

Chapter 1

Recent Developments in Phase Transitions in Small/Nano Systems

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Abstract

We report here some general advances made in phase transitions in small/nano systems which may also be utilized in analysis and understanding of phytonanotechnology systems. Experimental, simulation and theoretical methods for identification and prediction of solid-liquid and liquid-vapor phase transitions in simple molecular nano systems are reported. Through experimental and simulation studies it is shown that phase transition points (transition temperatures) by going from one phase to another and reverse differ and there is a hysteresis in nano systems phase transitions. The phenomena of fragmentation during phase transition from liquid to vapor phase is discussed and an experimental example is presented. Computer simulation has shown that the two-phase and critical regions in vapor-liquid transitions of nano systems differ from those of macroscopic systems. Van der Waals equation of state, which is already shown to be valid for nano systems through statistical mechanical derivation. Application of the van der Waals equation of state for nano systems can qualitatively predict the same phase behavior as observed by the computer simulation.

Keywords: Computer Simulation, fragmentation, hysteresis, Nano Systems, Nanoscience, Nanotechnology, Nano-Thermodynamics, Phase Transition, phytonanotechnology, Small Systems, statistical mechanical, Thermodynamics, van der Waals Equation of State

1. Introduction

Over the last four decades, nanoscience and nanotechnology have emerged as two of the pillars of the research that may lead us to the next industrial revolution, and together with molecular biology and information technology, would map the course of scientific and technological developments in the 21st century. This progress has been largely due to the development of sophisticated theoretical and experimental techniques, and practical tools, for understanding, characterizing and

manipulating nanoscale structures, processes and systems. Nano systems are made of countable (limited) number of atoms or molecules and their sizes are larger than individual molecules and smaller than micro-systems. In other words, nano, or small, systems are those where the linear dimension of the system is of the characteristic range of the interaction between the particles comprising the system. Nanoscale is a magical point on the dimensional scale: Systems in nanoscale are considered at the borderline of the smallest of human-made devices and the largest molecules of living things. One of the characteristic features of small/nano systems is their high surface-to-volume ratio. Nano systems can appear in all forms of matter, be it soft or hard, organic or inorganic and/or biological. They form the building blocks of nanotechnology, and their deep understanding is required for advancement of nanotechnology (Mansoori, 2005, 2017).

Phytonanotechnology, the agronomic application of nanotechnology in plants, has become synonyms with “green nanotechnology”, which is the section of nanotechnology dealing with the scope of engineering principles related to life cycle considerations, such as the use of more sustainable or renewable feedstocks and designing for end of life or the final disposition of the product (Poethig, 1990; Wang, 2016).

Understanding the principles of phase transitions in small/nano systems would enhance appreciably the development of phytonanotechnology, which is aimed to offer new and innovative development of growth and uses for plants, plant materials and biomass. Considering the fact that all the processes of living things, including plants, growth and function (Figure 1) is associated with chemical conversions and phase transitions in small/nano systems it is necessary to understand the principles behind such processes (Huijser & Schmit, 2011; Jaya et al. 2010; Poethig, 2010, 1990; Wang, 2016).

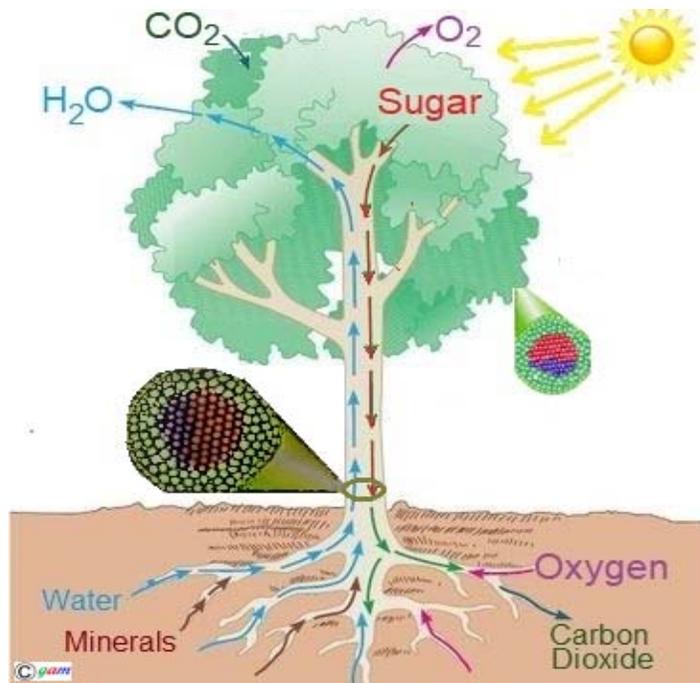


Figure 1. Phase transformations and chemical conversions of materials inside plants happen in small (micro and nano) capillary systems.

In the present paper we introduce some of the interesting features of phase transitions in small/nano systems, on which the authors and others have spent many years to develop their principles for analysis and predictions (Mansoori, 2002, 2005; Mansoori & Rice 2014).

In the macroscopic limit principles of phase separations / transitions are well-defined and formulated (Hamad & Mansoori, 1990; Hoffman & Tang, 2001; Kinderlehrer et al. 1993; Lan & Mansoori, 1977; Mansoori & Ely, 1985; Pourghesar et al. 1996).

