THEORY AND MODELLING OF NUCLEATION AND INTERFACIAL PHENOMENA

By

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DECLARATION

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree / diploma at this or any other Institution / University.

Satinet Ghon SATINATH GHOSH

Dedicated to.....

my parents

and

my wife

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SYNOPSIS

An understanding of the phenomena of nucleation and interfacial properties is of importance in a number of areas of research in chemistry, physics, materials science and allied subjects **[1-4]**. Nucleation is a process of formation of a nucleus from a bulk phase and usually involves the crossing of a free energy barrier known as the nucleation energy barrier. The dynamics of this first order phase transition depends on the finite nucleation energy barrier and therefore, an understanding of the nucleation barrier and the investigation of the effect of various parameters on this barrier is a very important and interesting topic of research.

The theory developed originally by Becker, Doring, Volmar, Farkas, and later modified by Zeldovich for the study of nucleation from vapor to liquid phase has been traditionally referred to as the classical nucleation theory (CNT) **[5-8]** based on the capillarity approximations which make the theory simple but introduce a considerable error in the results. Basic CNT has thus been modified and a number of improved theoretical techniques have been proposed from time to time to overcome this error for investigating the problem of vapor to liquid homogeneous nucleation **[9-15]** and heterogeneous nucleation phenomenon on flat as well as spherically curved solid surfaces **[16-23]**.

In this work, the phenomena of vapor-liquid nucleation has been systematically investigated from the most specified homogeneous nucleation phenomena to the more general and natural heterogeneous nucleation on spherically curved surfaces of different sizes. The theory applied in this work is the density functional theory (DFT) along with a model exponential density profile (diffuse density at the interface) and model Helmholtz free energy density functional. The conventional CNT has been also presented in the framework

of the present density functional formalism but with the use of step like density profile and equilibrium interfacial energy for a planar interface of the bulk fluid interface.

Interfacial properties such as surface tension, inhomogeneous density profile, surface thickness etc. are of immense scientific as well as technological importance in connection with various phenomena and processes ranging from macroscopic to microscopic length scales. In particular, the interfaces play a crucial role in some of the very important phenomena such as nucleation and hence in the fabrication of nanostructured materials. Although the experiment can be performed for bulk sized system (i.e, for planar interface), in order to get an idea of the interfacial properties for small sized systems (i.e, for curved interfaces), theoretical predictions are of crucial importance.

The density functional theory (DFT) is found to be the most versatile theory among the different theories and simulations for the interfacial properties of a planar interface [2-4,24-26] as well as spherically curved interface [27-31].

In the present work, the problem of interfacial properties have been addressed for both vapor-liquid planar interface as well as vapor-liquid droplet spherical interface using DFT along the lines of van der Waals and Cahn-Hilliard [**32-33**] density functional formalism for the inhomogeneous interface with the use of a model local Helmholtz free energy density for the two phase system and a model diffuse density profile at the interface. Analytical solutions to the problem of surface properties of planar as well as spherical interface have been derived here. The theory has been successfully applied to systems with model interaction potential as well as some real fluids such as water, heavy water and argon for a wide range of temperature ranging from the triple point to critical point.

The present work has also provided a simple way of evaluation of the size-dependent surface tension and temperature density $(T-\rho)$ curve for the liquid droplet-vapor equilibrium

analytically. The size dependent theory is then applied to the Lennard-Jones (L-J) fluid system and various interfacial properties such as surface tension, density profile, thickness of the interface etc. have been evaluated.

CHAPTER I

An appropriate introduction related to the work in the present thesis as well as a general introduction of the vapor to liquid nucleation and interfacial phenomena have been discussed in this chapter (chapter I). The background of the DFT used in the present work has also been briefed here. The earlier works (both theory and molecular simulations) by different authors on the same problem have been briefly reviewed. A number of methods and analytical instruments developed for the experimental measurement of the nucleation rate have been briefly discussed. The scope and motivation of the present work have then been outlined in this chapter.

CHAPTER II

Homogeneous nucleation involving vapor to liquid transition of the L-J fluid have been investigated here by employing DFT along with a model density profile (diffuse density at the interface) and a model Helmholtz free energy density functional [**34**]. The problem has also been investigated using CNT in the framework of the proposed DFT method but instead of diffuse density (in DFT method), a step density profile has been used. The model density profiles can be expressed as

 $\rho(r)_{DFT} = \rho_L - (1/2)(\rho_L - \rho_V) \exp[a(r - R_{av})]$ and $\rho(r)_{CNT} = \rho_L$ for $0 \le r \le R_{av}$ and $\rho(r)_{DFT} = \rho_V + (1/2)(\rho_L - \rho_V) \exp[-a(r - R_{av})]$ and $\rho(r)_{CNT} = \rho_V$ for $r > R_{av}$. Here, R_{av} is the distance from the centre, where the density is the average of the bulk liquid (ρ_L) and vapour (ρ_V) densities (i.e.

 $\rho(R_{av}) = (1/2)(\rho_L + \rho_V)$. The Helmholtz free energy of the final phase of the nonuniform density can be expressed by using DFT with square gradient approximation as $F_f = \int [f(\rho(r)) + K(\nabla\rho(r))^2] dr$. The Helmholtz free energy density functional, $f(\rho(r))$ has been expressed as Taylor series expansion with respect to the uniform fluid, retaining, for simplicity, terms up to first order, as $f(\rho(r)) = f(\rho(r)) \rho(r) = \rho_u + [d f(\rho(r))/d \rho(r)] \rho(r) = \rho_u (\rho(r) - \rho_u)$, where the subscript *U* refers to the uniform fluid. Thus, one has $\rho_U = \rho_L$ for $r \leq R_{av}$ and $\rho_U = \rho_V$ for $r > R_{av}$.

The expression of the free energy of formation of a droplet of any arbitrary size has been obtained analytically in this work and is given as

$$\Delta G_{R} = -\left(\frac{4\pi}{3}\right) R_{av}^{3} \rho_{L} \Delta \mu$$

+ $2\pi \Delta \mu \Delta \rho \left[\frac{R_{av}^{2}}{a_{0}} - \frac{2R_{av}}{a_{0}^{2}} + \frac{2}{a_{0}^{3}} - \frac{2\exp(-a_{0}R_{av})}{a_{0}^{3}}\right]$
+ $\frac{\pi}{2} K \Delta \rho^{2} a_{0}^{2} \left[\frac{2R_{av}^{2}}{a_{0}} + \frac{1}{a_{0}^{3}} - \frac{1}{2a_{0}^{3}} \exp(-2a_{0}R_{av})\right],$

where a_0 is the value of the parameter *a* (present in density profile), for which ΔG given by the above expression is minimum and $\Delta \mu = \mu_V - \mu_L$ and $\Delta \rho = \rho_L - \rho_V$ (the subscript *L* and *V* stands for liquid and vapor phase).

The classical droplet approximation is retained at the large value limit of the parameter *a*, for which the expression obtained for the free energy of formation is $\Delta G_R(\text{MCNT}) = -(4\pi/3) R^3 \rho_L \Delta \mu + 4\pi R^2 \gamma_{\text{MCNT}}$, where $\gamma_{\text{MCNT}} = \gamma_{\infty} [(\Delta \rho)^2 / (\Delta \rho_0)^2]$, and the theory is called here the modified classical nucleation theory (MCNT).

Temperature-density diagram $(T-\rho)$ using WCA perturbation scheme for the L-J fluid has been obtained. The formation free energy as a function of size and supersaturation ratio, density profile of the nucleating droplet, nucleation barrier and critical cluster size as a

function of supersaturation ratio and finally the comparison of the CNT, MCNT and DFT results have been presented in this chapter.

CHAPTER III

It is well known that the presence of a foreign body acting as a substrate has considerable influence on the process of nucleation. Accordingly, the vapor to liquid heterogeneous nucleation of L-J fluid on a flat solid substrate forms the subject matter for investigation in this chapter [**35**]. Density functional theory has been applied to investigate such heterogeneous nucleation on a flat solid surface, by invoking a model free energy density functional along with an exponential density model. The well-known CNT has been also employed within the framework of the present DFT method for the same investigations. The liquid droplet on the flat solid surface at a given contact angle (θ_C) has been presented as a spherical cap model. The effects of supersaturation of the vapor and the strength of the solid-fluid interaction on the nucleation barrier have been investigated for L-J fluid with 12-6 fluid-fluid and 9-3 solid-fluid interaction model.

The Helmholtz free energy of the final phase of the nonuniform density (liquid drop on the solid surface covered by the vapor phase) has been expressed by using DFT with square gradient approximation as $F_f = \int f(\rho(r,\theta)) dv + \frac{1}{2} K \int (\nabla \rho(r,\theta))^2 dv + \int \rho(r,\theta) V_{sf}(z) dv$.

The form of the density profile $\rho(r,\theta)$ and the Helmholtz free energy density functional $f(\rho(r,\theta))$ are similar to those used in the chapter II. The solid-fluid interaction $V_{sf}(z)$ has been obtained by considering the wall-fluid model [4]. In the case of L-J interaction, the total interaction energy experienced by each fluid particle due to the solid surface is given by the 9-3 potential as $V_{sf}(z) = 4\pi\varepsilon_{sf}\rho_w \sigma_{sf}^{3}[(1/45)(\sigma_{sf}/z)^9-(1/6)(\sigma_{sf}/z)^3]$, where ε_{sf} is the depth of the

wall-fluid interaction, σ_{sf} is the collision diameter (distance of zero potential) between fluid and solid and *z* is the perpendicular distance of the fluid particle from the wall.

Therefore the free energy of formation of a droplet of a given volume on a solid substrate, given by $\Delta G_V^{het}(DFT) = G_f - G_i$, can be expressed, after simplification, as

$$\Delta G_{V}^{het}(DFT) = -V_{L}\rho_{L}\Delta\mu + \frac{3}{2}\Delta\rho\Delta\mu V_{L}\left(\frac{1}{C} - \frac{2}{C^{2}} + \frac{2}{C^{3}} - \frac{2\exp(-C)}{C^{3}}\right) + \frac{\pi K\Delta\rho^{2}}{4}$$
$$\left(C + \frac{1}{2C} - \frac{\exp(-2C)}{4C}\right)_{0}^{\frac{\pi}{2}}\sin(\theta) \left[R(\theta) + \frac{1}{R(\theta)}\left(\frac{dR(\theta)}{d\theta}\right)^{2}\right]d\theta$$
$$+ 2\pi\Delta\rho\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\int_{0}^{R(\theta)}V_{sf}(z)r^{2}dr ,$$

where C is the parameter present in the density profile given by $\rho(r,\theta)_{DFT} = \rho_L - (1/2)(\rho_L - \rho_V)$ exp[$C(r/R(\theta)_{av}-1)$] for $\theta \le r \le R(\theta)_{av}$ and $\rho(r,\theta)_{DFT} = \rho_V + (1/2)(\rho_L - \rho_V) \exp[-C(r/R(\theta)_{av}-1)]$ for $r > R(\theta)_{av}$ with which the free energy is minimized and $R(\theta)$ is the polar radius in the spherical cap model which has been derived as $R(\theta) = -r_S \cos(\theta) \cos(\theta_C) + r_S (\cos^2(\theta) \cos^2(\theta_C) + \sin^2(\theta_C))^{1/2}$.

The Gibbs free energy of formation of a droplet of volume V_L on a solid planar surface, within the framework of CNT, is given by

$$\Delta G_{V_L}(\text{CNT}) = -V_L \rho_L \Delta \mu + 2\pi r_S^2 (1 - \cos(\theta)) \gamma_{\infty}$$
$$+ 2\pi \Delta \rho \int_0^{\frac{\pi}{2}} \sin(\theta) d\theta \int_0^{R(\theta)} V_{sf}(z) r^2 dr$$

The shape, density profile and the free energy of formation of droplets of any arbitrary size have been obtained in this work. The spinodal decomposition of the vapor has been observed at higher supersaturation or at higher strength of the solid-fluid interaction.

CHAPTER IV

Vapor to liquid homogeneous and heterogeneous nucleation on flat solid surface have been discussed in the previous two chapters. A more general and natural nucleation phenomena that is, vapor to liquid heterogeneous nucleation on spherically curved solid surface for example, of a seed particle has been investigated in this chapter [36]. The methodology used for this purpose is similar to those described in the earlier two chapters. A double spherical cap model has been proposed to handle the problem of a liquid droplet on the spherical surface of solid substrate at any arbitrary contact angle. In addition to DFT, the problem has been solved by applying the well-known CNT method within the present model. A general solid –fluid interaction energy between the fluid particle and the spherical solid of any arbitrary size has been derived here. The Helmholtz free energy of the final phase (F_f) , density profile $\rho(r, \theta)$ and the Helmholtz free energy density functional $f(\rho(r, \theta))$ are similar to those used in the last two chapters (ChapterII and Chapter III). The solid-fluid interaction has been derived as $V_{sf}(z) = 4\pi\varepsilon_{sf} \rho_w \sigma_{sf}^3 [(\sigma_{sf}^9/45) \{1/z_0^9 - 1/(z_0 + 2R_s)^9\} - (\sigma_{sf}^6/6) \{1/z_0^3 - 1/(z_0 + 2R_s)^9\}$ $V_{sf}(z_0)$ $1/(z_0+2R_s)^3$ - $(\sigma_{sf}^9/20a_1)$ { $1/z_0^8$ - $1/(z_0+2R_s)^8$ } + $(\sigma_{sf}^3/2a_1)$ { $1/z_0^2$ - $1/(z_0+2R_s)^2$ }, where $a_1=2(z_0+R_s)$ with z_0 as the distance of any fluid particle from the surface of the solid sphere and R_S is the radius of the solid sphere. The solid-fluid interaction, $V_{sf}(z_0) = 0$ when $R_s = 0$ (homogeneous system), whereas for flat surface, the limit $R_S \rightarrow \infty$ results into the well-known 9-3 potential for flat wall. The free energy of formation of a droplet of a given volume V_L on a seed surface can be expressed, after simplification, as

$$\Delta G_{V_L}(DFT) = -V_L \rho_L \Delta \mu + \pi \Delta \rho \Delta \mu \int_0^{\pi/2} \sin(\theta) d\theta \int_{R_S(\theta)}^{R_L(\theta)} \exp\left(C\left(\frac{r}{R_L(\theta)} - 1\right)\right) r^2 dr + I_2$$
$$+ 2\pi \Delta \rho \left[\int_0^{\pi/2} \sin(\theta) d\theta \int_{R_S(\theta)}^{R_L(\theta)} V_{sf}(z_0) r^2 dr - \frac{1}{2} \int_{R_S(\theta)}^{R_L(\theta)} V_{sf}(z_0) \exp\left(C\left(\frac{r}{R_L(\theta)} - 1\right)\right) r^2 dr\right]$$
$$+ \frac{1}{2} \int_{R_L(\theta)}^{\infty} V_{sf}(z_0) \exp\left(-C\left(\frac{r}{R_L(\theta)} - 1\right)\right) r^2 d$$

where R_L is the radius of curvature of the liquid drop on the spherical solid surface and $R_L(\theta)$ and $R_S(\theta)$ are the two polar radii for the double spherical cap model and have been shown in Chapter III. Here I₂ is given by

$$I_{2} = \frac{\pi K \Delta \rho^{2} C^{2}}{4} \begin{bmatrix} \frac{\pi}{2} \\ \int_{0}^{\pi} \sin(\theta) d\theta \\ \left\{ \frac{R_{L}(\theta)^{3}}{C} + \frac{R_{L}(\theta)^{3}}{2C^{3}} - \exp\left(2C\left(\frac{R_{s}(\theta)}{R_{L}(\theta)} - 1\right)\right) \\ \left(\frac{R_{L}(\theta)R_{s}(\theta)^{2}}{2C} - \frac{R_{L}(\theta)^{2}R_{s}(\theta)}{2C^{2}} + \frac{4R_{L}(\theta)^{3}}{4C^{3}}\right) \end{bmatrix} \begin{bmatrix} \frac{1}{R_{L}(\theta)^{2}} + \left(\frac{d\left(\frac{1}{R_{L}(\theta)}\right)}{d\theta}\right)^{2} \\ \frac{1}{d\theta} \end{bmatrix} \end{bmatrix}$$

The Gibbs free energy of formation of a droplet of volume V_L on a spherical solid surface, within the framework of CNT, is given by

$$\Delta G_{V_L}(\text{CNT}) = -V_L \rho_L \Delta \mu + 2\pi R_L^2 (1 - \cos(\theta_L)) \gamma_{LV} + 2\pi \Delta \rho \int_0^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R_S(\theta)}^{R_L(\theta)} V_{sf}(z_0) r^2 dr$$

The shape (i.e. contact angle) and formation free energy of droplets of any arbitrary size have been optimized in this work. The change of the shape (optimized) with variation of the size of the liquid droplet as well as the size of the solid substrate have been observed, which predicts the shape-size relationship in the course of vapor to liquid heterogeneous nucleation on a spherical solid substrate of any particular size. The spinodal decomposition of vapor has been also observed at higher strength of the solid-fluid interaction. The results have been compared with the results of the conventional classical nucleation theory (CNT). The extreme limiting cases of the seed size leads to the results of the particular nucleation phenomena, such as

homogeneous nucleation when the size of the seed is zero and heterogeneous nucleation on flat surface when the seed is infinitely large.

CHAPTER V

A new scheme to calculate the surface tension of real fluids at a wide range of temperature (from the triple point to the critical point) is proposed, the input being only the known value of surface tension at the triple point [37]. The calculation is based on the density functional theory with square gradient correction along the lines of van der Waals and Cahn and Hilliard density functional formalism of the interface which is known to be a successful theory for the study of interface with slowly varying density. A double well type Helmholtz free energy density functional and a slowly varying model density profile have been proposed here. The methodology has been used for the calculation of surface tension of different fluids such as water, heavy water as well as liquid argon and very good agreement between the calculated and experimental values is observed. The advantage of this approach is that the surface tension of the real fluids can be accurately and analytically obtained without handling the detailed microscopic features of the fluids. The proposed density profile for the planar interface given as $\rho(z) = \rho_L - (1/2)(\rho_L - \rho_V) \exp(az)$ for $-\infty \le z \le 0$ and $\rho(z) = \rho_V + (1/2)(\rho_L - \rho_V)$ exp(-az) for $0 \le z \le \infty$, where ρ_L and ρ_V are the coexistence densities of the liquid and vapor phases. A double well type Helmholtz free energy density has been proposed, which is written as $f(\rho(z)) = f_0 + \mu_0(\rho(z) - \rho_0) - d_2(\rho(z) - \rho_0)^2 + d_4(\rho(z) - \rho_0)^4$. The surface tension of the planar interface (γ_{∞}) obtained in the present DFT work is expressed as γ_{∞} =(11/96)^{1/2} $(d_2K)^{1/2}(\Delta\rho)^2$. This equation after applying suitable approximation for d_2 has been simplified to calculate the surface tension of real fluids quite accurately, and can be expressed as

$$\gamma_{\infty} = \gamma_{\infty,t} \frac{\left(\Delta \rho\right)^2}{\left(\Delta \rho_t\right)^2} \left(\frac{\left(T_C - T\right)}{\left(T_C - T_t\right)}\right)^{\frac{1}{2}}$$

Since $\Delta \rho = (\rho_L - \rho_V) \sim (Tc - T)^{1/2}$ when the temperature approaches the critical point [3], one has the result $\gamma_{\infty} \sim (Tc - T)^{3/2}$, which is also predicted by the mean field theory.

CHAPTER VI

The theory of interfacial phenomena is well studied for planar interface, but for many instances particularly for the problem of nucleation, the theory for the interfacial properties of small droplet is essential. This has already been discussed in the earlier chapters and the DFT for size dependent surface tension of L-J fluid has been presented in this chapter [**38**]. The density profile and Helmholtz free energy density functional used in this work are similar to those used in the case of planar interface (Chapter V). The problem has been solved analytically. The total interfacial energy of the droplet-vapor system has been obtained as

$$\Omega = d_4 (\Delta \rho)^4 \pi \left(\left(\frac{11}{24} \right) \frac{R_{av}^2}{a} + \left(\frac{635}{1728} \right) \frac{1}{a^3} - \frac{\exp(-2aR_{av})}{4a^3} \right) \\ + \frac{2\exp(-3aR_{av})}{27a^3} - \frac{\exp(-4aR_{av})}{128a^3} \right) \\ + \frac{\pi(\Delta \rho)^2 a^2 K}{2} \left(\frac{R_{av}^2}{a} + \frac{1}{2a^3} - \frac{\exp(-2aR_{av})}{4a^3} \right) .$$

The surface tension at the equimolar dividing surface γ_e , can be obtained by dividing the above equation by the interfacial area $(4\pi R_e^2)$, i.e. $\gamma_e = \Omega(R_e)/(4\pi R_e^2)$. The results of the planar interface can be retained by considering the limit $R_e = \infty$. The problem has been solved numerically in order to obtain the surface tension of the spherical droplet with an exact density profile using the free energy model. The thickness of the interface in the present

model has been obtained as $D = -2 \ln(0.2)/a$. The various size dependent interfacial properties such as surface tension, density profile, thickness of the interface and also the size dependent temperature-density (T- ρ) diagram have been obtained analytically in the present work.

