m$ on $N$ for Na clusters. Premelting effects have been found for Na clusters in the range between 8 and 147 atoms, using Monte Carlo thermodynamical analysis close to the solid-liquid transition with Gupta potentials. The literature is extensive in case of metallic cluster like Au clusters. Melting point depression in this case is strongly material dependent. Structural transitions and thermodynamic properties of small silicon clusters have been investigated, and good agreement has been found with the results on the thermodynamics of very small clusters found by means of empirical many body potentials. Although thermodynamics has achieved successful results in the study of free nanoclusters, in some cases there are discrepancies between the results of energetic and/or thermodynamic calculations, and the real experimental data. These observations indicate that kinetic effects must be taken into account to explain the actual or

experiments of free cluster formation.

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