The macroscopic limit is defined when the number of atoms and molecules in a large system is of the order of 10^{24} or more which is theoretically at infinite limit, known as thermodynamic limit [$(N \text{ and } V) \rightarrow \infty$ but $N/V = \text{finite}$]. Most of the existing theories of fluids, solids, mixtures and phase transitions are developed for systems at the thermodynamic limit using, mainly, canonical or grand-canonical ensembles of statistical mechanics (Haile & Mansoori, 1983; Matteoli & Mansoori, 1990; Pourghesar et al. 1996). However, for small systems consisting of limited number of particles principles governing the definition and separation of phases is not well understood yet. Actually, the thermodynamic property relations for small systems are also not clear and open for further study. The well-known thermodynamic property relations and data (Alem & Mansoori, 1984; Hall & Frenkel, 1998; Lan & Mansoori, 1977; Mansoori & Canfield 1969; Yan et al. 2001) are valid only for extensive large systems in the thermodynamic limit (Vakili-Nezhaad & Mansoori, 2004).

Investigation into phase separations, phase transitions and phase changes in macroscopic systems, both, experimentally and through the applications of statistical mechanics has a long tradition going back to 1800s. Andrews was probably the first person who studied the first order phase transition (with phase separation due to density difference and interfacial tension between phases) in 1869 ending the earlier notion of “permanent gases” (Mansoori & Haile, 1983). Before Andrews there was this ungrounded concept of “permanent gases” due to the fact that one could not condense a gas, like air, by simply compressing it without lowering its temperature. At that time the concept of critical point was not yet recognized and the understanding that a gas needs to go below its critical temperature to become condensable to a liquid was not discovered yet. J.D. van der Waals in 1873 worked on, probably, the first recorded predictive theory of phase transitions which resulted in the well-recognized van der Waals equation of state (vdW EOS),

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT. \quad (1)$$

This equation of state, when solved for pressure versus volume, produced all the necessary fluid phases which were experimentally observed by Andrews that could co-exist and gave a simple and, at that time, satisfactory account of phase transitions. Van der Waals was, probably the first scientist who proved that phases are changed between liquids and gases. The vdW EOS is now modified in various forms and its modifications have found many applications in the analysis of thermodynamic properties of pure fluids and mixtures in macroscopic systems (Filho et al. 1997; Kwak et al. 1987; Mansoori & Haile, 1983) of scientific and industrial interest. Its theoretically based extensions and modifications have been the subject of many theories of statistical mechanics (Haile & Mansoori, 1983; Hoffman & Tang, 2001; Kwak et al. 1987; Lan & Mansoori, 1977; Mansoori & Canfield 1969). The basic assumption in deriving the vdW EOS and majority of the other existing statistical mechanical theories of fluids and solids, is that the dimensions of the macroscopic system are very large when compared with those of the constituting atoms and

molecules. Recently it was shown that the vdW EOS is valid for nano systems (Keshavarzi et al. 2006) as it is presented in Section 3.2 of this report.

After the discoveries of van der Waals, investigations into phase transitions in macroscopic systems consisting of mixtures of many components in vapors, liquids and solid phases became a major subject for research in late 1800 until the early 1900. Among all such investigations, in line with phase transitions, one should mention the well-recognized research findings of J. Willard Gibbs (Gibbs, 1948) in late 1800. Gibbs gave the phase transitions in systems at equilibrium a firm theoretical ground and formulated his famous “phase rule” which is well known to all the fields of science and engineering today. The Phase Rule describes the possible number of degrees of freedom in a (closed) macroscopic system in thermodynamic limit at equilibrium. The general form of the phase rule for a multiphase-multicomponent-reacting system is $F=c-p-r+2$. In formulating the phase rule, the degrees of freedom, F , is defined by Gibbs as the number of independent intensive variables (*i.e.*, those that are independent of the quantity of material present) that need to be specified in value to fully determine the state of a macroscopic system.

In the case of small/nano systems due to the lack of experimental measurement techniques we have not been able to study phase transitions directly. However, investigations either through indirect experimental methods or by computer simulation and density functional theory techniques have been successful to distinguish various phases of matter in small systems, as small as clusters of a few atoms or molecules (Berry, 1999, 2002; Hill, 1994; Mansoori, 2002, 2005; Mansoori & Rice, 2014). Even though the principles of phase transitions are not well defined for small systems, however, there are many phenomena in small systems that resemble the phase transitions in large systems. This has been specially the case in the study of clusters of tens, hundreds and thousands of molecules by various investigators (Berry, 1999, 2002).

Considering that nanoscale systems consist of finite number of particles (intermediate in size between isolated atoms / molecules and bulk materials) principles of phase transitions, as formulated for large systems, need to be reformulated for nano systems (Berry, 1999, 2002; Mansoori, 2002, 2005; Mansoori & Rice, 2014; Vakili-Nezjaad & Mansoori 2004). While we can have control-mass (closed) nano systems, however due to the fact that such systems are not in thermodynamic limit and they may not be in equilibrium, from the point of view of Gibbsian thermodynamics we may not be able to use the Gibbs phase rule for such systems. Also, for nano systems, which are actually nonextensive (Mansoori 2005; Mohazzabi & Mansoori, 2005a, 2005b; Vakili-Nezjaad & Mansoori 2004; Tsallis et al. 1998) the definition and separation of extensive and intensive variables is not quite clear, and very possibly, they depend on the size of the system

2. Nano systems phase transitions

Understanding of phase transitions in systems composed of finite number of particles is a peculiar and unsolved problem, both, from experimental and theoretical points of view. Considering that nanoscale systems consist of finite number of particles (intermediate in size between isolated atoms /molecules and bulk materials) principles of phase transitions need to be reformulated for nano systems. For example, the PVT relation of pure systems and variety of mixtures are well defined and formulated in the thermodynamic limit. Thermodynamic property relations of nano systems are not well-defined and they are functions of the geometry, size and internal structure of the system under consideration (Mansoori, 2002, 2005; Mansoori & Rice, 2014).