CHAPTER VII

The over- all outcome (summary) and conclusions of the work reported in this thesis have been given in this chapter. The drawback and limitations have also been discussed. The scope of application of the present proposed methodology to other different kinds of systems (such as liquid to solid transition, precipitation etc.) has been discussed.

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CHAPTER 1

Nucleation Phenomena: An overview

Matter exists in different phases, the most common ones being gas, liquid and solid phases. The transition from one phase to another has been one of the most interesting and rich subject of investigation. Here, we first discuss nucleation in the context of metastability followed by the theory of nucleation.

1.1 Metastability and nucleation

When the density or the composition of a given phase of any system remains unaltered over a long period of time, then the phase of the system is either in the stable state or in metastable state depending upon the extent of stability of the phase [1]. If the phase change takes place due to a small perturbation in the state variable (density, composition etc.), the system is said to be in metastable state else it is in stable state (Fig.1.1). In the case of onecomponent system, the density of the phase can be regarded as a unique state variable. The density of a stable phase (or state) at a given temperature is called equilibrium density of that phase at that particular temperature. If the density is shifted from the equilibrium value, then the system (partly or completely) tries to attain the density of the nearest new equilibrium situation (i.e. the new phase) leading to a first order phase transition. The extent of the shift density from the equilibrium value controls the kinetics of phase transition (1st order). of The stability of matter can be quite well presented by the P-V isotherm corresponding to van der Waals equation of state (EOS) shown in Fig.1.2, where the equilibrium vapour and liquid densities (or equilibrium molar volumes $V_{V,eq}$ and $V_{L,eq}$) lie on the line known as binodal line below the critical temperature (T_C). The two humps of each of the P-V isotherm show the highest possible vapour density and lowest possible liquid density (or molar volume). The

line connecting these two humps of each isotherm is termed as spinodal line and the region inside the spinodal line is therefore indicates the unstable state whereas the area in between the binodal line and the spinodal line represents the metastable state of the matter. When the density of any phase is shifted from its equilibrium density at any particular temperature (below T_C) and falls in the region of metastability or unstability, a new phase is formed (first order phase transition) inside the bulk of the older phase and the densities of the coexisting phases lie on the two ends of the binodal line. Though the phase transition is a bulk phenomena, the mechanism is actually a microscopic event and it starts through the formation of a small droplet of liquid or solid (in case of vapour to liquid and liquid to solid transition respectively) or through the formation of microscopic cavity or gas bubble (in case of liquid to vapour transition). When the density of any particular phase falls in the region of metastability, the phenomenon of formation of the embryo of the new phase is called nucleation and the subsequent growth of the nucleated entity leads to the bulk of the new phase. Therefore, the phenomenon of nucleation involves the formation of an embryo of the new phase, larger than a particular size, the so called critical size, beyond which it can grow irreversibly resulting into the bulk new phase. Nucleation is therefore the process of crossing a free energy barrier known as the nucleation energy barrier. If the density of the older phase is not too far from equilibrium (i.e. in the metastable state), the finite nucleation energy barrier actually controls the dynamics of this first order phase transition. If the density of the older phase is far from the equilibrium (in the unstable region), there is no barrier to cross from older phase to new phase and the droplets or bubbles (bubble in case of liquid to vapor transition) grow irreversibly (from beginning) leading to the formation of the bulk of the new phase and the phenomenon is called spinodal decomposition.



Fig.1.1 Phase stability as a function of density. Stable, metastable and unstable states of phase I are shown in figure a, b and c respectively.



Fig.1.2. Pressure - volume phase diagram for one component system. The dome shaped curve with solid line is binodal whereas the dome shaped curve with dashed line is spinodal curve. The horizontal dotted line is a true isotherm (at temperature T_1) and the intersections with the binodal dome showing the equilibrium pressure and volumes of the coexisting vapor-liquid phases.

1.2 Diversity of nucleation phenomena

Nucleation is a widely spread phenomenon in various aspects of nature and technology including condensation, evaporation, crystal growth, deposition of thin film, phase change and segregation in alloys and in various soft mater and nanoparticles self-assemblies. The understanding of nucleation plays an important role in different areas of science and technologies such as in meteorology, the formation of rain drop from cloud and artificial production of rain by providing heterogeneity through the spray of seed of the appropriate material; the initiation and production of the new phase in metallurgy; super cooling, super heating, supersaturation and precipitation by chemical means in the field of chemical engineering, etc. Most importantly, the phenomenon of nucleation is involved in the area of nano-technology which is widely used in almost all the fields of research in recent years. The fabrication of nano-sized materials of different size and shape such as nanoparticles, nanotubes, nanorods, thin film and different architecture etc. are very much important in nano-technology. The size, shape and kinetics of nano material synthesis can be controlled through an understanding of the nucleation phenomena involved therein. The phenomenon is also believed to be involved in different domains [2] such as irradiation-induced formation of voids in nuclear reactors, rupture of foam, membrane and emulsion bilayers, formation of electron-hole liquid in semiconductors, earthquake, appearance of turbulence in liquid crystals subjected to strong electric fields, formation of particulate matter in space, crackmediated fracture of stressed solids and various cosmological phase transitions.

1.3 Historical background and classical nucleation theory (CNT).

Nucleation phenomenon is of importance in a number of areas of research in chemistry, physics, material science and allied subjects [2]. In the previous section (1.1), it is already mentioned that the nucleation involves a process of crossing a free energy barrier known as the nucleation energy barrier. Since the present dissertation focuses on the investigation of vapor to liquid transition, therefore the discussion is being limited mainly to the vapor to liquid condensation phenomena. The nucleation barrier is affected only by the degree of supersaturation of the vapor phase when there is one component vapor and the process is called homogeneous vapor to liquid nucleation. Since most of the natural systems are heterogeneous, where many other components (like impurities, surface of the wall etc.) are also present in the system, the new phase formation is commonly initiated on the surface of such foreign substrates and the phenomena is known as heterogeneous nucleation (see **Fig.1.3**). The condensation rate is therefore strongly affected by the presence of such foreign (solid) substrates. The size, shape and the strength of the solid- fluid interaction of such solid substrates control the nucleation barrier, critical size and shape of the nucleus at a given temperature and supersaturation.

The first attempt to understand the nucleation phenomena by applying thermodynamics was due to Gibbs [3] and many theoretical models and approaches have been proposed from time to time. The theory developed originally by Becker, Doring, Volmar, Farkas, and later modified by Zeldovich for the study of homogeneous nucleation from vapor to liquid phase has been traditionally referred to as the classical nucleation theory (CNT) [4-7]. The CNT assumes the capillarity approximation which considers that the small nucleated liquid droplet inside the vapor phase is same as a drop of bulk liquid with a well-defined radius R, with

bulk liquid density inside and bulk vapor density outside, corresponding to the assumption of a sharp interface between the vapor and the liquid drop. The free energy of this inhomogeneous state relative to the homogeneous vapor phase is expressed as a sum of two terms, viz. a negative contribution from the bulk free energy difference, proportional to the droplet volume and a positive contribution from the surface free energy, proportional to the surface area of the droplet of well-defined radius. The Gibbs free energy of formation of a droplet of radius R, in the conventional CNT (see Fig.1.4) is therefore written as $\Delta G_R(CNT)$ = - $(4\pi/3)R^3\rho_L\Delta\mu + 4\pi R^2\gamma_\infty$, where $\Delta\mu = \mu_V - \mu_L(\mu \text{ stands for chemical potential})$ is obtained in CNT by using the ideal gas equation, viz. $\Delta \mu$ so that $\Delta \mu = \mu_V - \mu_L = k_B T \ln(S)$, where $S (= \rho_V / I)$ $\rho_V^{\ 0}$ is the supersaturation, with ρ_V as the density of the supersaturated vapor and $\rho_V^{\ 0}$ as the vapor density at liquid-vapor coexistence. The classical theory assumes that the surface free energy is the same as that of the planar interface at coexistence at a given temperature. Thus at a given temperature, CNT uses the surface free energy corresponding to the vapor-liquid equilibrium state where the liquid drop is very large (resulting into planar interface). But during nucleation, a tiny liquid drop (spherical) is surrounded by supersaturated vapor (i.e., there is a spherical interface between the liquid and supersaturated vapor) and hence the interfacial energy should correspond to the supersaturated vapor-liquid spherical interface rather than liquid-vapor equilibrium state with planar interface which is used in CNT. The radius of the critical cluster, $R_{\rm C}$ as obtained through maximalisation of the free energy $\Delta G_R(\text{CNT})$, is given by $R_C = 2 \gamma_{\infty/} (\rho_L \Delta \mu)$ and the corresponding nucleation barrier, ΔG^*_{CNT} is expressed as $\Delta G^*_{CNT} = [(16\pi \gamma_{\infty}^3)/(3(k_B T \rho_L \ln(S))^2)]$. The free energy barrier to nucleation is then used in the transition state theory to calculate the nucleation rate, J, as given by J = A $\exp[-\Delta G^*_{CNT}/k_BT]$, where A is the preexponential factor.
The conventional classical theory developed for homogeneous nucleation is also applied to the process of heterogeneous nucleation, when a vapor starts condensing either on a flat solid surface or a curved solid surface. The first attempt initiated by Volmer, Fletcher (liquid nucleation on solid surface) and Turnbull (crystal nucleation on solid surface) for this purpose was of course through the classical theory of heterogeneous nucleation [8-12]. The same approximations as used in the case of homogeneous nucleation, were used, i.e. the properties of the tiny droplet were considered to be the same as that of the bulk liquid and the vapor-liquid interfacial energy was also treated as same as that of the planar interface at coexistence condition. The condensations on flat surfaces [8-10] as well as curved surfaces [11-12] of the solid substrate have been considered using the classical nucleation theory (CNT). The effect of particle size and surface properties on the nucleation efficiency was investigated by Fletcher [11]. A general result was derived in the framework of CNT, which is then applied to the case of condensation and sublimation. A rigorous thermodynamic formulation of Fletcher's model using a novel analytical approach within CNT was derived by Qian and Jie [12]. The two drastic approximations in CNT (for both homogeneous and heterogeneous nucleation) lead to considerable error in the calculation of nucleation barrier height and hence also in the nucleation rate. Attempts have been made to overcome this problem by proposing various theoretical approaches by passing these approximations which will be discussed in the next section.



Fig.1.3. Schematic description of homogeneous nucleation (labeled as a) and heterogeneous nucleation on flat surface and on spherically curved (convex) surface of solid substrate (labeled as b and c respectively).



Fig.1.4. Formation free energy vs size described by CNT

1.4 Progress on the theory of vapor-liquid nucleation

The drawback of CNT in the prediction of nucleation barrier height and hence the nucleation rate is due to the use of two crude approximations which has been already mentioned in the previous section (1.2). The theory proposed and developed by Oxtoby and co-workers [13-18] is the density functional theory (DFT) based on microscopic molecular interaction, thereby avoiding the phenomenological capillarity approximation to nucleation of vapor-liquid phase transition. Their theory is thus a nonclassical theory which is used for various fluid systems (interacting with Lennard-Jones, Yukawa potential etc.) encompassing one component fluid as well as binary fluid mixtures. They have developed an iteration technique [13] to obtain the density profile of the critical cluster from the energy equation for the inhomogeneous fluid. The DFT based theory of Iwamatsu has investigated the problem of homogeneous nucleation [19] using a double and more recently a triple parabola model [20]

for the free energy functional. Recently Lutsko **[21, 22]** has also proposed a DFT of inhomogeneous liquids and considered an approach to nucleation in liquid-vapor transition. A non-mean-field DFT based approach to nucleation has also been reported **[23]**.

A semi-phenomenological model, the so called mean-field kinetic nucleation theory, has also been proposed by Kalikmanov [24] and is known to be valid for all cluster sizes. Reguera and Reiss [25] have proposed a new phenomenological approach to nucleation based on an extended modified liquid drop model [26] and dynamical nucleation theory [27] which is able to predict successfully the free energy of formation of the critical nucleus, using only macroscopic thermodynamic properties. Another phenomenological approach to calculate the free energy of formation is the so-called diffuse interface model developed by Granasy [28] which assumes the center of the droplet to be bulk-like and the diffuse interface to have a size-independent thickness. Many other investigations using molecular simulation techniques have also been successful in predicting the nucleation in the context of vapor to liquid phase transition. The Monte Carlo (MC) simulation study of the formation free energy of clusters in vapor-liquid nucleation by Oh and Zeng [29], molecular dynamics (MD) simulation study of cluster evolution in suparsaturated vapor by Zhukhovitskii [30] and gas-liquid nucleation of Lennard-Jones (L-J) fluid by Laaksonen et.al. [31] are few examples of the development of molecular simulation on vapor to liquid homogeneous nucleation in the recent past. The classical theory, however, does not work well for the heterogeneous nucleation also and therefore several approaches have been developed within the frameworks of the widely used density functional theory (DFT) [32-37] as well as molecular simulation [38-46] based techniques to describe the various aspects of the phenomena of heterogeneous nucleation. Talanquer and Oxtoby employed DFT to calculate the rate of heterogeneous nucleation of the gas-to-liquid transition on a planar solid substrate [32] and to study the nucleation of gas-

liquid transition inside a slit pore in which a fluid is confined between two flat surfaces [33]. While the effect of flat surface of the solid substrate on nucleation has been the major concern most often, there are density functional theories, where the effect of microscopic or mesoscopic solid substrate (providing curved surface to the liquid droplet) have been discussed. Lattice density functional theory (LDFT) with suitable constraints had been applied by X. Zhang et.al to investigate the shape of the critical nucleus and height of the nucleation barrier and by applying the LDFT method, the nucleation behavior of vapor-liquid transition in nanosquare pores with infinite length was studied [35]. They also use the constrained LDFT to investigate how nanoscale seed particles affect heterogeneous vaporliquid nucleation [36] i.e. the effects of the physical properties of nanoscale seed particles (the seed size, the strength of seed-fluid attraction, and the shape of the seeds) on the structure of critical nuclei and nucleation barrier. A hybrid thermodynamic and density-functional theory for heterogeneous nucleation on mesoscopic wettable particles was developed by Bykov and Xeng [37]. Many molecular simulations have been carried out to study the heterogeneous nucleation on flat solid surface [38-40] as well as on the curved surfaces of small substrates [41-46].

Though the CNT provides much inaccurate results as compared to the theories and simulations discussed in this section, it has a very good acceptability in the case of complicated systems due to the simplicity of this description and because the application of other theories is much more cumbersome. The CNT can be further modified by retaining the simplicity but providing a simple theory of interfacial phenomena of curved interface of two phases and therefore the research and development on the theory of size dependent interfacial phenomena are also an interesting topic. The overview of the theory of interfacial phenomena of both flat and curved surfaces will be introduced in the next section.

1.5 Kinetic theory of nucleation

Kinetic theory of nucleation obtains the cluster distributions and nucleation rate by calculating the rate constants of association and dissociation of the cluster (nucleus) and thereby avoiding the explicit evaluation of cluster formation energies and surface tension. But the first task however, is the identification of the nucleus itself. In case of condensation of liquid droplet from a low density vapor, or solid crystallization from dilute solution, it is easy to identify the cluster or nucleus from the sharp difference in density or composition from their immediate surroundings. But if the temperature is near critical point, then it is difficult to draw a boundary between the cluster and the surrounding (high density vapor) which is also true for a nucleated crystal in the melt. In these cases, the identification of number of particles associated with a nucleus at a given time is difficult.

Restricting the discussion to the simpler cases in which the number of particles can be assigned to a nucleus, the kinetics of nucleation then involves a set of rate equations such as association and dissociation by which clusters of different sizes gain or lose particles which involves an assumption about lack of memory i.e. the probability of a particular change in size of a given cluster during a time interval is independent of its past history. The use of rate constants involves the implicit assumption that the temperature does not change as clusters grow or shrink.

Another assumption commonly considered is that the clusters grow or shrink by the attachment or loss of single particles and the other possibilities such as fusions of preexisting clusters and fissions of clusters into two or more other clusters (i >1) are ignored. This is reasonable for condensation at low pressures, where almost all particles are isolated 'monomers'.

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A set of coupled rate equations for the number densities n(i, t) of clusters of size i at time t, as obtained by considering the above approximation have the form [47]

$$\frac{\partial n(i,t)}{\partial t} = \alpha(i-1)n(i-1,t) - \beta(i)n(i,t) - \alpha(i)n(i,t) + \beta(i+1)n(i+1,t) , \qquad (1.1)$$

where $\alpha(i)$ and $\beta(i)$ are the forward and backward rate constant for the gain and loss of a monomer by a cluster of size *i* and n(i,t) is the number density of a cluster of size *i* at any particular time *t*. The forward rate depends on the concentration of the monomers and can be considered to be proportional to that concentration.

The net rate at which clusters of size i become clusters of size i + 1 is defined as a flux J(i + 1/2) and expressed as

$$J\left(i+\frac{1}{2},t\right) = \alpha(i)n(i,t) - \beta(i+1)n(i+1,t) , \qquad (1.2)$$

so that Eq.(1.1) can be rewritten as

$$\frac{\partial n(i,t)}{\partial t} = J\left(i - \frac{1}{2}, t\right) - J\left(i + \frac{1}{2}, t\right).$$
(1.3)

In the steady state, all fluxes are equal to a single constant flux J for all values of I and t, viz.

$$J\left(i+\frac{1}{2},t\right) = J,\tag{1.4}$$

which is the flux that is identified with the nucleation rate of interest in theory or experiment. A function f(i) is defined by the recursion relation as

$$f(i+1) = \left[\frac{\alpha(i)}{\beta(i+1)}\right] f(i) , \qquad (1.5)$$

with f(1) = 1. Dividing (1.2) by $\alpha(i) f(i) = \beta(i+1)f(i+1)$ and after setting J to a

constant in the steady state, gives

$$\frac{J}{\alpha(i)f(i)} = \frac{n(i)}{f(i)} - \frac{n(i+1)}{f(i+1)} .$$
(1.6)

Equation (1.6) can be summed from i = 1 to a limiting value $i = i_{max}$, leading to the results

$$J\sum_{i=1}^{i_{\max}} \frac{1}{\alpha(i)f(i)} = n(1) - \frac{n(i_{\max})}{f(i_{\max})} .$$
(1.7)

In order to examine the dependence of f(i) on *i*, the function f(i) can be rewritten as

$$f(i) = \prod_{j=1}^{i-1} \left[\frac{\alpha(j)}{\beta(j+1)} \right], \qquad (1.8)$$

The ratio $\alpha(i-1) / \beta(i)$ is the ratio of the rate at which a cluster of size (i - 1) gains a particle to the rate at which the cluster of size *i* loses a particle. These rates are equal exactly at phase coexistence, in the thermodynamic limit of large enough value of *i*. But during nucleation which occurs in the metastable state of the old phase, the new phase however, is thermodynamically stable, which means that for large enough *i* this ratio must be larger than 1 (i.e. the forward rate must be larger than the backward). Therefore f(i) must grow with *i* for large *i*, and increasing by a factor larger than 1 for each increase in *i* by 1which in fact corresponds to exponential growth of *f* with *i*. Since it has been assumed that there is a little depletion of monomer in the process of nucleation, one must clearly have $n(i_{max}) < n$ (1). The second term on the right side of (1.7) will then be negligible as compared to the first if i_{max} is chosen to be large enough. Because $\alpha(i)$ is a smooth (at least for large *i*) and increasing

function of *i*, the sum on the left side of this equation can be extended to infinity, with convergence guaranteed by the exponential fall-off of 1/f(i). This leaves

$$J = n(1) \left(\sum_{i=1}^{\infty} \frac{1}{\alpha(i)f(i)} \right)^{-1}$$
(1.9)

This equation gives a direct expression for the nucleation rate in terms of the forward and reverse rate constants.

1.6 Overview of the theory of vapor-liquid interface

Interfacial properties such as surface tension, density profile, surface thickness etc. are very much important in science and technology in connection with various phenomena and processes ranging from macroscopic to microscopic length scales. In particular, the interfaces play a crucial role in controlling the kinetics of nucleation and hence in the fabrication of nanostructured materials. A new phase appears in the bulk of the old phase in the process of nucleation leading to a two phase system and hence an interface is developed. The interfacial energy is actually guided by the density profile of the system and it is obvious that, higher the density difference, higher is the interfacial energy. In CNT, the liquid-vapor interfacial properties (density profile and thereby surface tension) is always considered as that of the bulk liquid-vapor interface at coexistence i.e. a planar interface with the sharpest density variation have been considered. But in actual case the droplet is tiny and therefore the interface is curved. Also since the vapor is supersaturated in the process of nucleation,

therefore the density difference is less than that at coexistence. The use of the latter leads to erroneous results in CNT. Proper understanding and application of the interfacial phenomena (density profile, surface tension etc.) is therefore very much important in the investigation of the phenomena of nucleation.