Due to nano size and confinement effect, fluid properties will be heterogeneous in space and the pressure will be of tensorial nature. For a nanoconfined simple molecular fluid the pressure

tensor, may reduce to a diagonal tensor with components p_{ii} ($i = x, y, z$). For example, to demonstrate the inhomogeneity of nanoconfined fluids at equilibrium with an external bulk phase we report Figure 2 which is *the normal pressure tensor* for the Lennard-Jones fluid (a fluid with molecules interacting according to the LJ intermolecular potential energy function, $\varphi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$) confined in a nanoslit pore with hard-walls versus distance from the hard-wall. This figure is the result of prediction using the density functional theory (Heidari et al. 2013).

According to this figure, pressure inside a confined nanoslit pore has oscillation characteristics. Detailed examples for various nanoconfined geometries and confined fluid natures are given in Refs. (Heidari et al. 2011a, 2011b, 2013; Kamalvand et al. 2008; Keshavarzi et al. 2010; Mansoori, 2002, 2005; Mansoori & Rice 2014).

In contrast to thermodynamics of large systems, thermodynamic properties and property relations of small systems will be generally different in different “environments”. As a result appropriate indirect methods for their observations and proper molecular simulation technique for their prediction must be used for different small/nano systems (Vakili-Nezhaad & Mansoori, 2004).

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2.1. An experimental example of melting and freezing transition in a nano system: In recent years the focus of many investigators has been on solid-liquid phase transitions (melting and freezing) in nano systems (Di Cicco, 1998; Klein & Kumacheva, 1998; Koga & Tanaka, 2005; Kuchta et al. 2004; Mansoori & Rice, 2014; Rice, 2009; Zhao et al. 1997). In general, experimental studies have shown that in nano systems melting and freezing points of pure compounds are different from one another, they are less than the bulk systems and there exist a hysteresis loop in melting and freezing transitions. An example for a simple molecule freezing and melting hysteresis loop is the work of Di Cicco (1998) on nanoconfined gallium (Di Cicco, 1998). In order to demonstrate the nano phase transition of gallium Di Cicco (1998) performed a series of experiments using confined gallium (Ga, Mw=69.7, m.p.=303K, b.p.=2477K) in a nano system. The reason for choosing gallium was apparently because it has the largest liquid range (2174°C) for a metal and a very low vapor pressure. Di Cicco produced a submicrometric gallium droplets confined in epoxy resin (Di Cicco, 1998). He also studied its melting and freezing changes by combining energy-dispersive x-ray diffraction (EDXRD), x-ray absorption fine structure, and single-energy x-ray absorption (see also Di Cicco et al. 1999; He et al. 2007; Li et al. 2011; Liu et al. 2004; Poloni et al. 2005).

The importance of this experiment is demonstration that gallium’s melting and freezing points are at two different temperatures contrary to macroscopic gallium. The restricted gallium liquid was shown to undercool down to 150 K before it was frozen. It was also shown the melting point of gallium was depressed down to 254 K (see Figure 3).

Figure 2. The normal pressure tensor for LJ confined fluids in nanoslit pore with hard-walls versus dimensionless distance ($Z^* \equiv Z/\sigma$) from the hard-wall, where σ is the LJ length parameter, H is the width of the nanoslit, and ρ^*_{bulk} is density of the bulk fluid in equilibrium with the fluid in nanoslit. (1): At $H^* = 6$ and $T^* = 2$ and for two different bulk densities $\rho^* = 0.6$ & 0.8 . (2): At $\rho^* = 0.6$ and $T^* = 2.5$ and for two different pore widths $H^* = 4$ & 6 . (3): At $\rho^* = 0.6$ and $H^* = 6$ for two different bulk temperatures $T^* = 2$ & 2.5 . (4): At $\rho^* = 0.6$, $T^* = 2.5$ and for two different pore widths $H^* = 4, 6$ (Heidari et al. 2013).