The liquid-vapor interface of classical fluids and related topics had been extensively discussed in the literature from time to time [48-50]. Different theories e.g. statistical mechanical theory [51-52], density functional theory (DFT) [53-57] etc. and molecular simulations [58-62], have been used for the investigation of interfacial properties of vapor liquid planar interface. It is found that the most versatile theory for this purpose is the DFT. While talking about the nanosized material, an idea of the interfacial properties for small sized systems (i.e, for curved interfaces) is needed, while most of the experiments are performed only for bulk sized system (i.e, for planar interface), the idea of considering a planar interface no longer works in the case of nanosized materials. For small liquid dropletvapor two phase system, it can be assumed that the interface is spherically curved. The curvature dependence of surface properties was first mentioned by Gibbs [63] and later developed by Tolman [64-66]. A simple relation between the surface tension γ and the radius R_s of the surface of tension was derived by Tolman and a parameter δ (known as Tolman length) was introduced which is the distance between this surface (R_s) and the equimolar dividing surface with radius R_e, which divides the fluid into two homogeneous parts, the inner one with the liquid density and the outer one, with the vapor density. A statistical thermodynamical approach for spherical droplets was introduced by Plesner [67] to investigate the dependence of surface tension on the droplet size. The problem was numerically solved by Guermeur et.al [68] by describing the inhomogeneous interface with

the help of a stress tensor within the framework of gradient theory. A DFT for the spherical droplet was considered by Hadjiagapiou [69] to examine the effect of drop size on various interfacial properties. The thermodynamic properties of planar and spherical liquid-vapor interface was calculated by Osman [70] who presented the results at the coexistence condition for both type of interfaces. A double parabola model based DFT had been reported earlier by Iwamatsu [71] to calculate the surface tension and Tolman length of a droplet. A patching model for the surface tension of a spherical droplet using the framework of DFT had been reported by Bykov and Zeng [72]. Li and Wu [73] illustrated the applications of a nonmean-field DFT to the ultra-small liquid droplets as formed during vapor-liquid nucleation, in which the size-dependence of surface tension had been examined. Many molecular simulation (Monte Carlo as well as molecular dynamics) strategies had also been developed to investigate the size dependence of interfacial properties [74-77]. Apart from the above literatures, many more studies have been reported, where the interfacial properties for both planar and spherical interfaces of one-component to multi-component systems of various fluid systems have been discussed. Although there have been a series of publications on the size-dependent surface tension, in the present thesis, a simple way of evaluation of the sizedependent surface tension and temperature density (T-p) curve for a droplet-vapor equilibrium have been presented.

1.7 Overview of DFT of inhomogeneous classical fluid

When a liquid droplet condenses inside the bulk of the vapor phase or a gas bubble forms inside the bulk of the liquid phase for one component system or in case of bulk vaporliquid coexistence condition, the system in CNT is treated as two distinct phases (i.e. liquid

and vapor phases) one component system. The system, however, is actually a single phase inhomogeneous fluid with a nonuniform density distribution (commonly diffuse density distribution) at the liquid-vapor interface, either for bulk system or for microscopic (droplet or bubble) system. It has been already mentioned (in section **1.3**) that the consideration of the two phase system (i.e. the use of a well-defined radius for the nucleated droplet) introduces a significant error in the results of CNT. The most widely used and accepted theory for such system is the density functional theory of inhomogeneous classical fluid (see Ref. **[48,78-80**]) where the system is considered as a single inhomogeneous fluid phase with a diffuse density distribution at the interface instead of the two phase with sharp interface (as used in CNT).

The density functional theory was first time applied by van der Waals [81] to study the inhomogeneous liquid–gas interface in 1894 and later it was classified as a local density approximation [48]. The subject is then moved to the field of quantum theory by Thomas [82] and Fermi [83] in their seminal development of the theory of the electron gas. The celebrated variational principle based DFT for the ground state energy of (quantum mechanical) electrons was derived by Hohenberg and Kohn [84] in 1964 and one year later this was generalized to non-zero temperature by Mermin [85]. The density functional variational method was then applied to classical fluids (see e.g. the work of Ebner and Saam [86,87] and Yang *et al* [88]). A more detailed historical discussion on DFT of inhomogeneous fluid can be found in [89].

The classical density functional theory is based on the grand canonical free energy functional $\Omega[\rho(r)]$ of the one-particle density $\rho(r)$ in the (one-component) system, which is expressed as

$$\Omega[\rho(r)] = F[\rho(r)] + \int d^3 r \rho(r) (V_{ext}(r) - \mu), \qquad (1.10)$$

where $F[\rho(r)]$ is the total Helmholtz free functional, μ is the chemical potential and $V_{ext}(r)$ is the external potential acting on the particles. The minimization of the functional (at fixed *T* and μ) with respect to one-particle density $\rho(r)$ results into the equilibrium density distribution, $\rho_0(r)$, i.e.

$$\frac{\delta\Omega[\rho]}{\delta\rho(r)}\Big|_{\rho(r)=\rho_0(r)} = 0 \quad , \tag{1.11}$$

which leads to the relation

$$\frac{\delta F[\rho]}{\delta \rho(r)} \bigg|_{\rho(r) = \rho_0(r)} - \mu + V_{ext}(r) = 0$$
(1.12)

and the corresponding value of the functional i.e. $\Omega[\rho_0(r)]$ is the equilibrium grand canonical energy. The Helmholtz free functional $F(\rho(r))$ is generally expressed as

$$F[\rho] = F_{id}[\rho] + F_{ex}[\rho] \quad .$$
(1.13)

The exact Helmholtz free energy functional of the ideal gas is expressed as

$$F_{id}[\rho] = k_{\rm B} T \int d^3 r \rho(r) \left[\ln \left(\Lambda^3 \rho(r) \right) - 1 \right], \qquad (1.14)$$

where Λ is the thermal wavelength of the particles and k_B is the Boltzmann's constant. For an ideal gas, the excess part of the Helmholtz free energy F_{ex} [ρ]= 0 and therefore the Helmholtz free energy density functional is known exactly for this system. For a non-ideal system, which is characterized by a non-vanishing inter particle interaction (e.g. by a pair potential $\Phi(r)$), the excess part $F_{\text{ex}}[\rho]$ is not exactly known and various approximations (see

ref **48,78-80,89**) have been developed for calculation of this excess part. The relation between $F_{\text{ex}}[\rho]$ and the direct correlation function $(c^{(2)}(r,r'))$ which is expressed as

$$c^{(2)}(\boldsymbol{r},\boldsymbol{r}') = -\frac{1}{k_{\rm B} \mathrm{T}} \frac{\delta^2 F_{ex}[\rho]}{\delta \rho(\boldsymbol{r}) \delta \rho(\boldsymbol{r}')},\tag{1.15}$$

is often made use of for approximating the $F_{ex}[\rho]$, as well as testing its accuracy.

The gradient expansion model of the Helmholtz free energy [**32**,**48**,**57**,**78**] is also used in many cases (nucleation, interfacial phenomena etc.), with the grand potential expressed as

$$\Omega[\rho(r)] = \int d^3r \left[f[\rho(r)] + \frac{1}{2} K \left[\nabla \rho(r) \right]^2 \right] + \int d^3r \rho(r) \left(V_{ext}(r) - \mu \right), \quad (1.16)$$

where $f[\rho(r)]$ is the local Helmholtz free energy density and the local excess free energy density associated with any effect from density inhomogeneity of the system is described by the square-gradient term $((K/2)[\nabla\rho(r)]^2)$. In the present thesis, the external potential $V_{ext}(r)$ describes the effect of substrate on the free energy of heterogeneous nucleation. Another way of expressing the Helmholtz free energy $F[\rho(r)]$ is [13,14],

$$F[\rho(r)] = \int d^3r f_h[\rho(r)] + \frac{1}{2} \iint d^3r \, d^3r' \, \rho(r) \, \rho(r') \, \Phi(|r-r'|) \,, \qquad (1.17)$$

where $f_h(\rho)$ is the Helmholtz free energy density of uniform hard sphere fluid of density ρ with an attractive perturbation contribution given by the second term in the equation.

1.8 Nucleation experiments

A number of methods and analytical instruments have been developed from time to time (see review **[90]**) for the experimental measurement of nucleation rates in a broad range (span

more than 20 orders of magnitude) from 10^{-4} to 10^{17} cm⁻³ s⁻¹. The differences between the experimental methods are mainly related to the way of achieving a supersaturated state. In the study of one component vapor to liquid nucleation, the supersaturated state of the initial phase (vapor) is obtained by cooling the vapor phase using either adiabatic expansion or a temperature gradient whereas in multicomponent systems, the turbulent mixing of vapors followed by fast cooling or in-situ generation of one of the nucleating vapors (chemically or photochemically) is preferred. Early studies of nucleation was done by using diffusion and expansion cloud chambers where the critical supersaturation required to attain the nucleation rate of unity (J = 1 cm⁻³ s⁻¹) had been measured [91] to calculate the kinetics of nucleation. Various particle detection techniques have been developed and implemented in later studies and the counting of the number of nucleated particles and thereby the calculation of the formation rate have been improved. The different approaches for the experimental study of vapor to liquid nucleation phenomena have been briefly discussed here.

1.8.1. Adiabatic expansion method

In this method, the supersaturation of the vapor is achieved through the cooling of the vapor by rapid adiabatic expansion to initiate nucleation. The nucleation in a fast expansion cloud chamber starts when a piston is moved to produce an adiabatic expansion in the nucleating vapor. Nucleation rates, in the range from 10^2 to 10^{10} cm⁻³ s⁻¹ can be determined from the number of particles depending on the specific design of the chamber. This method has been used to measure nucleation rates in a large number of single-vapor systems [**92-96**] as well as binary mixtures [**97**]. Shock tube method is the example of another expansion-based method of measurements of nucleation rates, consisting of two sections (driver and

driven sections) separated by a diaphragm. The driver section is maintained at higher pressure by vapor carrier gas mixture, whereas the driven section is maintained at low pressure. The adiabatic expansion from the driver to the driven section is produced by rupturing the diaphragm for making the vapor to be supersaturated and thereby initiating nucleation. Nucleation rates up to 10^{17} cm⁻³ s⁻¹ can be obtained by this approach .The supersonic nozzle based method is also used for both single and binary vapor systems to achieve very high supersaturation by utilizing adiabatic expansion of a flowing nucleating vapor-carrier gas mixture [**98**]. The growth of the clusters (due to nucleation and condensation) occurs as the flow passes out of the throat region of the nozzle and the local pressure raises due to the latent heat of condensation which allows the detection of the location of cluster and nucleation rates are determined by measuring this pressure trace and the cluster size. The cluster size is determined by various technique e.g. small angle neutron scattering, small angle X-ray scattering, tunable diode laser absorption spectroscopy etc. In this method, a very high supersaturation is achieved and the nucleation rates higher than 10^{16} cm⁻³ s⁻¹ are observed, which is much faster than the rates measured in other expansion techniques.

1.8.2. Diffusion chamber

The expansion chamber, discussed so far produces short nucleation pulses whereas the diffusion chambers operate continuously. The supersaturation is produced by introducing a temperature gradient between two parallel plates in a diffusion chamber, named as upward diffusion chember. The bottom plate is kept warm and covered with liquid, whereas the top plate is cool and the vapor from the warm bottom plate diffuses toward the top cool plate so that both temperature and partial pressure of the vapor decrease almost linearly with the distance from the liquid surface to the top plate. The saturation vapor pressure of the fluid

however depends exponentially on temperature, and the supersaturation ratio goes through a maximum at about $3/4^{\text{th}}$ of the chamber height. The temperature gradient is adjusted in such a way that a maximum rate of homogeneous nucleation is achieved. The nucleated droplets grow and settle down toward the bottom plate to be detected and counted with a laser beam. The desirable nucleation rate is obtained by adjusting the temperatures of the top and bottom plates. The rate is typically in the range of 10^{-4} to 10^3 cm⁻³ s⁻¹ in this upward diffusion method. This method can be used to measure critical supersaturations and nucleation rates of both single and mixed vapors, but it is most reliable for the one component systems.

1.8.3. Laminar flow chamber

In this chamber, the supersaturated state of vapor is achieved by utilizing the thermodynamic and transport properties of gas which is also known as the laminar flow tube reactor [99-100]. This chamber has a hot saturator section where the carrier gas is made saturated with the nucleating vapor and a condenser section where the vapor is made supersaturated by abrupt cooling so that the vapor nucleates to form the droplets which are then optically detected. Nucleation rates that can be measured in this method is typically in the range from 10^2 to 10^8 cm⁻³ s⁻¹. This method is particularly suitable for the vapors of high molecular weights. A transport model is required to calculate the temperature and saturation ratio which are then related to the measured nucleation rates.

1.8.4. Turbulent mixing chamber

This method is different from the above diffusion and expansion chamber method and makes use of turbulent mixing of two vapors and is therefore applicable to binary nucleation.

The turbulent mixing method is particularly useful for the systems where the applications of other techniques for the accurate measurement are difficult as for example, in case waterstrong acid (H₂O-H₂SO₄) mixture which is important in the atmosphere. This chamber consists of turbulent mixing section and laminar nucleation section. The temperature of turbulent mixing section is maintained at similar or higher relative to the laminar section. Two or more gas flows, carrying the nucleating vapors, are rapidly mixed in the turbulent section and the system becomes supersaturated enabling nucleation immediately after mixing [101]. In case of hot mixing section, the supersaturated state is followed by nucleation and growth is achieved when the gas mixture enters the colder laminar section. In order to quickly reduce the gas temperature, a chilled carrier gas is also used in some designs.

1.8.5 Comparison between the result of experiment and classical nucleation theories

Homogeneous nucleation of a large number of substances, including inert gases, vapors of metals and various inorganic and organic compounds [102] have been experimentally investigated. It has been found that, the nucleation rate J is a steep function of supersaturation ratio (S) for the vapors of all substances mentioned above. The nature of such strong dependence of nucleation rate on the supersaturation is not always predicted by the theory and a large disparities are often observed between theoretically predicted and experimentally measured nucleation rates. It is common to all nucleating systems that the critical supersaturation decreases with increasing temperature whereas the rate increases with temperature at a constant supersaturation. Though the dependence of the experimental nucleation rates on the supersaturation is often similar to the dependence predicted by CNT, the temperature dependences of experimental nucleation rate frequently differ from that of the theoretical nucleation rates. CNT typically underestimates the nucleation rates at low

temperatures and overestimates at high temperatures, with the errors of several orders of magnitude.

1.9 Molecular simulations

Unlike laboratory experiment discussed in Section 1.7, computer experiment i.e. molecular simulations like molecular dynamics (MD) and Monte Carlo (MC) are also popular for the study of the nucleation phenomena. These simulations apply first principles to calculate the structure, density profile and free energy of cluster formation [103,104]. The MC method is a stochastic method which simulates the evolution of an ensemble of molecules by sampling random molecular configurations, i.e., one molecule at a time, and it accepts or rejects the configurations depending upon the suitable criteria set for the system. The MD simulation on the other hand, uses Newton's laws for each particle to simulate the trajectories of all particles in the system undergoing a phase transition. The trajectories are determined by imposing the initial positions and momenta of the particles and by the inter-particle potential.

The appearance of a cluster of the new phase is identified by the particle density, chemical potential of the particles in the new phase, or by using other properties [**105**] which are used to calculate the association and decomposition rate coefficients, utilized to determine the nucleation rates. In case of direct MD simulations, the preparation and time evolutions of a metastable system continue until nucleation occurs [**31**], which is very much computationally expensive (true not only for molecular dynamics but also for the stochastic Monte Carlo simulation) due to the lack of analytical solution to the many body problem, necessary for solving for the interaction among numerous molecules. Due to this limitation, there is a constraint on the number of molecules that can be treated, the size of the spatial domain, and

the integration times. Since density fluctuations leading to nucleation are rare events on the simulation time scale, direct simulation of nucleation is therefore highly unusable. In order to overcome such difficulties a feasible alternative to the direct simulation is provided by biased sampling methods. Umbrella sampling method [106] is one such method first introduced into the field of nucleation by Frenkel and co-workers [107] which is widely used later. This method forces the metastable system to cross the free-energy barrier reversibly along a reaction coordinate in a manageable amount of time by means of biasing potential. The knowledge of the inter-particle potential is essential for both the classical MC and MD simulations. The model Lennard-Jones (LJ) potential function is the most widely used one which has been successfully applied to simple atoms and their mixtures particularly for inert gasses and sometimes also for other fluids with the suitable corrections.

1.10 Motivation of the thesis

The main objective of this thesis is to develop a simple theoretical methodology to investigate the nucleation phenomena beyond the conventional CNT by incorporating a more realistic density model for the vapor-liquid interface. Density functional theory has been found to be the most suitable tools for such problem where the liquid-vapor system can be considered as an inhomogeneous fluid with a continuous density distribution and thereby consideration of a sharp interface with the bulk value of density (of the liquid droplet) and consequent interfacial energy approximated in CNT could be avoided. Therefore a diffuse density profile model, which is quite realistic for liquid–vapor interface for microscopic as well as macroscopic interfaces and a simple Helmholtz free energy density functional for the inhomogeneous fluid have been approximated to obtain a simplified version of DFT for the

purpose of theoretical investigation of nucleation and interfacial phenomena. The theory (DFT) developed for the homogeneous nucleation phenomena is then extended to the case of heterogeneous nucleation on flat solid surface (normally on the surface of the container or wall) and also on the more general spherically curved surface of the solid substrate which may be the most common means of vapor to liquid condensation in nature. Motivated by the importance of the theory of interfacial phenomena, specially the size-dependent interfacial properties, which are very much significant while dealing with nucleation, a simplified version of both planar and size-dependent interfacial properties (that can be used for the replacement of the bulk interfacial energy term in the expression of CNT) of L-J system has been introduced. Though there are many theories available to calculate the surface tension of different model fluids, a detailed microscopic knowledge and rigorous calculations are required to obtain the surface tension of a real fluid (e.g. water) accurately over a wide range of temperature. In order to obtain a general expression for the surface tension of a real fluid a scheme has been proposed, in this thesis, to calculate the surface tension of real fluids without any detailed microscopic knowledge and calculations. This approach has been employed for calculating the surface tension of water, heavy water and liquid argon over a wide range of temperature from triple point to critical point with a significant accuracy.

1.11 Scope of the thesis

The thesis is organized as follows. In chapter 2, an analytical route of obtaining the properties of homogeneous nucleation phenomena for vapor to liquid transition of Lennard-Jones fluid using classical DFT with square gradient approximation along the lines of van der Waals [81] and Cahn and Hilliard [108] has been introduced [109]. An exponential density

profile model (with a parameter which measures the degree of diffuseness) and a model Helmholtz free energy functional which has been expressed as Taylor series expansion with respect to the uniform fluid have been proposed here. The free energy is variationaly minimized with respect to that parameter and the equilibrium density profile and corresponding free energy, which is the free energy of formation of droplet of a given radius, have been evaluated analytically. The problem has also been solved by using CNT in the frame of the present DFT. A modification of CNT has been introduced by applying the sharp interface approximation of CNT (through the large limit of the parameter in the model density profile) into the result of the DFT and the modified version has been named here as modified classical nucleation theory (MCNT). Temperature-density diagram (T- ρ) using Weeks, Chandler and Anderson (WCA) perturbation scheme for L-J fluid has been obtained. Formation free energy as a function of size and supersaturation ratio, density profile of the nucleating droplet, nucleation barrier and critical cluster size as a function of supersaturation ratio and finally the comparison of CNT, MCNT and DFT have been presented in this chapter.

The methodology is then applied to the vapor to liquid heterogeneous nucleation on flat solid surface [110] as presented in chapter 3. The liquid droplet on the flat solid surface at a given contact angle ($\theta_{\rm C}$) has been presented as spherical cap model. The well-known CNT has been also applied in the framework of the present DFT method for the same investigations. The effects of supersaturation of the vapor and the strength of the solid-fluid interaction on the nucleation barrier have been investigated for Lennard-Jones fluid with 12-6 fluid-fluid and 9-3 solid-fluid interaction model. The shape, density profile and the free energy of formation of droplets of any arbitrary size have been obtained in this work. The

spinodal decomposition of vapor has been observed at higher supersaturation or at higher strength of the solid-fluid interaction.

The vapor to liquid nucleation phenomena discussed in the last two chapters 2 and 3 however, are particular cases of the phenomena. The possibility of a more general situation viz. the heterogeneous nucleation on a spherical solid surface which can also be called seed mediated nucleation [111] has been discussed in chapter 4 where, in addition to the solidfluid interaction energy, the effect of the size of the seed has also been examined. The scheme of the work is similar to the methodology described in chapters 2 and 3. A double spherical cap idea has been proposed to model the liquid droplet on the spherically curved (convex) solid surface and solid-fluid interaction for such solid (spherical)-liquid system has been derived. The problem has been investigated by applying CNT as well and the outcome of both the theories (DFT and CNT) has been compared with the results of earlier proposed theories. The shape (i.e. contact angle) and formation free energy of droplets of any arbitrary size have been optimized in this work. The change of the shape (optimized) with the variation of the size of the liquid droplet as well as with the size of the solid substrate have been observed, which predicts the shape-size relationship in the course of vapor to liquid heterogeneous nucleation on a spherical solid substrate of any particular size. The spinodal decomposition of vapor has been also observed at higher strength of the solid-fluid interaction. The results have been compared with the results of the conventional CNT.

Since interfacial properties of fluids are inherently associated with (and also influence) the phenomena of nucleation, it is relevant to formulate a simple analytical theory to investigate the properties of interfacial phenomena in general. A new scheme of obtaining the interfacial properties of a planar interface by adopting the density functional formalism of

van der Waals and Cahn and Hilliard for the interface has been proposed in chapter 5. A double well type Helmholtz free energy density functional model and a slowly varying model density profile have been proposed here. The methodology has been used for the calculation of surface tension of different real fluids such as water, heavy water as well as argon [112] over a wide range of temperature (from the triple point to the critical point), the input being only the known value of surface tension at the triple point. A very good agreement between the calculated and experimental values is observed. The result near the critical point obtained in this work is $\gamma_{\infty} \sim (Tc - T)^{3/2}$ which is identical with the prediction of the mean field theory.