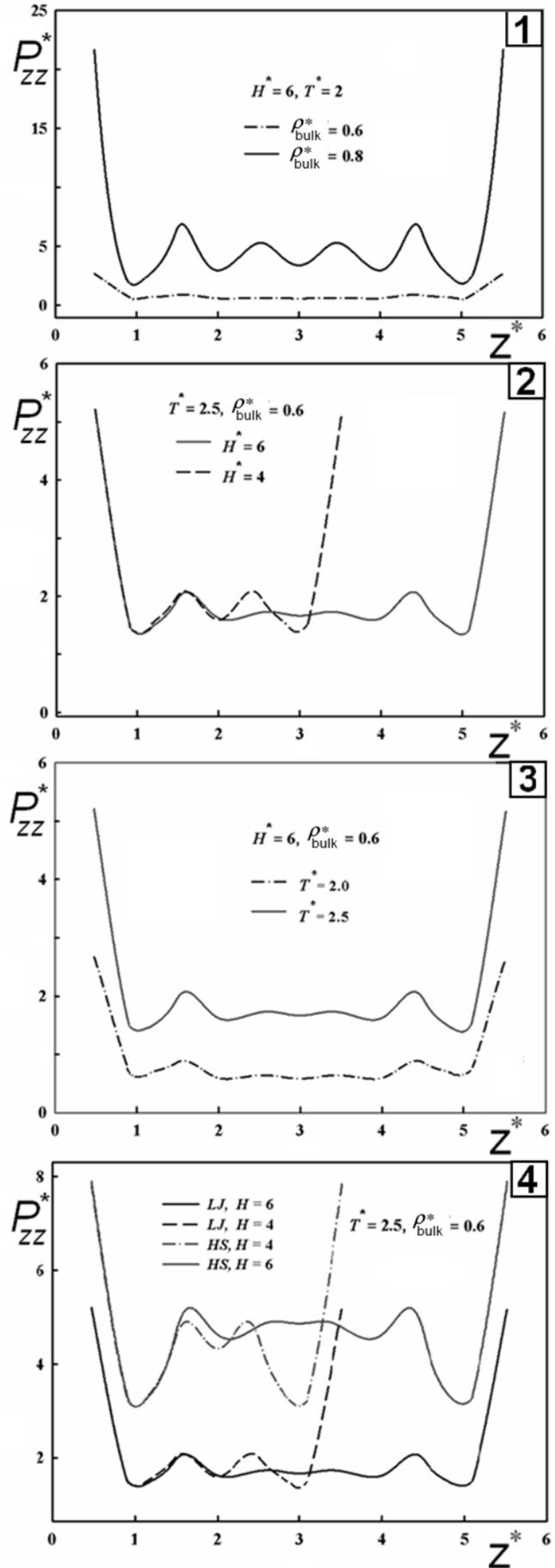
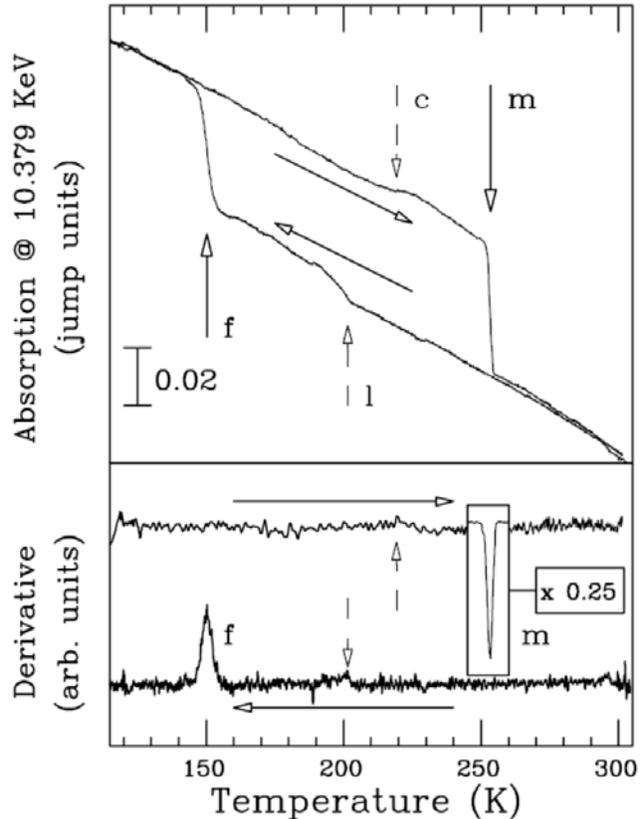


Figure 3. Upper panel: Temperature scan of the absorption coefficient at constant energy showing a clear hysteresis loop. Melting and freezing are indicated by arrows labeled as m and f, respectively. Lower panel: Derivative of the temperature scan shown in the upper panel (Di Cicco, 1998).



2.2. A computer-simulation example of melting and freezing transition in a nano system: Using molecular computer simulations Berry produced the two phase diagrams for solid-liquid transition of pure nano and macro systems (Berry, 1999, 2002) as shown in Figure 4.

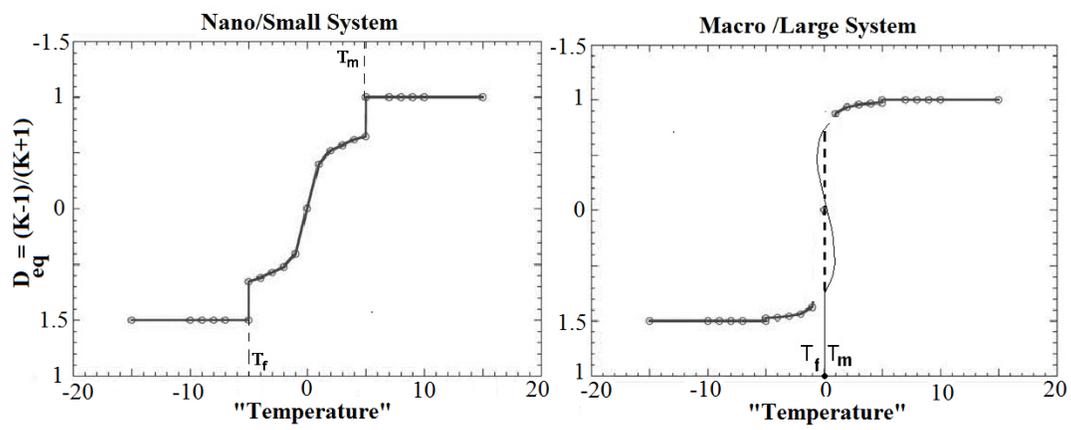


Figure 4. Left-side Figure. The coexistence of two phases of a nano system. Two distinct transition points, the freezing, T_f , and the melting, T_m , points are recognized for this system. Large discontinuities at T_f and T_m are observed. **Right-side Figure.** The coexistence of two phases of a macro system (in the thermodynamic limit). The two distinct transition points (freezing T_f and melting T_m) which were recognized in nano-size system have reduced to one point in this case and the discontinuities between the two phases have disappeared (Berry, 2002).

In Figure 4 the vertical coordinate of the two diagrams, D_{eq} , is defined as (Berry, 2002):

$$D_{eq} = \frac{K-1}{K+1} = \frac{[L]-[S]}{[L]+[S]} = \frac{e^{-\Delta\mu/kT} - 1}{e^{-\Delta\mu/kT} + 1},$$

which is a measure of the relative amounts of the molecules in solid $[S]$ and liquid $[L]$ phases and $K(T)=[L]/[S]$ is the equilibrium constant.

$$K(T) = \frac{[L]}{[S]} = \exp\left(-\frac{\Delta G}{NkT}\right), \quad (2)$$

where $\Delta G(T)$ is the difference in free energies of phases L and S at temperature T provided other system-variables are kept constant and uniform between the phases. The free energy difference can then be written in terms of the mean chemical potential difference $\Delta\mu(T)$ between the two phases and the number of particles, N , in the system as the following (Berry, 2002).

$$\Delta G(T) = N\Delta\mu(T). \quad (3)$$

In these figures the region of the graph corresponding to $D_{eq} = -1$ represents the solid phase, the region corresponding to $D_{eq} = +1$ represents the liquid phase. The transitions region between the freezing point, T_f , and melting point, T_m , is quite different between small, intermediate and large systems (Berry, 2002).

According to Figure 4 the phase diagram in the nano system has two distinct transition points, the freezing point, T_f , and the melting point, T_m . However, in macro system the melting and freezing points are the same at one point (Berry, 2002). These simulation findings are consistent with the experimental observations of Di Cicco (Di Cicco, 1998) reported in Section 2.1, above.

3. Vapor-liquid phase transition in a nano system

A widely study of phase transition in small (macro and nano) systems is the vapour to liquid transition in a confined small system known as the capillary condensation. The earliest study of capillary condensation is due to Derjaguin (Derjaguin, 1940). Later Bangham (Bangham, 1944) developed the thermodynamics of the hysteresis loop in capillary condensation. Later, Hill formulated the statistical mechanics of capillary condensation and the theory of hysteresis which occurs between condensation and evaporation (Hill, 1947). Many other investigators have worked on various aspects of capillary condensation prominent among them include Hirst (1947), Everett & Haynes (1972), Schmidt & Lowen (1997), Berim & Ruckenstein (2012) and the latest is by Keshavarzi & Helmi (2015). In what follows we report our findings of the concept of fragmentation during liquid to vapour phase transition in nano systems as observed experimentally together with computer simulation and equation of state modelling of nano systems.

3.1. An experimental example of liquid to vapor phase transition in a nano system (*Liquid fragmentation during liquid to vapor phase transition*): Fragmentation is considered a ubiquitous

phenomenon by many investigators and has been the focus of a great deal of study in the past. Such fragmentation processes as polymer degradation due to various physicochemical forces, crushing of rocks and other solid-state systems under stress and fragmentation of nuclear fuels observed during nuclear processes (now known as nuclear multifragmentation) are well known. Fragmentation as a real phase transition of first order in nuclei was theoretically interpreted and computationally simulated by several investigators. What is interesting is the fact of the breakup of continuous liquid phases in particular in small/nano systems during evaporation processes (Mansoori 2005; Vakili-Nezhaad & Mansoori, 2004).

An experimental example of liquid phase fragmentation during transition to vapor consists of evaporation of water inside a sealed multi-wall carbon nanotube. In Figures 5 and 6 the first order phase transition, evaporation of water, in a MWCNTs observed in a transmission electron microscope (TEM) is reported (Gogotsi et al. 2001).

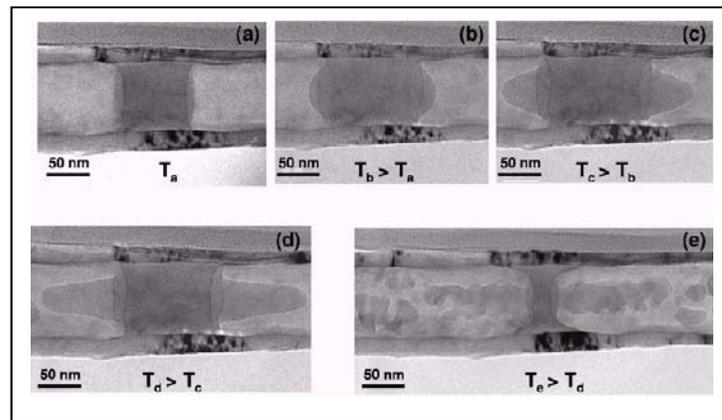


Figure 5. First order phase transition of water inside a multiwall carbon nanotube as photographed in a TEM (Gogotsi et al. 2001). We recognize fragmentation of the liquid phase as the temperature is increased.

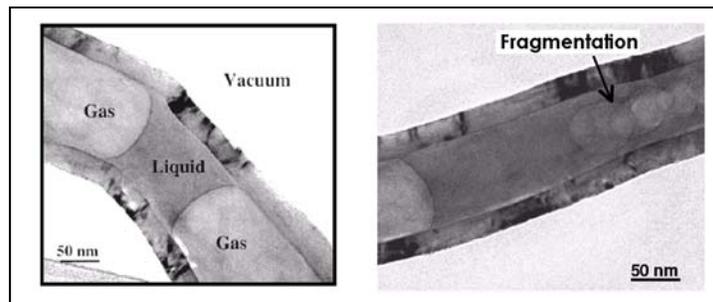


Figure 6: Demonstration of the phase separation and fragmentation in the first order phase transition of water inside a multiwall carbon nanotube. These figures correspond to the same experiment as shown by Figure 5 as photographed in a TEM (Gogotsi et al. 2001; Megaridis et al. 2002)

Fragmentation of the phases is well demonstrated in these figures as temperature is raised through electron beam. Figure 6 is TEM image of a peculiar behavior of water in a nanotube under variation of temperature. Whether these peculiarities are due to phase separations and transitions, interfacial effects, fragmentation and/or other unknown phenomena is not understood yet. Another recent observation of the behavior of fluid water in a MWCNT (Gogotsi et al. 2001; Megaridis et al. 2002) is what is shown in Figure 6. According to this figure the vacuum condition outside of the MWCNT is not removing the water molecules from the nanotube. This is an indication that the MWCNT wall is impenetrable by water molecules. Also shown in this figure is a more pronounced picture of liquid water phase fragmentation during its evaporation.