The above formulation is then generalized to obtain the size-dependent properties of interfacial phenomena [**113**] which have been presented in chapter 6. The size-dependent surface tension is very much significant in nucleation phenomena and can improve the result of CNT by replacing (γ_{∞}) by the size dependent surface tension (γ_R) in the bulk interfacial energy term. The various size-dependent interfacial properties such as surface tension, density profile, thickness of the interface and also the size-dependent temperature-density (T- ρ) diagram, obtained analytically have been presented in this chapter.

The summary and conclusions of the work reported in this thesis have been given in chapter 7. The drawback and limitations have also been discussed. The scope of the application of the present proposed methodology to other different kinds of systems and phenomena (such as liquid to solid transition, precipitation etc.) have been pointed out.

CHAPTER 2

Vapor to liquid homogeneous nucleation of Lennard-Jones fluids

2.1 Introduction.

The understanding of the nucleation phenomenon is of importance in a number of areas of research in chemistry, physics, material science and allied subjects [2]. This phenomenon was first treated by Gibbs by applying thermodynamics and thereafter the theory was further developed by Becker, Doring, Volmar, Farkas, and Zeldovich for the study of homogeneous nucleation from vapor to liquid phase which has been traditionally referred to as the classical nucleation theory (CNT) [3-6]. The CNT assumes the bulk density approximation for the small nucleated droplet and also the surface free energy to be the same as that of the planar interface at coexistence at a given temperature. But during nucleation, a tiny liquid drop (spherical) is surrounded by supersaturated vapor (i.e., there is a spherical interface between the liquid and supersaturated vapor) and hence the interfacial energy should correspond to the supersaturated vapor-liquid spherical interface rather than liquid-vapor equilibrium state with planar interface which is used in CNT. The CNT has been simple because of these two approximations but a considerable error in the calculation of nucleation barrier height and hence also in the nucleation rate has been introduced. Attempts have been made to overcome this problem by proposing various theoretical approaches bypassing these approximations. The widely used DFT for this purpose was developed by Oxtoby and co-workers [13-18] and later many DFT approaches have been proposed [19-23]. There are also semiphenomenological [24] and phenomenological [25-27] approaches which have been developed for this purpose. Many other investigations using simulation techniques [29-31]

have also been successful in predicting the nucleation in the context of vapor to liquid phase transition. It is interesting to have a theory which deals with the microscopic nature of the fluid and also can provide a simple scheme for calculating the properties of vapor to liquid nucleation phenomena.

In the present chapter DFT with square gradient approximation along the lines of van der Waals and Cahn and Hilliard **[81, 108]** has been used to solve the problem analytically with the use of a diffuse interface model to represent the density instead of a sharp interface considered in CNT and the actual density profile of the drop is obtained through variational minimization of the free energy functional. Thus, all the approximations in CNT have been dropped in this work. The theory is applied to the Lennard-Jones (L-J) fluid and the supersaturation is calculated by constructing the phase diagram of the L-J fluid. An analytical expression for the free energy of formation of the droplet of any arbitrary size has been derived. The sharp interface limit of this expression results into CNT but with a modification of the surface tension term which is now supersaturation dependent. This modification leads to better result than CNT in barrier height calculation and is referred to here as the modified classical nucleation theory (MCNT).

2.2. Classical nucleation theory (CNT)

The main features of the conventional CNT is the assumption of a sharp boundary between the liquid drop and vapor with a well-defined radius R and the density within the drop is same as the bulk liquid density. The model thus consists of two bulk fluids (liquid and vapor) on two sides of a sharp and planar interface (**Fig.2.1**). The fluid density profile $\rho(r)$ across the interface is thus given by

$$\rho(r) = \rho_L \quad \text{for } 0 \le r \le R \tag{2.1a}$$

and

$$\rho(r) = \rho_V \quad \text{for } r > R \quad , \tag{2.1b}$$

where ρ_L and ρ_V are the densities of the bulk liquid and supersaturated vapor respectively. Here the CNT has been expressed within the framework of DFT with the use of a sharp density profile (Eq.2.1) and due to which the Helmholtz free energy of the final state, i.e. a nucleated liquid droplet of radius *R* surrounded by the vapor of the same component, is expressed as

$$F_f = 4\pi \int_0^R f(\rho_L) r^2 dr + 4\pi \int_R^\infty f(\rho_V) r^2 dr + 4\pi R^2 \gamma_\infty$$
(2.2)

where $f(\rho_L)$ and $f(\rho_V)$ are the Helmholtz free energy density of the bulk liquid and bulk vapor phase respectively and γ_{∞} is the interfacial energy (surface tension) of a planar interface at coexistence. The Helmholtz free energy density can be written as, $f = \rho \mu - P$, where P and μ denote respectively the pressure and chemical potential of the fluid of interest. Equation (2.2) can thus be written as

$$F_{f} = 4\pi \int_{0}^{R} (\mu_{L}\rho_{L} - P_{L})r^{2}dr + 4\pi \int_{R}^{\infty} (\mu_{V}\rho_{V} - P_{V})r^{2}dr + 4\pi R^{2}\gamma_{\infty}$$
(2.3)

which, on using the relations $4\pi \int_{0}^{R} r^2 dr = \frac{4\pi}{3} R^3 = V_L$ and $4\pi \int_{R}^{\infty} r^2 dr = V_V$, where V_L

and V_V are the volume of liquid drop of radius *R* and the volume of vapor phase respectively, can be rewritten as

$$F_{f} = V_{L}\rho_{L}\mu_{L} - P_{L}V_{L} + V_{V}\rho_{V}\mu_{V} - P_{V}V_{V} + 4\pi R^{2}\gamma_{\infty} .$$
(2.4)

Here μ_L and P_L denote the chemical potential and pressure for the liquid phase while μ_V and P_V denote the same for the vapor phase.

The corresponding equation in terms of the Gibbs free energy (*G*) can also be written by using the relation G = F + PV and the Gibbs free energy of the final phase is thus given by

$$G_f = V_L \rho_L \mu_L + V_V \rho_V \mu_V + 4\pi R^2 \gamma_\infty \quad . \tag{2.5}$$

The total number of monomers (fluid particles), N can be written as $N = \int \rho(r) d\mathbf{r} = \rho_L V_L + \rho_V V_V.$

The Gibbs free energy of the initial uniform vapor phase (G_i) is thus given by

$$G_i = N\mu_V = V_L \rho_L \mu_V + V_V \rho_V \mu_V.$$
(2.6)

Hence the Gibbs free energy of formation of a droplet of radius *R*, within the framework of CNT, is given by

$$\Delta G_R(CNT) = -\left(\frac{4\pi}{3}\right) R^3 \rho_L \Delta \mu + 4\pi R^2 \gamma_{\infty}$$
(2.7)

where $\Delta \mu = \mu_V - \mu_L$. CNT uses the ideal gas equation to obtain $\Delta \mu$ so that $\Delta \mu = \mu_{V} - \mu_L = k_B T \ln(S)$, where $S = \rho_V / \rho_V^0$ is called supersaturation ratio or simply the supersaturation, with ρ_V as the density of the supersaturated vapor and ρ_V^0 as the vapor density at liquid-vapor coexistence.

The term $(4\pi/3) R^3 \rho_L \Delta \mu$ in Eq. (2.7) represents the volume energy of nucleation whereas the term $4\pi R^2 \gamma_{\infty}$ stands for the surface energy. Here, the volume energy term is negative and the surface energy term is positive, but since the surface to volume ratio is high at the beginning of nucleation when the drop size is very small, the free energy of formation of the droplet is positive and increases initially with size, passes through a maximum and then decreases. The maximum in the formation free energy determines the nucleation barrier and the cluster with this maximum free energy is called the critical cluster. The radius of the critical cluster, $R_{\rm C}$ as

obtained from Eq. (2.7) through maximaisation of the free energy with respect to R is given by $R_C = 2 \gamma_{\infty/} (\rho_L \Delta \mu)$ and the nucleation barrier, ΔG^*_{CNT} is given by

$$\Delta G^*_{CNT} = \frac{16\pi\gamma_{\infty}^3}{3(k_B T \rho_L \ln(S))^2} \quad .$$
 (2.8)

The free energy barrier to nucleation as obtained from Eq. (2.8) is then used in the transition state theory to calculate the nucleation rate, *J*, as given by

$$J = A \exp\left(\frac{-\Delta G^*_{CNT}}{k_B T}\right),$$
(2.9)

where A is the preexponential factor, the derivation of which has been discussed elsewhere [5].

As mentioned earlier (chapter I), the interfacial energy (γ_{∞}) used in CNT is the interfacial energy obtained at coexistence condition for the bulk system and therefore it does not depend on the supersaturation, *S*. The barrier height, predicted by Eq. (2.8) therefore vary incorrectly with the variation of supersaturation and never vanishes at finite supersaturation, i.e, no spinodal decomposition can be predicted at finite supersaturation, within the framework of this theory.

2.3 Modeling of the density profile

A continuous density profile for the one component spherical liquid droplet suspended in the supersaturated vapor phase has been modeled instead of the step like profile as used in CNT. A parameter has been used in the density expression which is a measure of the degree of diffuseness and is determined by minimizing the free energy of formation of the droplet of any size, with respect to the variation of this parameter. The density profile described by the proposed model, is given by

$$\rho(r) = \rho_L - \frac{\left(\rho_L - \rho_V\right)}{2} \exp(a(r - R_{\rm av})) , \text{ for } 0 \le r \le R_{\rm av}$$
(2.10a)

and

$$\rho(r) = \rho_V + \frac{\left(\rho_L - \rho_V\right)}{2} \exp(-a(r - R_{av})) , \text{ for } r > R_{av}$$
(2.10b)

corresponding to the final inhomogeneous phase. Here, ρ_V is the bulk density of the initial homogeneous supersaturated vapor phase and ρ_L is the bulk density of the liquid phase at coexistence and R_{av} is the distance from the center of the drop where the density is the average of the bulk liquid and vapor densities. In **Fig.2.1**, the density profile for this work is shown for specific value of the parameter a = 0.5 and $R_{av} = 5$. Thus, the density profile that has been assumed here is a continuous function of r and the expression for $\rho(r)$ and its first derivative with respect to r at $r = R_{av}$, as obtained from either of the Eqs.(2.10), are given respectively by

$$\rho(r) = \frac{\left(\rho_L + \rho_V\right)}{2} \qquad \text{at } r = R_{av} \qquad (2.11a)$$

and

$$\frac{d\rho(r)}{dr} = -\frac{a(\rho_L - \rho_V)}{2} \quad \text{at } r = R_{av} \,. \tag{2.11b}$$

Clearly an inhomogeneous density profile is obtained (instead of the bulk density value) for a drop of any arbitrary size. The relation between R_{av} and the radius R of the corresponding sharp interface droplet (as used in CNT) which is also called radius of equimolar dividing surface or equimolar radius, can be obtained from the conservation of density normalization, as given by

$$\int_{0}^{\infty} \rho(r)r^{2}dr = \int_{0}^{R} \rho_{L}r^{2}dr + \int_{R}^{\infty} \rho_{V}r^{2}dr .$$
(2.12)

For the given density profile $\rho(r)$ of Eqs. (2.10), the expression for R is given by

$$R = \left(3\left(\frac{2R_{\rm av}}{a^2} + \frac{\exp(-aR_{\rm av})}{a^3}\right) + R_{\rm av}^{-3}\right)^{\frac{1}{3}}.$$
(2.13)

This equimolar radius R, which is thus determined by the density profile, is considered here to be a measure of size of the droplet.



Fig.2.1. Density profile $\rho(r)$ of a liquid droplet. Solid line representing a model considered in CNT and dashed line is for the model used in the present DFT work with R_{av} = 5 and an arbitrary value of a = 0.5. Reduced units are used for the plot.

2.4 Density functional theory for vapor to liquid homogeneous nucleation

The Helmholtz free energy of the final phase of the nonuniform density i.e. liquid droplet suspended in the bulk of the supersaturated vapor (one component system) can be expressed by using DFT with square gradient approximation [48, 81] as

$$F_f = \int f(\rho(r))d\mathbf{r} + \frac{1}{2}K\int (\nabla\rho(r))^2 d\mathbf{r}, \qquad (2.14)$$

where $f(\rho(r))$ in the first term, is the local Helmholtz free energy density and the second term represents the square gradient correction. Equation (2.14) can be rewritten as

$$F_{f} = 4\pi \int_{0}^{R_{av}} f(\rho(r)) r^{2} dr + 4\pi K \int_{0}^{R_{av}} (\nabla \rho(r))^{2} r^{2} dr + 4\pi K \int_{R_{av}}^{\infty} f(\rho(r)) r^{2} dr + 4\pi K \int_{R_{av}}^{\infty} (\nabla \rho(r))^{2} r^{2} dr$$
(2.15)

The free energy density functional contribution given by the first term of Eq.(2.14) is unknown in general for an inhomogeneous density distribution. However, it is often known for some model system at homogeneous density and this knowledge can be used for evaluating this quantity for inhomogeneous density through some suitable weighted density approximation or a perturbative approach, since local density approximation has been known to be unsuitable for such systems.

A perturbative approach has been proposed to express $f(\rho(r))$ as Taylor series expansion with respect to the uniform fluid, retaining for simplicity terms up to first order, as

$$f(\rho(r)) = f(\rho(r))_{\rho(r)=\rho_U} + \left[\frac{df(\rho(r))}{d\rho(r)}\right]_{\rho(r)=\rho_U} (\rho(r)-\rho_U)$$
(2.16)

where the subscript *U* stands for the uniform fluid and therefore, one has $\rho_U = \rho_L$ for $r \le R_{av}$ and $\rho_U = \rho_V$ for $r > R_{av}$.

Using Eqs. (2.10) and (2.16), Eq.(2.15) can be written as

$$F_{f} = 4\pi \int_{0}^{R_{av}} f_{L}r^{2}dr - 2\pi\mu_{L}\Delta\rho \int_{0}^{R_{av}} \exp(a(r - R_{av}))r^{2}dr$$
$$+\pi(\Delta\rho)^{2}a^{2}K \int_{0}^{R_{av}} \exp(2a(r - R_{av}))r^{2}dr$$

F + PV, as

$$+4\pi \int_{R_{av}}^{\infty} f_V r^2 dr + 2\pi \mu_V \Delta \rho \int_{R_{av}}^{\infty} \exp(-a(r-R_{av})) r^2 dr +\pi (\Delta \rho)^2 a^2 K \int_{R_{av}}^{\infty} \exp(-2a(r-R_{av})) r^2 dr , \qquad (2.17)$$

where $f_L = f(\rho_L)$, $f_V = f(\rho_V)$ and $\Delta \rho = \rho_L - \rho_V$.

Using the relation, $f = \rho \mu - P$, Eq.(2.17) can be further rewritten as

$$F_{f} = \rho_{L}V_{L}\mu_{L} - P_{L}V_{L} - 2\pi\mu_{L}\Delta\rho I_{1}(a, R_{av}) + \pi(\Delta\rho)^{2}a^{2}KI_{1}(2a, R_{av}) + \rho_{V}V_{V}\mu_{V} - P_{V}V_{V} + 2\pi\mu_{V}\Delta\rho I_{2}(a, R_{av}) + \pi(\Delta\rho)^{2}a^{2}KI_{2}(2a, R_{av}),$$
(2.18)

where the integrals denoted by I_1 and I_2 are given by

$$I_1(a, R_{av}) = \int_0^{R_{av}} \exp(a(r - R_{av}))r^2 dr = \frac{R_{av}^2}{a} - \frac{2R_{av}}{a^2} + \frac{2}{a^3} - \frac{2\exp(-aR_{av})}{a^3}$$
$$I_2(a, R_{av}) = \int_{R_{av}}^\infty \exp(-a(r - R_{av}))r^2 dr = \frac{R_{av}^2}{a} + \frac{2R_{av}}{a^2} + \frac{2}{a^3}.$$

Equation (2.18) can be expressed in terms of the Gibbs free energy by using the relation G =

$$G_{f} = F_{f} + P_{L}V_{L} + P_{V}V_{V}$$

= $\rho_{L}V_{L}\mu_{L} - 2\pi\mu_{L}\Delta\rho I_{1}(a, R_{av}) + \pi(\Delta\rho)^{2}a^{2}KI_{1}(2a, R_{av})$
+ $\rho_{V}V_{V}\mu_{V} + 2\pi\mu_{V}\Delta\rho I_{2}(a, R_{av}) + \pi(\Delta\rho)^{2}a^{2}KI_{2}(2a, R_{av}).$ (2.19)

Since the total number of monomers (individual fluid particles), *N*, is conserved, one has $N = \int \rho(r) d\mathbf{r} = \text{constant}$. Thus, the Gibbs free energy of the initial uniform vapor phase can be written as $G_i = N \mu_V$, i.e.

$$G_i = \mu_V \int \rho(r) d\mathbf{r} \quad , \tag{2.20}$$

which on using Eq. (2.10) leads to the expression

$$G_{i} = 4\pi\mu_{V} \int_{0}^{R_{av}} \rho_{L}r^{2}dr - 2\pi\mu_{V}\Delta\rho \int_{0}^{R_{av}} \exp(a(r-R_{av}))r^{2}dr + 4\pi\mu_{V} \int_{R_{av}}^{\infty} \rho_{V}r^{2}dr + 2\pi\mu_{V}\Delta\rho \int_{R_{av}}^{\infty} \exp(-a(r-R_{av}))r^{2}dr, \qquad (2.21)$$

that can be further written as

$$G_{i} = \rho_{L} V_{L} \mu_{V} - 2\pi \mu_{V} \Delta \rho I_{1}(a, R_{av}) + \rho_{V} V_{V} \mu_{V} + 2\pi \mu_{V} \Delta \rho I_{2}(a, R_{av}) .$$
(2.22)

The difference in free energy between the final and initial states, $\Delta G = G_f - G_i$, is thus given by

$$\Delta G = -\left(\frac{4\pi}{3}\right) R_{av}^{3} \rho_L \Delta \mu + 2\pi \Delta \mu \Delta \rho I_1(a, R_{av}) + \pi K \Delta \rho^2 a^2 (I_1(2a, R_{av}) + I_2(2a, R_{av})), \qquad (2.23)$$

which, on minimization with respect to the parameter a, provides ΔG_R , the free energy of formation of a fluid droplet of radius R. The final expression of ΔG_R is given by

$$\Delta G_{R} = -\left(\frac{4\pi}{3}\right) R_{av}^{3} \rho_{L} \Delta \mu$$

$$+ 2\pi \Delta \mu \Delta \rho \left[\frac{R_{av}^{2}}{a_{0}} - \frac{2R_{av}}{a_{0}^{2}} + \frac{2}{a_{0}^{3}} - \frac{2\exp(-a_{0}R_{av})}{a_{0}^{3}}\right]$$

$$+ \frac{\pi}{2} K \Delta \rho^{2} a_{0}^{2} \left[\frac{2R_{av}^{2}}{a_{0}} + \frac{1}{a_{0}^{3}} - \frac{1}{2a_{0}^{3}} \exp(-2a_{0}R_{av})\right], \qquad (2.24)$$

where a_0 is the value of the parameter a, for which ΔG as given by Eq.(2.23), is minimum.

Here $\Delta \mu = \mu_V - \mu_L$ and $\Delta \rho = \rho_L - \rho_V$, with ρ_L , representing the equilibrium bulk density of liquid at a given temperature and ρ_V denoting the density of supersaturated vapor i.e, $\rho_V = \rho_V^0 S$, where *S* is the supersaturation. The liquid and vapor densities at coexistence, ρ_L and ρ_V^0 are

obtained from the phase diagram. The coefficient of the square gradient term, K, in Eq. (2.14) can be approximately written as **[114,115]**

$$K = -\left(\frac{1}{12}\right) \int \Phi(r) r^2 d\mathbf{r}$$
(2.25)

where $\Phi(r)$ denotes the attractive potential, and for the L-J fluid system, one has

$$\Phi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right] , \qquad (2.26)$$

which is attractive in the range of $r \geq \sigma$.

Equations (2.10)-(2.24) thus provide a scheme for obtaining the free energy of formation as the difference between the droplet and initial supersaturated vapor phase as a function of the droplet size at any chosen temperature.