3.2. Computer simulation and analytic modeling of liquid-vapor phase transition in nano systems: The state of a confined (control mass) substance in a macroscopic system is defined using up to two degrees of freedom (Berry et al. 2001; Gibbs, 1948; Hill, 1994; Vakili-Nezhaad & Mansoori 2004). For a confined substance in a small/nano system we may not be able to define its state using only two degrees of freedom. This difference, between confined macroscopic and confined small systems, is due to the relatively much larger fraction of molecules adjacent to walls of nanoconfined systems as compared to a macroscopic system. As a result, in such small systems the interaction of molecules with their external environment (or walls) will have to be taken into account. Due to walls effect it is believed that additional degrees of freedom will be necessary to define the state of a nanoconfined system. The wall effects of a confined fluid in a uniform and constant diameter nanotube, or constant thickness nanoslit pore, may be incorporated at least in one additional degree of freedom. Therefore, an additional term resulting from the surface effects will appear in the expressions for the thermodynamic functions of a nanoconfined system.

Helmholtz free energy of the confined fluid systems due to confinement wall effects is (Keshavarzi et al. 2006; Vakili-Nezhaad & Mansoori, 2004):

$$A = N\mu - \sum_i p_{ii} d\varepsilon_{ii} V + \psi U N_{\psi} \quad (4)$$

Where N is the number of particles, μ is their chemical potential, N_{ψ} is the number of molecules interacting with the wall, U is unit wall-molecules interaction energy, and ψ is the wall area. Depending on the geometry of nanoconfinement under consideration (such as cylindrical or slit-like nanopores) and the nature of the walls the equation of state and its solution will vary.

An equation of state is needed to derive the expressions for chemical potential and other thermodynamic functions of the nano fluid. Statistical mechanic theories of non-extensive systems (Mohazzabi & Mansoori, 2005a, 2005b; Vakili-Nezhaad & Mansoori, 2004) may be used to derive the equation of state of nanofluids. Generally, the many available equations of states for bulk fluids may not be valid for nanofluids. It is showed that (Keshavarzi et al. 2006) the van der Waals equation of state (vdW EOS), Eq. (1), which is developed for macroscopic systems is equally valid for small/nano systems. Of course, the numerical values of parameters a and b of the vdW EOS will vary with the size of the system for the same reason that the critical point of nanofluids may vary with size as well as geometry as it is shown through computer simulations (Brovchenko et al. 2001). Expression for the chemical potential based on the van der Waals equation of state is,

$$\mu = \left[\frac{\partial A}{\partial N} \right]_{T,V} = f(T) - kT \ln(V - Nb) + \frac{kTNb}{V - Nb} - \frac{2aN}{V}. \quad (5)$$

The pressure tensor coordinates can be then calculated from the Helmholtz free energy, Eq. 6,

$$-p_{ii} = \frac{1}{V} \left(\frac{\partial A}{\partial \varepsilon_{ii}} \right)_{T,N,A} \quad (6)$$

Using the van der Waals equation of state, the following expressions for the components of pressure tensor of confined fluids in a nanotube is derived (Keshavarzi et al. 2006):

$$P_{zz}^* = \frac{T^*}{V^* - 1} - \frac{1}{V^{*2}} + \frac{2U^* N_{\psi}}{r^*} \ln V^*, \quad (7)$$

$$P_{rr}^* = \frac{T^*}{V^* - 1} - \frac{1}{V^{*2}} - \frac{2U^* N_{\psi}}{N^{1/2} r^*}, \quad (8)$$

where,

$$p^* = \frac{pa}{b^2}, T^* = \frac{kTb}{a}, V^* = \frac{V}{Nb}, U^* = \frac{Ub^{5/3}}{a}, r^* = \frac{r}{b^{1/3}},$$

and k is the Boltzmann constant. Similarly expressions for the components of pressure tensor of confined fluids in a nanoslit (p_{zz}^* and $p_{xx}^* = p_{yy}^*$) may be derived. Then plots of (p_{zz}^* & p_{rr}^*) and (p_{zz}^* & $p_{xx}^* = p_{yy}^*$), along with macroscopic pressure, p_{Macro}^* , versus V^* are shown in Figure 7.