2.5 Modified classical nucleation theory (MCNT)

The value of interfacial energy used in CNT is the value, obtained at coexistence condition of vapor and liquid bulk system though the vapor is supersaturated in the process of vapor to liquid nucleation (already mentioned in section 2.1). In the present work, the supersaturation term has been introduced in the expression of surface tension by considering a large limit of the parameter a (present in the density profile see Eq.(2.10)) in the result obtained by the DFT (Eq.(2.23), and obtained another simplified version of the theory, which we call MCNT. The density profile will approach the sharp interface limit (like CNT) for large value of a, and one can neglect (1/a) terms in Eqs. (2.13) and (2.23), and have the expression for the free energy difference given by

$$\Delta G_R = -\left(\frac{4\pi}{3}\right) R^3 \rho_L \Delta \mu + 4\pi R^2 \left(\frac{K(\Delta \rho)^2 a}{4}\right),\tag{2.27}$$

which is identical in form with the expression of CNT (Eq. (2.7)), except that the bracketed quantity in the last term which can be identified as the interfacial energy is not constant but is supersaturation dependent, viz.

$$\gamma = \frac{K(\Delta \rho)^2 a}{4}.$$
(2.28)

In CNT, the surface tension used is the one at coexistence when supersaturation *S*=1 and thus $\Delta \rho = \rho_L - \rho_V^{\ 0} = \Delta \rho_0$, which indicates that on substituting $\Delta \rho_0$ in Eq. (2.28), one has $\gamma = \gamma_\infty$, viz.

$$\gamma_{\infty} = \frac{K(\Delta \rho_0)^2 a}{4} \tag{2.29}$$

From Eqs. (2.28) and (2.29), one obtains the relation

$$\gamma_{MCNT} = \gamma_{\infty} \frac{(\Delta \rho)^2}{(\Delta \rho_0)^2} \quad . \tag{2.30}$$

Therefore a supersaturation dependence of surface tension has been obtained though it has a size-dependence as well. The investigation of a proper size-dependence of the surface tension in presence of supersaturation is an interesting problem in itself.

The expression for γ given by Eq.(2.30) therefore can be used to obtain nucleation free energy in the form of MCNT given by

$$\Delta G_R(MCNT) = -\left(\frac{4\pi}{3}\right) R^3 \rho_L \Delta \mu + 4\pi R^2 \gamma_{MCNT} . \qquad (2.31)$$

An analogous modification was earlier arrived at by Lutsko [21] through a different approach.
The free energy barrier obtained From Eq. (2.31), is expressed as

$$\Delta G^*_{MCNT} = \frac{16\pi (\gamma_{MCNT})^3}{3(k_B T \rho_L \ln(S))^2} .$$
(2.32)

These two equations (2.31) and (2.32) are the results corresponding to MCNT and can be compared with Eqs. (2.7) and (2.8) of CNT.

2.6 Calculation of temperature-density diagram (phase diagram) of L-J fluid

The vapor to liquid bulk phase transition followed by microscopic nucleation or spinodal decomposition occurs when the vapor is supersaturated. The height of the nucleation barrier is controlled by the extent of supersaturation, which may be vanished at very high value of supersaturation when the densities of the vapor enter to the spinodal region (see **Fig.2**). It has been seen that (earlier sections of chapter 2) the knowledge of supersaturation ratio is essential to calculate the nucleation free energy and therefore one has to calculate the coexistence densities temperature-density diagram). At a given temperature the coexistence bulk densities of liquid and vapor (ρ_L and ρ_V^0) are obtained by solving the following simultaneous equations involving equalization of the pressure and chemical potential of the two phases,viz.

$$p_L(\rho_L) = p_V(\rho_V^0), \ \mu_L(\rho_L) = \mu_V(\rho_V^0), \ p = p_h - \frac{1}{2}\alpha\rho^2, \ \mu = \mu_h - \alpha\rho, \ \text{with} \ \alpha = -\int \Phi(r) \ \mathrm{d}\mathbf{r}.$$
 (2.33)

Here, p_h and μ_h are the hard sphere pressure and chemical potential represented, for example by Carnahan-Starling form of the equation of state [**116**], with $p_h = \rho k_B T (1 + \eta + \eta^2 - \eta^3)/(1 - \eta)^3$, where $\eta = (\pi/6)\rho d^3$ is the packing fraction. The chemical potential is obtained by solving the equation $(\partial p_h/\partial \rho) = \rho (\partial \mu_h/\partial \rho)$, which gives $\mu_h = k_B T [ln \eta + (8\eta - 9\eta^2 + 3\eta^3)/(1 - \eta)^3]$. Thus, the phase diagram can easily be obtained by plotting temperature vs. density of both the phases, obtained from the solution of Eq. (2.33). The proposed formalism is implemented

here by considering application to a model L-J system, whose interatomic potential (see Eq.(2.26)) is given by $\Phi_{L,J}(r) = 4\varepsilon [(\sigma/r)^{1/2} \cdot (\sigma/r)^6]$ with ε and σ as the characteristic energy and length parameters of the L-J system. Hence for convenience, these two parameters are used to express the temperature and density in reduced units, viz., the reduced temperature $T^* = k_B T / \varepsilon$, and the reduced density $\rho^* = \rho \sigma^3$. For the calculation of temperature-density diagram, which provides the ρ_L and ρ_V^0 values at any given temperature, the conventional Weeks, Chandler and Anderson (WCA) perturbation scheme has been employed, where the repulsive term, $\Phi_I(r)^{WCA} = 0$ for $r \ge r_{min}$ and $\Phi_I(r)^{WCA} = -\varepsilon$ for $r < r_{min}$, and the attractive term, $\Phi_2(r)^{WCA} = \Phi_{L,J}(r)$ is minimum. The repulsive term $\Phi_I(r)^{WCA}$ is replaced by that of an equivalent system of hard sphere with temperature-dependent diameter $d(T) = \sigma (a_1T + b)/(a_2T + a_3)$, with $a_I = 0.56165 k_B/\varepsilon$, $a_2 = 0.60899 k_B/\varepsilon$, $a_3 = 0.92868 k_B/\varepsilon$ and b=0.9718.



Fig. 2.2. Vapor-liquid coexistence phase diagram and spinodal curve of L-J fluid. The triangles are for coexistence and the squares are for spinodal curve.

At a given temperature, the hard sphere term in pressure and chemical potential expression is obtained from the repulsive term of the WCA perturbation scheme and hence from the temperature-dependent diameter mentioned above. The attractive part in pressure and chemical potential of L-J fluid denoted by α and is obtained from the attractive term of the WCA perturbation scheme. The spinodal curve has been obtained by solving the equation

$$\frac{\partial p}{\partial \rho} = 0. \tag{2.34}$$

The calculated phase diagram for the L-J system in reduced unit is shown in Fig.2.2.

2.7 Results and discussions

As already mentioned, the formation free energy at a given supersaturation and for a given size can be obtained by minimizing Eq.(2.24) with respect to the parameter *a* which also yields the optimized density profile. The parameter *a* for a given size *R*, determines the diffuseness of the density, with larger *a* corresponding to sharper density profile. Here, the density of the small drop is not forced to be equal to the bulk liquid density (even at the center), as is used in CNT and the density of the drop, which is inhomogeneous, can take any value within the range of bulk liquid to bulk vapor density so as to yield the minimum value for the formation free energy. The procedure is followed to calculate the various quantities of interest for L-J fluid system for different values of the system parameter. From the plot of the calculated (optimized) density profiles in **Fig.2.3**, it is observed that as the droplet size increases, the sharpness of density at the interface also increases and as its size decreases, the density even at the center of the drop becomes less than the bulk liquid density which is in agreement with observation in other earlier works **[13, 117]**.



Fig. 2.3. Density profiles of liquid drops of different sizes ($R^*=R/\sigma$) at T*=0.7 and S=4.0. Indicated as ρ_L^* denotes the value of bulk density of liquid.



Fig. 2.4. Formation free energy as a function of size at different Supersaturation (S) at $T^*=0.7$, as calculated using the present model.

The free energy of formation of various sized clusters has then been calculated at a given temperature for different supersaturation by evaluating Eq.(2.24) with optimized value of the parameter a in each case. This equation can be used for any size of the droplet although the evaluation is not needed beyond the critical size for calculating the nucleation rate. In **Fig.2.4**, free energy profiles at different supersaturations have been plotted. Both the critical size and the barrier height are found to decrease as the supersaturation increases. It is also interesting to note that for a given size, the optimized value of the parameter a increases slowly with supersaturation. Since the barrier height and its dependence on supersaturation plays a crucial role in the investigation of nucleation phenomena, it will be of interest to study the nature of this dependence in further details.



Fig. 2.5. Comparison of the calculated nucleation barrier vs vapor density at $T^*=0.67$ with simulation work reported by Oh and Zeng [**29**]. The squares correspond to results obtained from the present study and the circles refer to the Monte Carlo data from Ref. **29**.

Therefore, in **Fig.2.5**, we have plotted the barrier height as a function of the density of the supersaturated vapor phase for better insight into this aspect. It is found that the plot is almost linear in the supersaturation range investigated. For comparison, we have also included the Monte Carlo simulation results of Oh and Zeng **[29]**. It may be noted that the dependence of the present calculated nucleation barrier on density is very similar to that obtained from simulation, although the calculated results are consistently slightly ($\approx 4\%$) higher, which is in fact a very good agreement.

Another quantity of interest is the size of the critical cluster (liquid droplet) in nucleation. The cluster is associated with a continuously varying density profile $\rho(\mathbf{r})$ which is extended over a long distance and hence the definition of size is somewhat nonunique, and is usually based on a partitioning of the space into the liquid droplet domain and vapor domain. In order to obtain the number of particles belonging to the liquid droplet, one has to integrate the density profile up to a certain suitable distance R_N , which is chosen here such that the integral of the decaying density profile equals the integral of a step like density with $\rho=\rho(0)$ for $r\leq R_N$ and $\rho=\rho_V$ for $r>R_N$. The number (N^*) of particles belonging to the critical liquid droplet, as obtained from the present density profile using this consideration, are shown in **Figs. 2.6(a)** and **2.6(b)** and are compared with the results of simulation by Oh and Zeng [**29**] and other DFT (both mean-field and non-mean-field) [**23**] as well as simulation results reported earlier. It is again clear that the results obtained from the present theory compare quite well with simulation and other DFT results.



Fig. 2.6. (a) Plot of critical size vs vapor density at reduced temperature $T^*=0.67$. The squares denote present DFT results and the circles refer to the Monte Carlo simulation data of Oh and Zeng [**29**]. (b) Plot of critical size vs Supersaturation at reduced temperature $T^*=0.7$. The squares denote present DFT results, circles and triangles refer respectively to mean-field and non mean-field DFT results [**23**], and open circles and open triangles denote simulation results [**31**], as reported in Ref.[**23**].

It will also be of interest to compare the present results with the prediction of CNT as well as the modified version MCNT, which is proposed here. Therefore, we have plotted, in **Fig. 2.7**, the free energy profile calculated based on the present DFT prescription as well as MCNT and have compared the results with those of CNT. From the plots, it is clear that the present DFT results show much lower energy barrier and larger critical size as compared to CNT. It is gratifying to note that the simulation results of Oh and Zeng [**29**], when compared with the CNT prediction, also show the same trend.



Fig. 2.7. Formation free energy vs particle size at T*=0.7 and at S=10 using different theories. The γ_{∞} value used for both CNT and MCNT based calculation is 1.24 ϵ/σ^2 (from Zeng and Oxtoby [14]).

This is clearly a consequence of the fact that two of the major approximations used in CNT are avoided here and thus the result for free energy barrier is expectedly much better than that obtained from CNT. In CNT, the effect of supersaturation comes through the

volume term only and not the surface term whereas in the present work, the supersaturation affects both the terms. Thus, the effect of supersaturation is more pronounced here than in CNT. The modified classical nucleation theory as proposed in Eq. (2.31) leads to lowering of the free energy barrier but the result is not as good as the one predicted by density functional theory with our model. The MCNT, however, considers the surface tension in a more realistic way because here the surface tension is not calculated at coexistence (as in CNT) but at supersaturated state and hence the supersaturation affects the surface term as well.

According to CNT, the free energy barrier as given by Eq.(2.8) is zero only at infinite supersaturation which is a totally unphysical situation but in MCNT, the barrier (Eq.(2.32)) is zero at finite supersaturation but still it is incorrect. But if we don't consider the extreme spinodal condition and concentrate at lower supersaturation, then MCNT results are better than CNT without loss of the simplicity of calculation.

2.8. Conclusion

A new theoretical approach for vapor to liquid homogeneous nucleation using DFT with square gradient approximation for the free energy functional has been presented, which is rather common for the study of nonuniform fluids, interfaces and spinodal decomposition. The analytical model for the density profile and expressing the free energy at any density by Taylor expansion with respect to the bulk density have made it simpler to perform the evaluation analytically. The procedure of variational minimization of the free energy functional using a parametric expression for the density profile has been advantageous in comparison to the numerical solution of the corresponding Euler equation. Besides leading to analytical expressions, the variational approach is shown to be particularly useful when the free energy functional used is rather approximate, since the boundary conditions or physical

features of the interfacial density can be easily built in through a proper choice of the density expression. Thus, the optimized density inside the nucleated small droplet is predicted to be lower than the bulk liquid in consistency with the other earlier works. Also, the calculated results demonstrate that the supersaturation effect is much better and realistically represented as compared to CNT, in good agreement with simulation and other results. The simple MCNT prescription is shown to predict the spinodal condition at finite supersaturation and also a supersaturation dependence in the surface tension, in contrast to CNT.

CHAPTER 3

Vapor to liquid heterogeneous nucleation of Lennard-Jones fluids on flat surface of solid substrate

3.1. Introduction.

The theory for the phenomena of nucleation was first introduced by Gibbs [3], developed further by Becker, Doring , Volmar , Farkas, and later modified by Zeldovich for the study of homogeneous nucleation from vapor to liquid phase. These approaches already discussed in Chapters 1 and 2, form the basis of what is known as the classical nucleation theory (CNT) [4-7]. As we know, nucleation involves a process of barrier crossing phenomena (nucleation barrier), and therefore, an understanding of the nucleation barrier and the effect of various parameters on this barrier is very important and needs to be explored. The degree of supersaturation is the only parameter that can affect the nucleation process, when the system is homogeneous. But most of the natural systems are heterogeneous, where many other components (like impurities, surface of the wall etc.) are also present in addition to the main component of interest. Therefore, apart from the supersaturation, the presence of such foreign substances can also affect the nucleation barrier and thereby control the condensation rate. The nucleation in such case can begin on the surface of a substrate and the nucleation barrier, critical size and shape of the nucleus at a given temperature and supersaturation will thus be governed by the shape and size of the substrate and the strength of substrate- fluid interaction.

As was the case for homogeneous nucleation, the first attempt to understand heterogeneous nucleation phenomena also was through the classical theory of heterogeneous nucleation [8-12] based on those approximations (see chapter 2) as used in CNT of

homogeneous nucleation. Since those approximations have been found to lead to significant error in calculating the nucleation properties (i.e. nucleation barrier, critical size etc), several approaches have been developed within the framework of density functional theory (DFT) [**32-37**] and several investigations have been carried out using molecular simulation [**38-46**] based techniques to describe the various aspects of the phenomena of heterogeneous nucleation.

In the present chapter, the effect of a flat solid substrate on the properties of vapor to liquid nucleation (i.e. heterogeneous nucleation on the flat surface of a solid substrate) has been discussed. Along the lines of treatment for homogeneous nucleation, a density functional theory with square gradient approximation for the free energy functional has been proposed here to investigate the heterogeneous nucleation of vapor to liquid phase transition of Lennard-Jones (L-J) fluid on a flat solid surface [110]. The density profile and the local Helmholtz free energy density have been modeled in a way similar to that used for homogeneous nucleation [109]. The standard 9-3 interaction (which corresponds to L-J potential) energy between a fluid particle and the flat solid substrate (L-J system) has been used to incorporate the effect of flat solid surface on the free energy of the fluid. The free energy of formation of a given volume of a liquid drop on the solid surface has been minimized with respect to both the contact angle and the parameter present in the density profile. Therefore, the optimized shape, density profile and free energy of formation of a droplet of any given volume can be obtained. The strength of the wall-fluid interaction as well as the extent of supersaturation control the nucleation barrier significantly and also make it vanish (spinodal) at their large values. The CNT for such system has also been presented within the framework of the proposed DFT and the results have been compared with the results of DFT.

3.2 Spherical cap model for the liquid drop on the flat surface of a solid substrate

The liquid droplet placed on the flat surface of a solid substrate, which makes a contact angle with the surface, is considered for simplicity to be part of a sphere. This model, called a spherical cap, is shown in **Fig 3.1**, where the solid, liquid and vapor regions are denoted by 1, 2 and 3 respectively. As shown in the figure, in the present model the origin of the sphere is its center O', whereas the origin for defining the coordinates of the spherical cap is O (the center of the interface of the solid and liquid phase), which will be mainly used for the calculation in the present work. The radius of the sphere (i.e. the radius of curvature of the cap) is denoted by r_s and $\mathbf{R}(\theta)$ is the polar radial vector with respect to origin at O (distance of the droplet surface from O) which is a function of the polar angle θ . The contact angle between the liquid and the solid surface is θ_c . Since the origin (point O) of the spherical cap will be used for the calculation, it is essential to have an expression for $\mathbf{R}(\theta)$, which has been obtained here from simple geometrical consideration.

In **Fig 3.1**, P is an arbitrary point on the surface of the spherical cap. Due to the cylindrical symmetry the problem can be considered in two dimensions and therefore one can consider X and Z axis only.

$$OA = r_{s} \sin(\theta_{c}) ; OO' = r_{s} \cos(\theta_{c}) ; OB = r_{s} (1 - \cos(\theta_{c}))$$
(3.1)



Fig3.1 A liquid droplet (2), formed on a flat solid surface (1) with a contact angle θ_C , and surrounded by the vapor phase (3).

The X coordinate of the point P with respect to the two origins are $X_{SC} = R(\theta)$ sin(θ) and $X_S = r_S \sin(\theta')$, where the subscript S stands for spherical case, i.e. with respect to the origin at O' and SC denotes spherical cap, i.e. with respect to the origin at O. Since $X_{SC} = X_S$, one has

$$r_{s} \sin(\theta') = R(\theta) \sin(\theta)$$
 (3.2)

Analogously one has $Z_{SC} = R(\theta) \cos(\theta)$ and $Z_S = r_S \cos(\theta')$. Since $Z_S = Z_{SC} + O'O$, one obtains

$$R(\theta)\cos(\theta) + r_{s}\cos(\theta_{c}) = r_{s}\cos(\theta')$$
(3.3)

Equation (3.2) can be rewritten as

$$r_{S} \cos(\theta') = \sqrt{\left(r_{S}^{2} - R(\theta)^{2} \sin^{2}(\theta)\right)}$$
(3.4)

Using Eq.(3.4) in Eq.(3.3), one has $R(\theta) \cos(\theta) + r_S \cos(\theta_C) = (r_S^2 - R(\theta)^2 \sin^2(\theta))^{1/2}$, which on squaring and after some rearrangement, leads to the result

$$R(\theta)^2 + 2R(\theta)r_s\cos(\theta)\cos(\theta_c) - r_s^2\sin^2(\theta_c) = 0.$$
(3.5)

The solution of Eq.(3.5) for the variable $R(\theta)$ is given by

$$R(\theta) = -r_{S} \cos(\theta) \cos(\theta_{c}) + r_{S} \sqrt{\left(\cos^{2}(\theta) \cos^{2}(\theta_{c}) + \sin^{2}(\theta_{c})\right)}, \qquad (3.6)$$

which can be used to calculate the polar radius $R(\theta)$ as a function of the polar angle θ .

The volume of the spherical cap as obtained by using this expression of $R(\theta)$ is given by the expression

$$V = \int_{0}^{2\pi} d\Phi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{0}^{R(\theta)} r^{2} dr$$

$$= \frac{2\pi}{3} \int_{0}^{\frac{\pi}{2}} R^{3}(\theta) \sin(\theta) d\theta \quad .$$
(3.7)

Another expression for the volume of the spherical cap which is commonly employed, using the radius of the sphere as r_s , is

$$V = \frac{4\pi r_s^3}{3} \left(\frac{(\cos(\theta_c) - 1)^2 (\cos(\theta_c) + 2)}{4} \right).$$
(3.8)

Since the radius of the spherical cap for a given volume varies with the contact angle, the volume (and not the radius) is used as the size of the droplet in case of heterogeneous nucleation. In the present work, the radius (r_s), for a given volume (V) of the droplet on solid surface with contact angle (θ_c) can be obtained from Eq.(3.8) and will be used in Eq.(3.6) to

calculate $R(\theta)$. The calculated $R(\theta)$ for different values of the contact angle has been plotted in **Fig 3.2**.



Fig 3.2 Plot of $R(\theta)$ in 2-D for a given volume $V=10\sigma^3$ (σ is a parameter in the Lennard- Jones potential) at different values of the contact angle. Please note that only half of the droplet surface profile in the xz-plane is shown for convenience

3.3 Classical nucleation theory of vapor to liquid heterogeneous nucleation on a flat surface of solid substrate.

Heterogeneous vapor to liquid nucleation for the droplet formation on the planar surface of a solid substrate along the lines conventional CNT has been considered here. According to CNT, there is a sharp boundary (interface of the regions 2 and 3 in Fig. **3.1**) between the liquid drop (region 2 on the surface of the substrate 1) and vapor (region 3 covering the liquid drop 2) with a well-defined polar radius $\mathbf{R}(\theta)$, so that the density within the drop is same as the bulk liquid density and outside the drop, it is same as that of supersaturated vapor. The

fluid density profile $\rho(r, \theta)$ (see Fig. 3.3) in the present spherical cap model, is thus written as

$$\rho(r,\theta) = \rho_L \quad \text{for } 0 \le r \le R(\theta) \tag{3.9}$$

and

$$\rho(r,\theta) = \rho_v \quad \text{for} \quad r > R(\theta) \qquad , \tag{3.10}$$

for all values of θ ranging from 0 to $\pi/2$, where ρ_L and ρ_V are the densities of the bulk liquid and supersaturated vapor respectively.