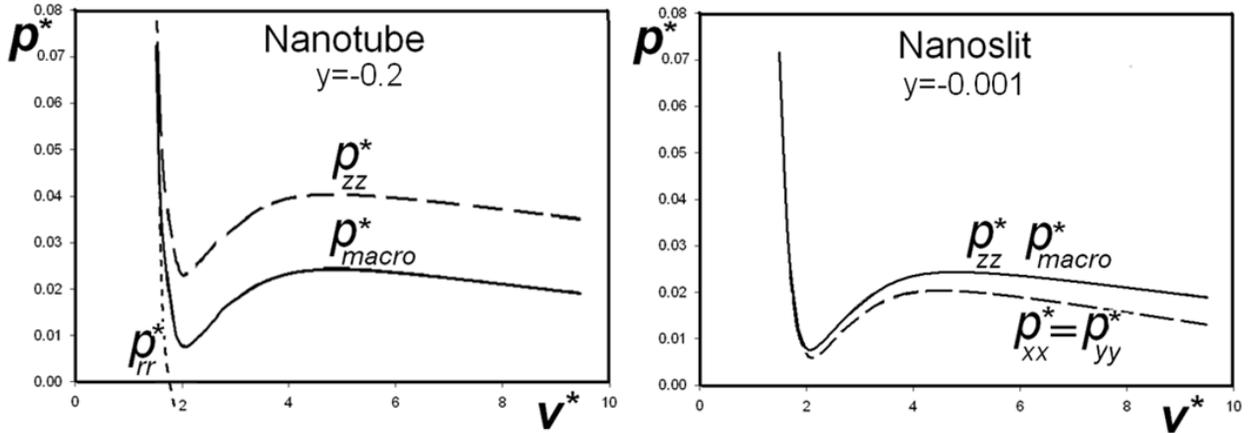


Figure 7. Dimensionless pressure tensor components ($p_{ii}^* = p_{ii} a / b^2$) of nanoconfined van der Waals fluid, versus the dimensionless volume ($V^* = V / Nb$) inside a nanotube and nanoslit pore at $T^* = 0.25$ and at various values of $y = U^* N_{\psi} / r^*$. Note that in the case of nanoslit pore values of p_{rr}^* and p_{macro}^* are graphically indistinguishable from one another (Keshavarzi et al. 2006).

According to Figure 7 the pressures vs. volume possess the vdW phase transition S-shaped loops. Using the Maxwell construction principle (equality of temperatures, pressures and chemical potentials in the two phases in equilibrium), the properties of phases in equilibrium are obtained and they are reported in Figures 8-10.

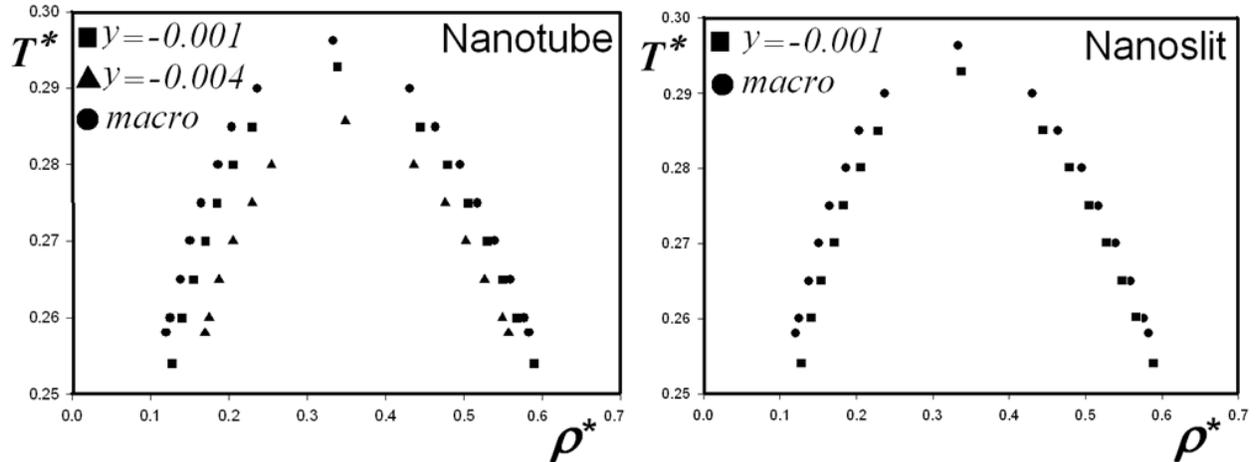


Figure 8. The coexistence curves (dimensionless temperature versus dimensionless density) for the nanoconfined van der Waals fluid inside a nanotube and a nanoslit for various $y = U^* N_s / r^*$ values as compared with the coexistence curve for the van der Waals fluid in macroscopic/bulk scale (Keshavarzi et al. 2006).

According to Figure 8 the coexisting loop is sensitive to geometry of nanoconfinement and nature of walls. It is also demonstrated in Figures 9 and 10 that critical temperature and critical volume of a confined fluid vary with the size of confinement and they increase as the size of the confinement increases (Zarragoicochea & Kuz, 2002).

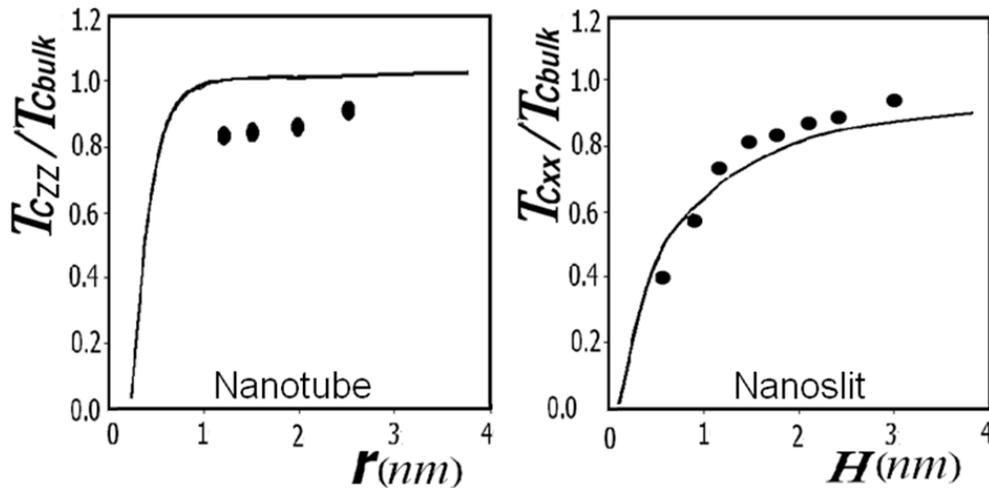


Figure 9. The ratio of critical temperature of the van der Waals fluid in a nanotube and a nanoslit over the macroscopic/bulk critical temperature (T_{Czz} / T_{Cbulk}) as a function of nanoslit pore width (H) and nanotube radius (r), respectively. The solid line is calculated based on the van der Waals equation of state and for $y = -0.001$. The solid circles are the MD simulation data for confined water in nanoslit pore and nanotube (Keshavarzi et al. 2006).