The Helmholtz free energy of the final phase is expressed as

$$F_{f} = 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{0}^{R(\theta)} f\left(\rho_{L}\right) r^{2} dr + \int_{R(\theta)}^{\infty} f\left(\rho_{V}\right) r^{2} dr + \right] + 2\pi r_{S}^{2} (1 - \cos(\theta)) \gamma_{\infty}$$
$$+ 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{0}^{R(\theta)} \rho_{L} V_{sf}(z) r^{2} dr + \int_{R(\theta)}^{\infty} \rho_{V} V_{sf}(z) r^{2} dr \right] , \qquad (3.11)$$

where $f(\rho_L)$ and $f(\rho_V)$ in the first term (volume energy term) are the Helmholtz free energy density of the one-component bulk liquid and bulk vapor phase respectively, and γ_{∞} in the second term (vapour-liquid surface energy term) is the surface tension of the vapour-liquid planar interface at coexistence. The third term in Eq.(3.11) is the energy due to solid-fluid interaction, where $V_{sf}(z)$ is the interaction energy experienced by each fluid particle due to the solid substrate at a distance z from the surface of the solid plane and z can be replaced byz $= r \cos(\theta) + \sigma_W$ (where σ_W is the collision diameter between fluid and solid) in the present model. A standard 9-3 model for the L-J interaction potential between the solid wall and fluid particles has been used in this work.

The Helmholtz free energy density can be written as, $f = \rho \mu - P$, where P and μ denote respectively the pressure and chemical potential of the fluid of interest. Equation (3.11) can thus be written as

$$F_{f} = 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{0}^{R(\theta)} (\mu_{L}\rho_{L} - P_{L})r^{2}dr + \int_{R(\theta)}^{\infty} (\mu_{V}\rho_{V} - P_{V})r^{2}dr + \right] + 2\pi r_{S}^{2} (1 - \cos(\theta))\gamma_{\infty} + 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{0}^{R(\theta)} \rho_{L}V_{sf}(z)r^{2}dr + \int_{R(\theta)}^{\infty} \rho_{V}V_{sf}(z)r^{2}dr \right] .$$
(3.12)

Using the relations $2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{0}^{R(\theta)} r^2 dr = V_L$ and $2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R(\theta)}^{\infty} r^2 dr = V_V$ (see

Eq.(3.7)), where V_L and V_V are the volume of the liquid droplet on the solid substrate and the volume of vapor phase respectively, Eq.(3.12) can be rewritten as

$$F_{f} = V_{L}\rho_{L}\mu_{L} - P_{L}V_{L} + V_{V}\rho_{V}\mu_{V} - P_{V}V_{V} + 2\pi r_{S}^{2}(1 - \cos(\theta))\gamma_{\infty} + 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta)d\theta \left[\int_{0}^{R(\theta)} \rho_{L}V_{sf}(z)r^{2}dr + \int_{R(\theta)}^{\infty} \rho_{V}V_{sf}(z)r^{2}dr\right].$$
(3.13)

Here μ_L and P_L denote the chemical potential and pressure for the one-component liquid phase, while μ_V and P_V denote the same for the one-component vapor phase. One also has the relation $N = \int \rho(r, \theta) d\mathbf{r} = \rho_L V_L + \rho_V V_V$, where N denotes the total number of monomers (fluid particles).

The corresponding equation for the Gibbs free energy (*G*) can also be written, on using the relation G = F + PV. The Gibbs free energy of the final phase is thus given by

$$G_{f} = V_{L}\rho_{L}\mu_{L} + V_{V}\rho_{V}\mu_{V} + 2\pi r_{S}^{2}(1 - \cos(\theta))\gamma_{\infty} + 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta)d\theta \left[\int_{0}^{R(\theta)} \rho_{L}V_{sf}(z)r^{2}dr + \int_{R(\theta)}^{\infty} \rho_{V}V_{sf}(z)r^{2}dr\right] .$$
 (3.14)

The Gibbs free energy of the initial uniform vapor phase G_i , can similarly be expressed as the sum of the free energy of one-component vapor phase and the solid-fluid interaction experienced by all the vapor particles as the perturbative term. The initial Gibbs free energy G_i , is thus given by

$$G_{i} = V_{L}\rho_{L}\mu_{V} + V_{V}\rho_{V}\mu_{V} + 2\pi\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta \left[\int_{0}^{R(\theta)}\rho_{V}V_{sf}(z)r^{2}dr + \int_{R(\theta)}^{\infty}\rho_{V}V_{sf}(z)r^{2}dr\right],$$
(3.15)

which is written in a form analogous to the expression of G_f as given by Eq.(3.14). Hence, the Gibbs free energy of formation of a droplet of volume V_L on a solid planar surface, within the framework of CNT, is given by

$$\Delta G_{V_L}(\text{CNT}) = -V_L \rho_L \Delta \mu + 2\pi r_S^2 (1 - \cos(\theta)) \gamma_{\infty} + 2\pi \Delta \rho \int_0^{\frac{\pi}{2}} \sin(\theta) d\theta \int_0^{R(\theta)} V_{sf}(z) r^2 dr \quad , \qquad (3.16)$$

where $\Delta \mu = \mu_V - \mu_L$ and $\Delta \rho = \rho_L - \rho_V$. Within CNT, one uses the ideal gas equation to obtain $\Delta \mu$ so that $\Delta \mu = \mu_V - \mu_L = k_B T \ln(S)$, where *S* is the supersaturation ratio, $S = \rho_V / \rho_V^0$, with ρ_V and ρ_V^0 denoting the density of the supersaturated vapor and the vapor density at liquid-vapor coexistence respectively.

3.4 Modeling of the density profile for heterogeneous nucleation on a flat surface

The density profile model proposed for homogeneous nucleation (section 2.3 in chapter 2) has been implemented here with some modification related to the polar angle (θ) dependent distance of the boundary (R(θ)) from the center in the present case instead of a constant value of R in the case of homogeneous droplet model. The density profile for the final nonuniform state, as described by the proposed model, is given by

$$\rho(r,\theta) = \rho_L - \frac{\left(\rho_L - \rho_V\right)}{2} \exp\left[C\left(\frac{r}{R(\theta)_{av}} - 1\right)\right], \text{ for } 0 \le r \le R(\theta)_{av}$$
(3.17a)

and

$$\rho(r,\theta) = \rho_{V} + \frac{\left(\rho_{L} - \rho_{V}\right)}{2} \exp\left[-C\left(\frac{r}{R(\theta)_{av}} - 1\right)\right], \text{ for } r > R(\theta)_{av}$$
(3.17b)

Here, ρ_V is the bulk density of the initial homogeneous supersaturated vapor phase and ρ_L is the bulk density of the liquid bulk phase at coexistence and $R(\theta)_{av}$ is the distance from the centre of the drop on the solid surface (i.e, point O in Fig. **3.1**), at any particular polar angle θ (see Eq.(3.6)), to a point on the liquid-vapor interface where the density is the average of densities of the bulk liquid and the vapor. The parameter C is a measure of the diffuseness of the density at the interface. The density at the origin, i.e., at r=0 (at point O in **Fig.3.1**) is $\rho (0, \theta) = \rho_L - (\rho_L, \rho_V)/2 \exp(-C)$ clearly independent of θ . Since the density at the origin has to be same for all values of the polar angle θ , at a given contact angle θ_C , the parameter *C* is therefore constant (independent of θ) at any particular contact angle (θ_C).

In **Fig.3.3**, the model density profile for a droplet of volume V= 400 σ^3 placed on a flat surface with a contact angle $\theta_C = \pi/6$ is shown for specific value of the parameter C = 4 at two different values of the polar angle $\theta = 0$ and $\theta = \pi/2$. The expressions relating the radius of

curvature (r_s) of the droplet on the planar surface (origin O') and the polar angle (θ) dependent radius (R(θ)) (origin O) for a given volume (V) of the liquid drop on a planar surface have already been discussed in section 3.2.



Fig.3.3. Density profile $\rho(r,\theta)$ of a liquid droplet of an arbitrary volume V=400 σ^3 on a flat surface of the solid substrate. Solid and dash-dot-dash lines correspond to the model for the present work for the polar angle θ = 0 and $\pi/2$ respectively, while dash and dot lines are densities corresponding to CNT for the polar angle θ = 0 and $\pi/2$ respectively.

The density profile assumed here is a continuous function of r and the expression for $\rho(r,\theta)$ and its first derivative with respect to r at $r = R(\theta)_{av}$, as obtained from either of Eqs.(3.17), are given respectively by

$$\rho(r,\theta) \big|_{r=R(\theta)_{av}} = \frac{\left(\rho_L + \rho_V\right)}{2}$$
(3.18a)

and

$$\frac{d\rho(r,\theta)}{dr} \mid_{r=R(\theta)_{av}} = -\frac{C}{R(\theta)_{av}} \frac{\left(\rho_L - \rho_V\right)}{2}$$
(3.18b)

Therefore, the proposed model provides an inhomogeneous density profile (instead of the bulk density value) for a drop of any arbitrary size. For the sake of simplicity, the $R(\theta)_{av}$, hereafter, will be denoted as $R(\theta)$.

3.5 Density functional theory of vapor to liquid heterogeneous nucleation

The Helmholtz free energy of the final phase of the nonuniform density (liquid drop on the solid surface covered by the vapor of the same component) can be expressed by using DFT with square gradient approximation [**32**] as

$$F_{f} = \int f(\rho(r,\theta))d^{3}r + \frac{1}{2}K\int (\nabla\rho(r,\theta))^{2}d^{3}r + \int \rho(r,\theta) V_{sf}d^{3}r$$
(3.19)

where $f(\rho(r, \theta))$, in the first term, is the local Helmholtz free energy density, while the second term represents the square gradient correction to it and the third term arises from solid wall- fluid interaction, with the quantity V_{sf} (z) denoting the interaction energy experienced by each fluid particle due to the solid substrate. The third term will be calculated here by considering the drop as a classical drop with the sharp density at interface, i.e. the contribution by the solid surface is considered to be the same for both CNT and DFT methods.

Equation (3.19) can be further written as

$$F_{f} = 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{0}^{R(\theta)} f\left(\rho(r,\theta)\right) r^{2} dr + \int_{R(\theta)}^{\infty} f\left(\rho(r,\theta)\right) r^{2} dr \right]$$

+ $\pi K \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{0}^{R(\theta)} \left(\nabla \rho(r,\theta)\right)^{2} r^{2} dr + \int_{R(\theta)}^{\infty} \left(\nabla \rho(r,\theta)\right)^{2} r^{2} dr \right]$
+ $2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{0}^{R(\theta)} \rho_{L} V_{sf}(z) r^{2} dr + \int_{R(\theta)}^{\infty} \rho_{V} V_{sf}(z) r^{2} dr \right].$ (3.20)

The form of the local Helmholtz free energy density $f(\rho(r,\theta))$ used here is expressed (see also Eq.(2.16) in chapter 2) as Taylor series expansion with respect to the uniform fluid up to 1st order [109], as

$$f\left(\rho(r,\theta)\right) = f\left(\rho(r,\theta)\right)_{\rho(r)=\rho_U} + \left[\frac{df\left(\rho(r,\theta)\right)}{d\rho(r,\theta)}\right]_{\rho(r)=\rho_U} \left(\rho(r,\theta)-\rho_U\right), \quad (3.21)$$

where the subscript *U* refers to the uniform fluid and therefore $\rho_U = \rho_L$ for $r \le R(\theta)$ and $\rho_U = \rho_V$ for $r > R(\theta)$.

The square gradient term for such density is written as

$$\left(\nabla\rho(r,\theta)\right)^2 = \left(\frac{d\rho(r,\theta)}{dr}\right)^2 + \frac{1}{r^2} \left(\frac{d\rho(r,\theta)}{d\theta}\right)^2 . \tag{3.22}$$

The Helmholtz free energy of the final nonuniform phase is obtained by substituting Eqs (3.21) and (3.22) into Eq.(3.20), and can be expressed as

$$F_{f} = 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{0}^{R(\theta)} \left[f_{L} + \mu_{L} \left(\rho(r,\theta) - \rho_{L} \right) \right] r^{2} dr$$

$$+ 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R(\theta)}^{\infty} \left[f_{V} + \mu_{V} \left(\rho(r,\theta) - \rho_{V} \right) \right] r^{2} dr$$

$$+ \pi K \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{0}^{R(\theta)} \left[\left(\frac{d\rho(r,\theta)}{dr} \right)^{2} r^{2} + \left(\frac{d\rho(r,\theta)}{d\theta} \right)^{2} \right] dr$$

$$+ \pi K \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R(\theta)}^{\infty} \left[\left(\frac{d\rho(r,\theta)}{dr} \right)^{2} r^{2} + \left(\frac{d\rho(r,\theta)}{d\theta} \right)^{2} \right] dr$$

$$+ 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{0}^{R(\theta)} \rho_{L} V_{sf}(z) r^{2} dr + \int_{R(\theta)}^{\infty} \rho_{V} V_{sf}(z) r^{2} dr \right] . (3.23)$$

Using the model density given by Eqs.(3.17) in Eq.(3.23), one has the result

$$F_{f} = 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{0}^{R(\theta)} \left[f_{L} - \frac{\Delta \rho}{2} \mu_{L} \exp\left(C\left(\frac{r}{R(\theta)} - 1\right)\right) \right] r^{2} dr$$

$$+ 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R(\theta)}^{\infty} \left[f_{V} + \frac{\Delta \rho}{2} \mu_{V} \exp\left(-C\left(\frac{r}{R(\theta)} - 1\right)\right) \right] r^{2} dr$$

$$+ \frac{\pi K \Delta \rho^{2}}{4} \left(C + \frac{1}{2C} - \frac{\exp(-2C)}{4C}\right) \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[R(\theta) + \frac{1}{R(\theta)} \left(\frac{dR(\theta)}{d\theta}\right)^{2} \right]$$

$$+ 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{0}^{R(\theta)} \rho_{L} V_{sf}(z) r^{2} dr + \int_{R(\theta)}^{\infty} \rho_{V} V_{sf}(z) r^{2} dr \right], \quad (3.24)$$

where $f_L \equiv f(\rho_L)$, $f_V \equiv f(\rho_V)$ and $\Delta \rho = \rho_L - \rho_V$.

Using the relations $2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{0}^{R(\theta)} r^2 dr = V_L$ and $2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R(\theta)}^{\infty} r^2 dr = V_V$ (see

Eq.(3.7)) and $f = \rho \mu - P$, Eq.(3.24) can be used to express the Gibbs free energy of the final phase as

$$G_{f} = V_{L}\rho_{L}\mu_{L} - \pi\Delta\rho\mu_{L}\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\int_{0}^{R(\theta)}\exp\left(C\left(\frac{r}{R(\theta)}-1\right)\right)r^{2}dr$$

$$+ V_{V}\rho_{V}\mu_{V} + \pi\Delta\rho\mu_{V}\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\int_{R(\theta)}^{\infty}\exp\left(-C\left(\frac{r}{R(\theta)}-1\right)\right)r^{2}dr$$

$$+ \frac{\pi K\Delta\rho^{2}}{4}\left(C + \frac{1}{2C} - \frac{\exp(-2C)}{4C}\right)\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\left[R(\theta) + \frac{1}{R(\theta)}\left(\frac{dR(\theta)}{d\theta}\right)^{2}\right]$$

$$+ 2\pi\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\left[\int_{0}^{R(\theta)}\rho_{L}V_{sf}(z)r^{2}dr + \int_{R(\theta)}^{\infty}\rho_{V}V_{sf}(z)r^{2}dr\right]. \quad (3.25)$$

Since the total number of monomers (individual fluid particles), *N*, is conserved, one has $N = \int \rho(r, \theta) d\mathbf{r}$ = constant. The free energy of the initial uniform phase can be expressed as the sum of the free energy of the one component pure vapor and the solid- vapor perturbative term, as

$$G_{i} = \mu_{V} \int \rho(r,\theta) d\mathbf{r} + 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{0}^{R(\theta)} \rho_{V} V_{sf}(z) r^{2} dr + \int_{R(\theta)}^{\infty} \rho_{V} V_{sf}(z) r^{2} dr \right].$$
(3.26)

Using the relations given by Eqs. (3.7) for V_L and V_V and Eqs.(3.17), Eq.(3.26) can be rewritten as,

$$G_{i} = V_{L}\rho_{L}\mu_{V} - \pi\Delta\rho\mu_{V}\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\int_{0}^{R(\theta)}\exp\left(C\left(\frac{r}{R(\theta)}-1\right)\right)r^{2}dr$$

+ $V_{V}\rho_{V}\mu_{V} + \pi\Delta\rho\mu_{V}\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\int_{R(\theta)}^{\infty}\exp\left(-C\left(\frac{r}{R(\theta)}-1\right)\right)r^{2}dr$
+ $2\pi\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\left[\int_{0}^{R(\theta)}\rho_{V}V_{sf}(z)r^{2}dr + \int_{R(\theta)}^{\infty}\rho_{V}V_{sf}(z)r^{2}dr\right].$ (3.27)

Therefore, the free energy of formation of a droplet of a given volume on a solid substrate, as given by ΔG_V^{het} (DFT) = $G_f - G_i$, can be expressed, after simplification, as

$$\Delta G_{V}^{het}(DFT) = -V_{L}\rho_{L}\Delta\mu + \frac{3}{2}\Delta\rho\Delta\mu V_{L}$$

$$\left(\frac{1}{C} - \frac{2}{C^{2}} + \frac{2}{C^{3}} - \frac{2\exp(-C)}{C^{3}}\right)$$

$$+ \frac{\pi K\Delta\rho^{2}}{4} \left(C + \frac{1}{2C} - \frac{\exp(-2C)}{4C}\right)$$

$$\frac{\frac{\pi}{2}}{\int_{0}^{\pi} \sin(\theta)} \left[R(\theta) + \frac{1}{R(\theta)} \left(\frac{dR(\theta)}{d\theta}\right)^{2}\right] d\theta$$

$$+ 2\pi\Delta\rho \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{0}^{R(\theta)} V_{sf}(z)r^{2}dr \quad , \qquad (3.28)$$

which, on minimization with respect to the parameter *C*, provides $\Delta G_V^{het}(DFT)$, the free energy of formation of a fluid droplet of volume *V*.

Here $\Delta \mu = \mu_V - \mu_L$ and $\Delta \rho = \rho_L - \rho_V$, with ρ_L , representing the equilibrium bulk density of liquid at a given temperature and ρ_V denoting the density of supersaturated vapor, i.e., $\rho_V = \rho_V^0 S$, where *S* is the supersaturation ratio. The liquid and vapor densities at coexistence, ρ_L

and ρ_V^0 are obtained from the phase diagram. The coefficient of the square gradient term, *K* used in Eq.(3.19) is given by in Eq. (2.25) of chapter 2.

The solid-fluid interaction $V_{sf}(z)$ has been obtained by considering the wall-fluid model [50]. In the case of L-J interaction, the total interaction energy experienced by each fluid particle due to the solid surface is given by the 9-3 potential,

$$V_{sf}(z) = 4\pi\varepsilon_{sf}\rho_w\sigma_w^3 \left[\frac{1}{45}\left(\frac{\sigma_w}{z}\right)^9 - \frac{1}{6}\left(\frac{\sigma_w}{z}\right)^3\right] , \qquad (3.29)$$

where ε_{sf} is the depth of the solid-fluid interaction potential curve, σ_W is the collision diameter between fluid and solid and z is the perpendicular distance of the fluid particle from the wall. In the present model, z is written as $z = r \cos(\theta) + \sigma_W$, where θ is the polar angle. Therefore, the minimum distance (z) between the particle and wall is now σ_W and not zero, so that the integral in Eq.(3.28) can be run from r = 0. The density of the solid at the wall (ρ_w) has been considered here for simplicity as unity so that $\rho_w \sigma^3 = 1$ and the depth the solid-fluid interaction ε_{sf} is expressed as the ratio of the depth of the solid-fluid to fluid-fluid ($\varepsilon_{sf} / \varepsilon_{ff}$) interaction potential.

3.6 Results and discussions

The present formalism is applied to a model L-J system, with interatomic potential $\Phi_{L-J}(r) = 4\varepsilon [(\sigma/r)^{12} \cdot (\sigma/r)^6]$ with ε and σ as the characteristic energy and length parameters of the L-J system (see Eq.(2.26)). The coexistence densities of vapor and liquid of L-J system at any particular temperature which are required for the calculation of degree of

supersaturation has been obtained from the temperature-density diagram (see **Fig.2.2**) shown in section 2.6 of chapter 2.

In order to obtain the optimized density profile for a given volume of droplet on the solid surface, the parameter C (in Eq.(3.17)) has to be evaluated, which has been obtained by minimizing the free energy of heterogeneous nucleation (Eq.(3.28)) with respect to this parameter. The minimized free energy is thus the free energy of formation of that droplet and the corresponding C is used to calculate the optimized density profile as shown in **Fig.3.4**. From the plot, it is observed that as the polar angle increases, the sharpness of density at the interface decreases and the density even at the centre of the drop becomes less than the bulk liquid density which is commonly observed in the case of tiny droplet .



Fig.3.4. Density profiles of liquid drops of volume V=400 σ^3 on the solid surface with contact angle $\theta_C = \pi/6$ at T*=0.7 and S=2.0 for different values of the polar angle θ_c

The free energy of formation of the droplets of different volumes at different conditions such as supersaturation and strength of the solid-fluid interaction has been obtained. It has

been observed that the contact angle for the minimum free energy of formation of the droplet decreases as the volume of the droplet increases. The free energy of heterogeneous nucleation using the present DFT at different supersaturation has been plotted in Fig.3.5 at reduced temperature $T^*=0.7$. The free energy of both heterogeneous and homogeneous nucleation at T*=0.7 and S=5 using classical nucleation theory (CNT) is also shown in Fig.3.6. Form Figs. 3.5 and 3.6, it is clear that, although the nucleation barrier is much less in the case of heterogeneous nucleation, as compared to the same for homogeneous nucleation, as predicted by CNT, the barrier predicted by the present DFT method is still lower. The spinodal decomposition is also observed at higher supersaturation as shown in Fig. 3.5. The effect of substrate on the free energy of heterogeneous nucleation has been shown in Fig. 3.7, where the free energy of heterogeneous nucleation using both CNT and DFT have been plotted at different values of ε_{sf} . The nucleation barrier is found to vanish with increase in ε_{sf} . From Figs. 3.5, 3.6 and 3.7, it is clear that the nucleation is favoured on the surface of the substrate. It has been observed that, even at a given ε_{sf} , the optimized shape of the droplet on the solid surface varies with the different volumes of the droplet. In Fig. 3.8, the shape of the droplet on the flat surface, i.e. the contact angle has been plotted against the volume of the droplet. The contact angle is found to sharply fall with increase of the volume when the droplet is very small and then it varies slowly to reach a constant value when it becomes a macroscopic droplet.



Fig. 3.5. Formation free energy as a function of volume at different supersaturation (S) at $T^*=0.7$ with $\varepsilon_{sf}=1.0$, as calculated using the present model.



Fig. 3.6.Comparison of classical heterogeneous and homogeneous nucleation at T*=0.7, S= 5 with $\varepsilon_{sf} = 1.0$. The γ_{∞} value used for both types of nucleation is 1.24 ε/σ^2 , as obtained from DFT by Zeng and Oxtoby [14].



Fig. 3.7. Heterogeneous nucleation with different values of ε_{sf} at T*=0.7 and S=2. The symbols denote results of CNT, while the symbols connected with line denote results of DFT, in the present model.



Fig. 3.8 Optimised contact angle vs volume at T*=0.7, S=1.5 and $\varepsilon_{sf} = 1.0$.

3.7 Conclusions

A method for the calculation of the free energy of heterogeneous nucleation for the vapor to liquid phase transition of L-J fluid using DFT with square gradient approximation for the free energy functional has been introduced. This type of DFT is commonly used for the study of nonuniform fluids, interfaces and spinodal decomposition. Although the present work is not completely analytical, with the use of a simple numerical integration, the formalism is overall simple due to the consideration of a model for the density profile and evaluation of the free energy has been minimized variationally with respect to the bulk density. The free energy has been minimized variationally with respect to the parameter present in the density profile as well as the contact angle to obtain the minimum free energy of formation of a drop on the surface of the substrate. Therefore, this method can be used to predict the shape, density profile and free energy of a given volume of the droplet including a critical droplet which provides an idea about the kinetics of nucleation. Spinodal decomposition is observed either by increasing supersaturation or by increasing the strength of the solid-fluid interaction.

CHAPTER 4

Vapor to liquid heterogeneous nucleation on spherical solid substrate: Seed mediated vapor condensation

4.1 Introduction

In chapter 3, vapor to liquid heterogeneous nucleation on the flat surface of a solid substrate has been discussed. The phenomenon of droplet formation on flat surface is a particular case of droplet formation on a spherically curved surface with infinite radius of curvature. Nucleation on curved surface is therefore a general case of heterogeneous nucleation which is also known as seed mediated nucleation. The zero value of the radius of the solid substrate (foreign particle or seed) corresponds to the homogeneous nucleation (chapter 2) while the infinite radius of curvature corresponds to the heterogeneous nucleation on flat surface (chapter 3). In the present chapter the features of vapor to liquid heterogeneous nucleation on convex surface of solid substrate has been discussed. The theory is then applied to the case of Lennard-Jones fluid.

The conventional classical theory with the well-known approximations for density and interfacial energy has been applied earlier [**10-12**] for such heterogeneous nucleation. The effect of particle size and surface properties upon nucleation efficiency was investigated by Fletcher [**11**]. A general result was derived in the framework of CNT which was then applied to condensation, sublimation etc. A rigorous thermodynamic formulation of Fletcher's model using a novel analytical approach within CNT was derived by Qian and Jie [**12**]. The classical theory, however, does not work well because of the use of unrealistic approximations, and therefore several approaches have been developed to solve the problem in a more realistic

manner. Density functional theory (DFT) [**35-37**] as well as molecular simulation [**41-46**] based techniques have been employed to describe various aspects of the phenomena of heterogeneous nucleation on curved solid surface. Lattice density functional theory (LDFT) with suitable constraints had been applied by Zhang et.al to investigate the shape of the critical nucleus as well as the height of the nucleation barrier corresponding to the nucleation behavior of vapor-liquid transition in nanosquare pores with infinite length [**35**]. They have also used the constrained LDFT to investigate how nanoscale seed particles affect heterogeneous vapor-liquid nucleation[**36**], i.e. the effects of the physical properties of nanoscale seed particles (the seed size, the strength of seed-fluid attraction, and the shape of the seeds) on the structure of critical nuclei and nucleation barrier. A hybrid thermodynamic and density-functional theory for heterogeneous nucleation on mesoscopic wettable particles was developed by Bykov and Xeng [**37**].

In the present work, the effect of the size and surface properties of seed on the nucleation of Lennard-Jones (L-J) fluid has been investigated by employing DFT with square gradient approximation for the free energy functional. The well-studied exponential density profile model which has been known to work quite well in the case of liquid droplet- vapor system [109-110,112-113] and a model Helmholtz free energy density for the local part of the free energy density functional have been employed in the present work. Homogeneous nucleation has been obtained in the limiting condition of the seed size equal to zero (i.e. no seed particle) whereas the infinite radius of seed size provides the heterogeneous nucleation on flat solid substrate. The present work is therefore the generalization of our earlier work on homogeneous [109] and heterogeneous nucleation on flat surface [110], discussed in chapter 2 and 3 .Unlike the standard 9-3 interaction (corresponds to L-J potential) energy between each fluid particle and the flat solid substrate (radius of seed = ∞) in case of heterogeneous

nucleation on flat surface, a general formula for the interaction between each fluid particle and the spherical substrate has been derived. Minimization of the free energy of formation of a liquid drop on the spherical solid surface (of given radius) with respect to both contact angle as well as the parameter present in the density profile has been carried out for a given volume of the drop. This leads to the optimized shape and free energy of formation of a droplet of any given volume. The dependence of the optimized shape of the liquid droplet on the size of the solid substrate (spherical) at constant volume of the liquid and also on the volume (size) of the liquid droplet at constant size of the solid substrate have been studied using both CNT and DFT, which has been mentioned here as shape-size relation. This shapesize relation gives an idea of shape wise mechanistic pathway of growing droplets. The strength of the wall-fluid interaction as well as the size of the solid substrate controls the nucleation barrier significantly. The spinodal decomposition has also been observed at different conditions. The unconstrained density profile used in the present DFT gives different results as compared to the results obtained by the approximation of step like constraint density profile used in CNT, which is an additional achievement of this DFT based study as compared to the earlier work of Fletcher [11] and Qian [12]. The size of the seed of any particular material for the lowest nucleation free energy barrier can also be predicted by the present formalism.





Fig.4.1 Double spherical cap model representing the liquid drop formation on a spherical solid substrate. Vapor, liquid and solid phases are denoted by region 1,2 and 3 respectively in the figure.

The liquid droplet placed on the spherical surface of a solid substrate, which makes a contact angle ($\theta_{\rm C}$) with the surface, is considered here as a spherical cap and denoted as CAPL. The cap is constructed by the portion of the solid substrate covered by the CAPL and denoted as CAPS. This model which has been called here as a double spherical cap model is shown in **Fig. 4.1**, where the vapor, liquid and solid regions are denoted by 1, 2 and 3 respectively. The CAPL and CAPS are therefore part of two different spheres with the origin of the solid sphere at O_S, whereas the origin of the liquid droplet on the solid surface is at O_L, in the present model. The origin of both the spherical caps (CAPS and CAPL) is chosen to be at the
point O, which will be used for the calculation in the present work. The radius of the solid sphere (i.e. the radius of curvature of the CAPS) and the liquid droplet (i.e. the radius of curvature of the CAPL) are denoted by R_S and by R_L respectively. $\mathbf{R}(\theta)$ is the polar radial vector with respect to origin at O (distance of the surface of the cap from O) which is clearly a function of the polar angle θ . $\mathbf{R}(\theta)$ is actually $\mathbf{R}_L(\theta)$ when CAPL is considered and $\mathbf{R}_S(\theta)$ in case of CAPS. The contact angle between the liquid and the solid surface is θ_C . Since the origin of the spherical cap (O) will be used for the calculation, it is essential to have the expressions for $\mathbf{R}_L(\theta)$ and $\mathbf{R}_S(\theta)$. In order to obtain the expressions of these radii, the two caps can be treated separately so that the calculation can be done by considering the single spherical cap model as used in section 1, Chapter 3 and the expressions are therefore given by

$$R_{s}(\theta) = -R_{s}\cos(\theta)\cos(\theta_{s}) + R_{s}\sqrt{\left(\cos^{2}(\theta)\cos^{2}(\theta_{s}) + \sin^{2}(\theta_{s})\right)}$$
(4.1)

$$R_{L}(\theta) = -R_{L}\cos(\theta)\cos(\theta_{L}) + R_{L}\sqrt{\left(\cos^{2}(\theta)\cos^{2}(\theta_{L}) + \sin^{2}(\theta_{L})\right)}$$
(4.2)

Equations (4.1) and (4.2) can be used to calculate the polar radius $R(\theta)$ as a function of the polar angle θ for both solid and the liquid caps from origin O. The volume of the liquid droplet on the surface of the solid is therefore the difference in volume between CAPL and CAPS and can be written as

$$V = \int_{0}^{2\pi} d\Phi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R_{S}(\theta)}^{R_{L}(\theta)} r^{2} dr .$$

$$(4.3)$$

Another expression for the volume of the liquid droplet on a spherical solid surface in terms of the radius of the spheres as R_s and R_L , is given by

$$V_{L} = \frac{1}{3}\pi R_{L}^{3} (2 - 3\cos(\theta_{L}) + \cos^{3}(\theta_{L})) - \frac{1}{3}\pi R_{S}^{3} (2 - 3\cos(\theta_{S}) + \cos^{3}(\theta_{S}))$$
(4.4)

In the present model θ_{C_1} , θ_{L_2} , θ_{S} and R_L , R_S are related as

$$\theta_L = \theta_S + \theta_C \text{ and } R_L = R_S \left[\frac{\sin(\theta_S)}{\sin(\theta_L)} \right], \text{ for } 0 < R_S < \infty.$$
(4.5)

From the above relations, it is clear that for a particular volume (V) of the liquid droplet, there are only two unknown parameters in Eq.(4.4), viz. the radius of the solid substrate (R_s) and the contact angle (θ_c). Since the radius of the spherical cap, for a given volume, varies with the contact angle, the volume is used here as the size of the droplet and not the radius in this case of heterogeneous nucleation.

4.3. Effect of seed size and surface properties on the vapour to liquid nucleation

4.3.1 Solid fluid interaction energy

It is essential to derive an expression for the solid-fluid interaction energy in order to investigate the effect of solid substrate on the nucleation of vapor. The widely used solid-fluid interaction energy due to the interaction between a fluid particle and a solid object with flat surface (both are L-J system) which is also known as wall-fluid interaction is the well-known 9-3 interaction potential. Since in the present system, liquid is placed on the surface of a spherical seed, it is necessary to derive a general interaction energy expression for the interaction energy between each fluid particle with the whole seed substrate.



Fig.4.2. A fluid point particle labeled as L, placed at a distance z_0 from the surface of the solid sphere of radius R_s . Here S is an arbitrary point particle of the solid sphere.

The problem has been solved by using cylindrical coordinate. From **Fig. 4.2**, it is clear that, $r^2 = z^2 + \rho^2$, where z and ρ are the two cylindrical coordinates of the point S with respect to the point L. Here, ρ_m , i.e. the maximum value of ρ can be written as $\rho_m = [R_S^2 - (z_0 + R_S - z)^2]^{1/2}$. For L-J system, the interaction potential is written as $\Phi(r) = 4\varepsilon[(\sigma/r)^{12} - \sigma/r)^6]$. Total interaction energy experienced by each fluid particle by the spherical solid substrate ($V_{sf}(z_0)$) is therefore expressed as

$$V_{sf}(z_0) = 2\pi \int_{z_0}^{z_0 + 2R_s} dz \int_0^{\rho_m} \rho_s 4\varepsilon_{sf} \left[\left(\frac{\sigma_{sf}}{r} \right)^{12} - \left(\frac{\sigma_{sf}}{r} \right)^6 \right] \rho \, d\rho \,, \tag{4.6}$$

where ρ_S is the density of the solid substrate, ε_{sf} is the depth of the solid-fluid interaction potential and σ_{sf} is the collision diameter between fluid and solid and z_0 is the minimum distance of the fluid particle from the surface of the solid. After simplification, the expression of $V_{sf}(z_0)$ becomes

$$V_{sf}(z_{0}) = 4\pi\varepsilon_{sf}\rho_{S}\sigma^{3} \begin{bmatrix} \frac{\sigma^{9}}{45} \left\{ \frac{1}{z_{0}^{9}} - \frac{1}{\left(z_{0} + 2R_{S}\right)^{9}} \right\} - \frac{\sigma^{3}}{6} \left\{ \frac{1}{z_{0}^{3}} - \frac{1}{\left(z_{0} + 2R_{S}\right)^{3}} \right\} \\ - \frac{\sigma^{9}}{20a_{1}} \left\{ \frac{1}{z_{0}^{8}} - \frac{1}{\left(z_{0} + 2R_{S}\right)^{8}} \right\} + \frac{\sigma^{3}}{2a_{1}} \left\{ \frac{1}{z_{0}^{2}} - \frac{1}{\left(z_{0} + 2R_{S}\right)^{2}} \right\} \end{bmatrix},$$

$$(4.7)$$

where $a_1 = 2(z_0 + R_S)$

For a flat surface, $R_S \rightarrow \infty$, and Eq.(4.7) becomes the well-known 9-3 potential as

$$V_{sf}(z_0) = 4\pi \varepsilon_{sf} \rho_S \sigma_{sf}^{3} \left[\frac{1}{45} \left(\frac{\sigma_{sf}}{z_0} \right)^9 - \frac{1}{6} \left(\frac{\sigma_{sf}}{z_0} \right)^3 \right] .$$
(4.8)

In order to make the problem simple the collision diameter σ_{sf} has been considered to be the same as σ and the density of the solid (ρ_s) has been considered here as unity so that $\rho_s \sigma^3 = 1$. The depth the solid-fluid interaction ε_{sf} is expressed as the ratio of the depth of the solid-fluid to fluid-fluid ($\varepsilon_{sf} / \varepsilon_{ff}$) interaction potential.

4.3.2: A general theory of seed mediated vapor to liquid nucleation $(0 \le R_S \le \infty)$

4.3.2A. Classical nucleation theory

The phenomenon of seeding is first investigated here by applying the conventional CNT approach. The liquid droplet is formed on the spherically curved surface of the available seed particles has been considered in the present work. Following the CNT, a sharp boundary (interface of region 1 and 2 in **Fig. 4.1**) between the liquid drop (region 2 on the surface of

the seed 3) and the vapor (region 1 covering the liquid drop 2) with a well-defined polar radius $\mathbf{R}_L(\theta)$ has been considered. In the present double spherical cap model, the density within the drop is same as the bulk liquid density while outside the drop, the density is the same as that of supersaturated vapour and have the fluid density profile $\rho(r, \theta)$ of the drop, is given by

$$\rho(r,\theta) = \rho_L$$
, for $R_S(\theta) \le r \le R_L(\theta)$, $0 \le \theta \le \frac{\pi}{2}$
(4.9a)

and

$$\rho(r,\theta) = \rho_V \quad , \text{ for } r > R_L(\theta) \quad , \qquad 0 \le \theta \le \frac{\pi}{2}$$
(4.9b)

where ρ_L and ρ_V are the densities of the bulk liquid and supersaturated vapor respectively.

The Helmholtz free energy of the final phase can thus be expressed as

$$F_{f} = 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} f(\rho_{L}) r^{2} dr + \int_{R_{L}(\theta)}^{\infty} f(\rho_{V}) r^{2} dr + \right] + 2\pi R_{L}^{2} (1 - \cos(\theta_{L})) \gamma_{LV} + 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} \rho_{L} V_{sf}(z_{0}) r^{2} dr + \int_{R_{L}(\theta)}^{\infty} \rho_{V} V_{sf}(z_{0}) r^{2} dr \right] , \qquad (4.10)$$

where the total energy has been divided into three energy terms. The first term is the volume energy term with $f(\rho_L)$ and $f(\rho_V)$ being the local Helmholtz free energy density of the onecomponent bulk liquid and bulk vapor phase respectively. The second term is the vaporliquid surface energy term which involves the surface tension γ_{LV} of the vapour-liquid planar interface at coexistence. The third term is the energy due to solid-fluid interaction, where $V_{sf}(z_0)$ is the interaction energy experienced by each fluid particle due to the solid substrate at a distance z_0 from the spherical surface of the seed (see Eq. 4.7 and **Fig. 4.2**).

The Helmholtz free energy density can be written as, $f = \rho \mu - P$, where P and μ denote respectively the pressure and chemical potential of the fluid of interest. Equation (4.10) can thus be written as

$$F_{f} = 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} (\mu_{L}\rho_{L} - P_{L})r^{2} dr + \int_{R_{L}(\theta)}^{\infty} (\mu_{V}\rho_{V} - P_{V})r^{2} dr + \right] \\ + 2\pi R_{L}^{2} (1 - \cos(\theta_{L}))\gamma_{LV} + 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \\ \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} \rho_{L} V_{sf}(z_{0})r^{2} dr + \int_{R_{L}(\theta)}^{\infty} \rho_{V} V_{sf}(z_{0})r^{2} dr \right].$$
(4.11)

Equation (4.11), on using the relations of volume of liquid and vapor part (see Eq. (4.3)) can be rewritten as

$$F_{f} = V_{L}\rho_{L}\mu_{L} - P_{L}V_{L} + V_{V}\rho_{V}\mu_{V} - P_{V}V_{V} + 2\pi R_{L}^{2}(1 - \cos(\theta_{L}))\gamma_{LV} + 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta)d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} \rho_{L}V_{sf}(z_{0})r^{2}dr + \int_{R_{L}(\theta)}^{\infty} \rho_{V}V_{sf}(z_{0})r^{2}dr\right], \qquad (4.12)$$

with μ and P, the chemical potential and pressure for the one-component fluid (subscripts L and V stand for the liquid and vapor phases respectively).

Total number of monomer (fluid particles) N in the classical drop model can be expressed as

$$N = \int \rho(r,\theta) d\mathbf{r} = \rho_L V_L + \rho_V V_V$$

The Gibbs free energy of the final phase (G_f) , on using the relation G = F + PV, is given by

$$G_{f} = V_{L}\rho_{L}\mu_{L} + V_{V}\rho_{V}\mu_{V} + 2\pi R_{L}^{2}(1 - \cos(\theta_{L}))\gamma_{LV} + 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta)d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} \rho_{L}V_{sf}(z_{0})r^{2}dr + \int_{R_{L}(\theta)}^{\infty} \rho_{V}V_{sf}(z_{0})r^{2}dr\right] .$$
(4.13)

The Gibbs free energy of the initial uniform vapor phase G_i , can be expressed as the free energy of one-component vapor phase ($\mu_V N$) with the perturbation by the solid-fluid interaction experienced by all the vapor particles. The initial Gibbs free energy G_i , can be expressed in a form analogous to the expression of G_f as given by Eq. (4.13) and is therefore, written as

$$G_{i} = V_{L}\rho_{L}\mu_{V} + V_{V}\rho_{V}\mu_{V} + 2\pi\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)}\rho_{V}V_{sf}(z_{0})r^{2}dr + \int_{R_{L}(\theta)}^{\infty}\rho_{V}V_{sf}(z_{0})r^{2}dr\right],$$
(4.14)

The Gibbs free energy of formation of a droplet of volume V_L on seed surface, within the framework of CNT, is given by

$$\Delta G_{V_L}(\text{CNT}) = -V_L \rho_L \Delta \mu + 2\pi R_L^2 (1 - \cos(\theta_L)) \gamma_{LV} + 2\pi \Delta \rho \int_0^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R_S(\theta)}^{R_L(\theta)} V_{sf}(z_0) r^2 dr,$$
(4.15)

where $\Delta \mu = \mu_V - \mu_L$ and $\Delta \rho = \rho_L - \rho_V$. Within CNT, the term $\Delta \mu$ is obtained by using the ideal gas equation so that $\Delta \mu = \mu_V - \mu_L = k_B T \ln(S)$, where *S* is the supersaturation ratio, $S = \rho_V / \rho_V^0$, with ρ_V and ρ_V^0 denoting the density of the supersaturated vapor and the vapor density at liquid-vapor coexistence respectively.