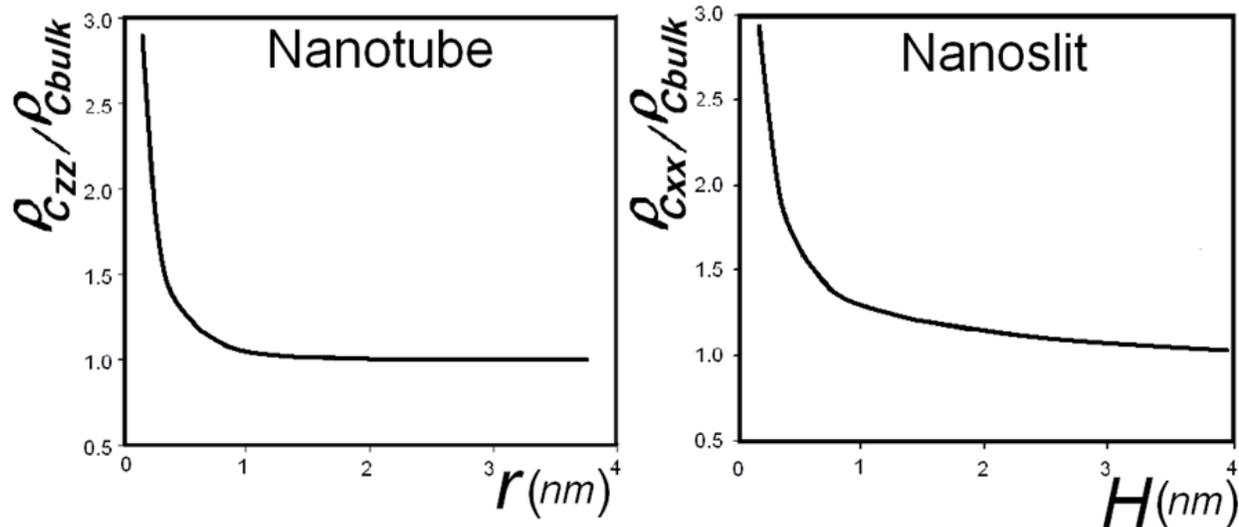


Figure 10. The ratio of critical density of the nanoconfined van der Waals fluid in a nanotube and a nanoslit over the macroscopic/bulk critical density as a function nanotube radius (r), and of nanoslit pore width (H), respectively, as calculated based on the van der Waals equation of state and for $y = -0.001$ (Keshavarzi et al. 2006).

The agreement between the results of the vdW EOS for nanoconfined fluid and result of the MD simulation for confined water is surprisingly good in Figure 9 even though the vdW EOS is based on a very simple potential model and a simplified perturbation theory of statistical mechanics (Keshavarzi et al. 2006; McQuarrie, 1976). It is also demonstrated that the coexistence curve for nanoconfined fluids is sensitive to the nature of confinement wall in agreement with the literature data (Brovchenko 2004).

4. Discussion and conclusions

In this report we have presented some highlights of the advances made in understanding the nano-systems phase behavior which are important in science and technology. We already have a good qualitative and quantitative understanding of phase behaviors in macroscopic / bulk systems.

Well-defined quantitative experimental observations about nano systems phase behavior are limited. In order to develop some better understandings about nano-confined system, and due to the limited available experimental data, we also have reported computer simulation results and density functional theory approaches, of assemblies of atoms and molecules which are reported by various investigators.

There have been many other kinds of nano-confined systems investigations including ionic fluids, hydrogen-bonding fluids (other than water), confined polymers, variety of confined colloids and micelles, biological ion-channels just to name a few. However, due to the limitation of space and the vast number of such systems we have limited our discussion to rather simple fluids.

Due to lack of thermodynamic limit and appreciable fluctuations in temperature and pressure in small systems, as compared to macroscopic systems, the following peculiarities in small systems are expected to happen during phase transitions (Mansoori 2002, 2005; Mansoori & Rice, 2014; Vakili-Nezhaad & Mansoori, 2004):

- Phase transition in nanoscale systems is, generally, a dynamic phenomenon and not of the static (equilibrium) nature as it is in macroscopic phase transition which is called phase equilibrium.
- Coexistence of phases in small systems are expected to occur over bands of temperatures and pressures, rather than only at a sharp point as is the case for large systems.
- 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.
- Like large systems, various forms of phase transitions, including the first order, second order, and more, are expected to occur in small systems.
- Small systems have additional degrees of freedom unknown to large (infinite) systems. In addition to the well-known structural phase transitions as melting or boiling, fragmentation into several large fragments and possibly also into many monomers or small clusters is characteristic for the disintegration of finite systems. It is similar to boiling in macro systems but has many new features due to the important size fluctuations and correlations which distinguish fragmentation from the simpler evaporation.

A better understanding of phase transitions in small systems will help the development of molecular self-assembly which is the fundamental of bottom-up nanotechnology.

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