Fig.4.3 A liquid droplet covering a solid sphere (seeding) of radius R_S , while the radius of the liquid including the solid is R_L .

When the liquid completely covers the seed particle (**Fig. 4.3**), the contact angle becomes zero ($\theta_C = 0$), and the phenomenon corresponds to complete wetting .

The Gibbs free energy of formation of liquid drop of volume V_L due to complete wetting (**Fig. 4.3**) is written along the lines of CNT as

$$\Delta G^{wet} V_L(CNT) = -V_L \rho_L \Delta \mu + 4\pi R_L^2 \gamma_{LV} + 4\pi \Delta \rho \int_{R_S}^{R_L} V_{sf}(z_0) r^2 dr \qquad (4.16)$$

4.3.2B Density functional theory

Unlike a sharp density profile in CNT, a slowly varying continuous density profile of a liquid droplet on the surface of the seed has been modeled here, which is one of the main features of this thesis. The fluid system, i.e. the droplet on the seed surface covered by the vapor phase is treated as a nonuniform liquid. The free energy of such an inhomogeneous fluid with slowly varying density has been expressed through the framework of density functional theory using square gradient correction. The density profile and the local part of the Helmholtz free energy density that are being used here correspond to an extension of our earlier work on nucleation [Chapter 2 and Chapter 3]. The degree of diffuseness of the density is determined by a parameter present in the density expression which is optimized by minimizing the free energy of formation of the droplet of any size, with respect to the variation of this parameter. The density profile for the final nonuniform state in the proposed model is expressed as

$$\rho(r,\theta) = \rho_L - \frac{\left(\rho_L - \rho_V\right)}{2} \exp\left[C\left(\frac{r}{R_L(\theta)_{av}} - 1\right)\right], \text{ for } R_S(\theta) \le r \le R_L(\theta)_{av}$$
(4.17a)

and

$$\rho(r,\theta) = \rho_V + \frac{\left(\rho_L - \rho_V\right)}{2} \exp\left[-C\left(\frac{r}{R_L(\theta)_{av}} - 1\right)\right], \text{ for } r > R_L(\theta)_{av}$$
(4.17b)

Here, ρ_V and ρ_L are the bulk density of the initial homogeneous supersaturated vapor phase and that of the liquid bulk phase respectively at coexistence and $R_L(\theta)_{av}$ is the distance from the point O (in **Fig. 4.1**) at any particular polar angle θ , where the density is the average of the bulk liquid and vapor densities. The model density profile for a droplet of volume V= 200 σ^3 placed on the surface of a seed with a contact angle $\theta_C = \pi/5$ is shown in **Fig. 4.4** for specific value of the parameter C = 4 at two different values of the polar angle $\theta = 0$ and $\theta = \pi/3$.



Fig.4.4 Density profiles of liquid drops of volume $V=200\sigma^3$ on the spherical solid surface with contact angle $\theta_C = \pi/5$ at T*=0.7 and S=2.0 for different values of the polar angle θ .

The model density profile $\rho(r,\theta)$, which is thus a continuous function of r, and its first derivative with respect to r at $r = R_L(\theta)_{av}$, as obtained from Eqs. (4.17), are given respectively by

$$\rho(r,\theta)|_{r=R_{L}(\theta)_{av}} = \frac{\left(\rho_{L} + \rho_{V}\right)}{2}$$
(4.18a)

and

$$\frac{d\rho(r,\theta)}{dr} \mid_{r=R_{L}(\theta)_{av}} = -\frac{C}{R_{L}(\theta)_{av}} \frac{\left(\rho_{L} - \rho_{V}\right)}{2} \qquad (4.18b)$$

The proposed model, therefore, provides an inhomogeneous density profile for a drop of any arbitrary size. For sake of simplicity, the quantity $R_L(\theta)_{av}$, denoting the distance corresponding to angle θ , at which $\rho(r,\theta) = (\rho_L + \rho_V)/2$ hereafter, will be denoted as $R_L(\theta)$.

The final phase of the nonuniform density thus corresponding to the liquid drop on the spherical solid surface covered by the vapor of the same component. The Helmholtz free energy of this phase can now be expressed by using DFT with square gradient approximation as

$$F_f = \int f(\rho(r,\theta))dv + \frac{1}{2}K\int (\nabla\rho(r,\theta))^2 dv + \int \rho(r,\theta) V_{sf}(z_0)dv$$
(4.19)

The quantity $f(\rho(r, \theta))$ in the first term and $V_{sf}(z_0)$ in the third term are already mentioned while discussing about CNT and the second term represents the square gradient correction to first term. Equation (4.19) based on the present density model can be further written as

$$F_{f} = 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} f\left(\rho(r,\theta)\right) r^{2} dr + \int_{R_{L}(\theta)}^{\infty} f\left(\rho(r,\theta)\right) r^{2} dr \right] + \pi K \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} \left(\nabla \rho(r,\theta)\right)^{2} r^{2} dr + \int_{R_{L}(\theta)}^{\infty} \left(\nabla \rho(r,\theta)\right)^{2} r^{2} dr \right] + 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} \rho(r) V_{sf}(z_{0}) r^{2} dr + \int_{R_{L}(\theta)}^{\infty} \rho(r) V_{sf}(z_{0}) r^{2} dr \right] .$$
(4.20)

The local Helmholtz free energy density $f(\rho(r,\theta))$ which has been proposed earlier [Chapter 2 and Chapter 3], has been expressed as Taylor series expansion with respect to the uniform fluid up to 1st order term as

$$f\left(\rho(r,\theta)\right) = f\left(\rho(r,\theta)\right)_{\rho(r)=\rho_U} + \left[\frac{df\left(\rho(r,\theta)\right)}{d\rho(r,\theta)}\right]_{\rho(r)=\rho_U} \left(\rho(r,\theta) - \rho_U\right), \quad (4.21)$$

where the subscript *U* refers to the uniform fluid and therefore $\rho_U = \rho_L$ for $R_S(\theta) \le r \le R_L(\theta)$ and $\rho_U = \rho_V$ for $r > R_L(\theta)$.

The square gradient term for the present density is written as, $\left(\nabla\rho(r,\theta)\right)^2 = \left(\frac{d\rho(r,\theta)}{dr}\right)^2 + \frac{1}{r^2} \left(\frac{d\rho(r,\theta)}{d\theta}\right)^2$ (4.22)

The Helmholtz free energy of the final nonuniform phase is obtained by substituting Eqs (4.21) and (4.22) into Eq. (4.20) and can be expressed as

$$F_{f} = 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R_{s}(\theta)}^{R_{t}(\theta)} \left[f_{L} + \mu_{L} \left(\rho(r,\theta) - \rho_{L} \right) \right] r^{2} dr$$

$$+ 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R_{s}(\theta)}^{\infty} \left[f_{V} + \mu_{V} \left(\rho(r,\theta) - \rho_{V} \right) \right] r^{2} dr$$

$$+ \pi K \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R_{s}(\theta)}^{R_{t}(\theta)} \left[\left(\frac{d\rho(r,\theta)}{dr} \right)^{2} r^{2} + \left(\frac{d\rho(r,\theta)}{d\theta} \right)^{2} \right] dr$$

$$+ \pi K \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R_{t}(\theta)}^{\infty} \left[\left(\frac{d\rho(r,\theta)}{dr} \right)^{2} r^{2} + \left(\frac{d\rho(r,\theta)}{d\theta} \right)^{2} \right] dr$$

$$+ 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{R_{s}(\theta)}^{R_{t}(\theta)} \rho_{L} V_{sf}(z) r^{2} dr + \int_{R_{t}(\theta)}^{\infty} \rho_{V} V_{sf}(z) r^{2} dr \right]$$

$$(4.23)$$

Using the model density given by Eqs.(4.17) in Eq.(4.23), one has the result

$$F_{f} = 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R_{S}(\theta)}^{R_{L}(\theta)} \left[f_{L} - \frac{\Delta \rho}{2} \mu_{L} \exp\left(C\left(\frac{r}{R(\theta)} - 1\right)\right) \right] r^{2} dr$$

$$+ 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{R_{L}(\theta)}^{\infty} \left[f_{V} + \frac{\Delta \rho}{2} \mu_{V} \exp\left(-C\left(\frac{r}{R(\theta)} - 1\right)\right) \right] r^{2} dr + I_{2}$$

$$+ 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} \rho_{L} V_{sf}(z) r^{2} dr + \int_{R_{L}(\theta)}^{\infty} \rho_{V} V_{sf}(z) r^{2} dr \right], \qquad (4.24)$$

where $f_L \equiv f(\rho_L)$, $f_V \equiv f(\rho_V)$ and $\Delta \rho = \rho_L - \rho_V$ and

$$I_{2} = \frac{\pi K \Delta \rho^{2} C^{2}}{4} \begin{bmatrix} \pi/2 \\ \int_{0}^{\pi/2} \sin(\theta) d\theta \begin{cases} \frac{R_{L}(\theta)^{3}}{C} + \frac{R_{L}(\theta)^{3}}{2C^{3}} - \exp\left(2C\left(\frac{R_{S}(\theta)}{R_{L}(\theta)} - 1\right)\right) \\ \left(\frac{R_{L}(\theta)R_{S}(\theta)^{2}}{2C} - \frac{R_{L}(\theta)^{2}R_{S}(\theta)}{2C^{2}} + \frac{R_{L}(\theta)^{3}}{4C^{3}}\right) \end{bmatrix} \\ \left\{ \frac{1}{R_{L}(\theta)^{2}} + \left(\frac{d\left(\frac{1}{R_{L}(\theta)}\right)}{d\theta}\right)^{2} \\ \left\{ \frac{1}{R_{L}(\theta)^{2}} + \left(\frac{d\left(\frac{1}{R_{L}(\theta)}\right)}{d\theta}\right)^{2} \\ \frac{1}{R_{L}(\theta)^{2}} + \left(\frac{1}{R_{L}(\theta)^{2}}\right)^{2} \\ \frac{1}{R_{L}(\theta)^{2}} \\ \frac{1}{R_{L}(\theta)^{2}} + \left(\frac{1}{R_{L}(\theta)^{2}}\right)^{2} \\ \frac{1}{R_{L}(\theta)^{2}} \\ \frac{1}{R_{L}($$

The expression for the Gibbs free energy, can thus be written as

$$G_{f} = V_{L}\rho_{L}\mu_{L} - \pi\Delta\rho\mu_{L}\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta \int_{R_{S}(\theta)}^{R_{L}(\theta)}\exp\left(C\left(\frac{r}{R_{L}(\theta)}-1\right)\right)r^{2}dr$$

$$+ V_{V}\rho_{V}\mu_{V} + \pi\Delta\rho\mu_{V}\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta \int_{R_{L}(\theta)}^{\infty}\exp\left(-C\left(\frac{r}{R_{L}(\theta)}-1\right)\right)r^{2}dr + I_{2}$$

$$+ 2\pi\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)}\rho(r)V_{sf}(z_{0})r^{2}dr + \int_{R_{L}(\theta)}^{\infty}\rho(r)V_{sf}(z_{0})r^{2}dr\right] \quad . \quad (4.26)$$

In analogy to the present version of CNT, the Gibbs free energy of the initial uniform phase has been expressed as the sum of the free energy of the one-component pure vapor ($\mu_V N$) and the solid- vapor perturbative term, as

$$G_{i} = \mu_{V} \int \rho(r,\theta) d\mathbf{r} + 2\pi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \left[\int_{R_{S}(\theta)}^{R_{L}(\theta)} \rho_{V} V_{sf}(z_{0}) r^{2} dr + \int_{R_{L}(\theta)}^{\infty} \rho_{V} V_{sf}(z_{0}) r^{2} dr \right], (4.27)$$

which can be rewritten by applying Eqs.(4.17)) as

$$G_{i} = V_{L}\rho_{L}\mu_{V} - \pi\Delta\rho\mu_{V}\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\int_{R_{S}(\theta)}^{R_{L}(\theta)}\exp\left(C\left(\frac{r}{R_{L}(\theta)}-1\right)\right)r^{2}dr$$

$$+ V_{V}\rho_{V}\mu_{V} + \pi\Delta\rho\mu_{V}\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\int_{R_{L}(\theta)}^{\infty}\exp\left(-C\left(\frac{r}{R_{L}(\theta)}-1\right)\right)r^{2}dr$$

$$+2\pi\int_{0}^{\frac{\pi}{2}}\sin(\theta)d\theta\left[\int_{R_{S}(\theta)}^{R_{L}(\theta)}\rho_{V}V_{sf}(z_{0})r^{2}dr + \int_{R_{L}(\theta)}^{\infty}\rho_{V}V_{sf}(z_{0})r^{2}dr\right] \qquad (4.28)$$

The free energy of formation of a droplet of a given volume on a seed surface, given by $\Delta G_V^{Seed} = G_f - G_i$, can be expressed, after simplification, as

$$\Delta G_{V_L}(DFT) = -V_L \rho_L \Delta \mu + \pi \Delta \rho \Delta \mu$$

$$\int_{0}^{\pi/2} \sin(\theta) d\theta \begin{bmatrix} \frac{R_L(\theta)^3}{C} - \frac{2R_L(\theta)^3}{C^2} + \frac{2R_L(\theta)^3}{C^3} \\ -\left(\frac{R_L(\theta)R_S(\theta)^2}{C} + \frac{2R_L(\theta)^3}{C^3} - \frac{2R_L(\theta)^2R_S(\theta)}{C^2}\right) \\ \exp\left(C\left(\frac{R_S(\theta)}{R_L(\theta)} - 1\right)\right) \end{bmatrix} + I_2 + 2\pi \Delta \rho$$

$$\int_{0}^{\pi/2} \sin(\theta) d\theta \begin{bmatrix} R_L(\theta) \\ R_S(\theta) \\ R_S(\theta) \end{bmatrix} + I_2 + 2\pi \Delta \rho$$

$$\frac{\pi_L(\theta)}{R_L(\theta)} + I_2 + 2\pi \Delta \rho \\ \exp\left(C\left(\frac{R_S(\theta)}{R_L(\theta)} - 1\right)\right) \\ + I_2 + 2\pi \Delta \rho \\ \exp\left(C\left(\frac{R_S(\theta)}{R_L(\theta)} - 1\right)\right) \\ + I_2 + 2\pi \Delta \rho \\ \left(\frac{R_L(\theta)}{R_L(\theta)} - 1\right) \\ + \frac{R_L(\theta)}{R_S(\theta)} + \frac{R_L(\theta)}{R_S(\theta)} + \frac{R_L(\theta)}{R_S(\theta)} + \frac{R_L(\theta)}{R_S(\theta)} + \frac{R_L(\theta)}{R_S(\theta)} \\ + \frac{R_L(\theta)}{R_S(\theta)} + \frac$$

which is then minimized with respect to the parameter *C* to obtain ΔG_V^{het} , i.e. the free energy of formation of a fluid droplet of volume V.

The problem becomes simple when the liquid phase completely covers the seed (i.e. $\theta_C=0$), which is also known as complete wetting and can be considered as the nucleation due to seeding effect by the substrate (see **Fig. 4.3**). Due to the spherical symmetry of the seeding condition the density can be simply modeled as

$$\rho(r) = \rho_L - \frac{\left(\rho_L - \rho_V\right)}{2} \exp\left[a\left(r - R_{L, av}\right)\right], \text{ for } R_S \le r \le R_L, av$$
(4.30a)
and

$$\rho(r) = \rho_V + \frac{\left(\rho_L - \rho_V\right)}{2} \exp\left[-a\left(r - R_L, av\right)\right], \text{ for } r > R_L, av \quad , \tag{4.30b}$$

where, a is a parameter which is the measure of the degree of diffuseness of density at the

interface which is related to the parameter C present in the density profile model (Eqs.(4.17)) by $C = aR_L$.

The Helmholtz free energy of the final phase due to the completing seeding (wetting) can also be expressed by using DFT with square gradient approximation as

$$F_{f} = \int f(\rho(r))dv + \frac{1}{2}K\int (\nabla \rho(r))^{2}dv + \int \rho(r) V_{sf}(z_{0})dv$$
(4.31)

Substituting Eqs.(4.30) and Eq.(4.21) into Eq.(4.31) and after simplification and elimination of the free energy of the initial phase, the free energy of formation of a given volume of liquid on a solid seed particle of radius R_s can be written as

$$\Delta G_{V}^{wet}(DFT) = -V_{L}\rho_{L}\Delta\mu + 2\pi\Delta\rho\Delta\mu \left[\frac{R_{L}^{2}}{a} - \frac{2R_{L}}{a^{2}} + \frac{2}{a^{3}} - \left(\frac{R_{S}^{2}}{a} - \frac{2R_{S}}{a^{2}} + \frac{2}{a^{3}}\right) \exp\left(a\left(R_{S} - R_{L}\right)\right)\right] + \frac{\pi K\Delta\rho^{2}a^{2}}{2} \left[\frac{R_{L}^{2}}{a} + \frac{1}{2a^{3}} - \left(\frac{R_{S}^{2}}{2a} - \frac{R_{S}}{2a^{2}} + \frac{1}{4a^{3}}\right) \exp\left(2a\left(R_{S} - R_{L}\right)\right)\right] + 4\pi\Delta\rho \left[\int_{R_{S}}^{R_{L}} V_{sf}(z_{0})r^{2}dr - \frac{1}{2}\int_{R_{S}}^{R_{L}} \exp\left(a(r - R_{L})\right)V_{sf}(z_{0})r^{2}dr\right] + 2\pi\Delta\rho \int_{R_{L}}^{\infty} \exp\left(-a\left(r - R_{L}\right)\right)V_{sf}(z_{0})r^{2}dr$$
(4.32)

The above scheme (from Eq. (4.17) to Eq.(4.32)), therefore, can be used to obtain the free energy of heterogeneous nucleation on a spherical solid substrate for any contact angle ranging from $\theta_C = 0 \rightarrow 180$.

In the present model (**Fig.4.1**), the parameter z_0 in the expression of $V_{sf}(z_0)$, can be replaced by *r* is given as

$$z_0 = (r^2 + 2rR_S \cos(\theta_S) \cos(\theta) + R_S^2 \cos^2(\theta_S))^{\frac{1}{2}} - R_S + \sigma .$$
(4.33)

Therefore, the minimum distance (z_0) between the particle and surface of the solid is now σ and not zero, so that the integral in Eq.(4.29) can be run from $r = R_S(\theta)$ (see **Fig.4.1**). While considering the wetting phenomena, the replacement of z_0 by r is given as $z_0 = r - R_S + \sigma$, so that the integral can be run from $r = R_S$ in Eq.(4.32).

4.3.3 Nucleation in absence of solid substrate ($R_s = 0$)

The nucleation without solid substrate can be alternatively represented by the seeding phenomena where the radius of the solid substrate (R_S) has been reduced to zero. It is clear from Eq.(4.7), that the solid fluid interaction energy term $V_{sf}(z_0) = 0$ when $R_S = 0$. The nucleation free energy of seeding by CNT (Eq.(4.16)) can therefore be written as

$$\Delta G_{V_L}(CNT) = -V_L \rho_L \Delta \mu + 4\pi R_L^2 \gamma_{LV} \quad , \tag{4.34}$$

which is nothing but the expression of nucleation free energy for homogeneous nucleation described by CNT.

The free energy of nucleation without substrate in the present DFT method can be obtained by applying the solid fluid interaction energy term $V_{sf}(z_0) = 0$ at $R_S = 0$ into Eq. (4.32) which is now expressed as

$$\Delta G_{V}(DFT) = -V_{L}\rho_{L}\Delta\mu + 2\pi\Delta\rho\Delta\mu \left[\frac{R_{L}^{2}}{a} - \frac{2R_{L}}{a^{2}} + \frac{2}{a^{3}} - \frac{2}{a^{3}}\exp(-aR_{L})\right] + \frac{\pi K\Delta\rho^{2}a^{2}}{2} \left[\frac{R_{L}^{2}}{a} + \frac{1}{2a^{3}} - \frac{1}{4a^{3}}\exp(-2aR_{L})\right].$$
(4.35)

The results of both CNT and DFT of nucleation without substrate obtained from the present general formulation are exactly identical with the results of the earlier work [see Chapter 2] on the theory of homogeneous nucleation.

4.3.4 Nucleation on spherical solid substrate of infinite radius $(R_S = \infty)$

It is clear from **Fig.4.1** that the angle $\theta_S = 0$ as $R_S \to \infty$ and therefore $R_S(\theta) = 0$ and $\theta_L = \theta_C$ (see Eq.(4.1)). The double spherical cap model is therefore converted to single spherical cap, where the cap is constructed only by the liquid and the polar radius vector $R_L(\theta)$ can be simply written as $R(\theta)$. The volume of the droplet, thus can be written as

$$V = \int_{0}^{2\pi} d\Phi \int_{0}^{\frac{\pi}{2}} \sin(\theta) d\theta \int_{0}^{R(\theta)} r^2 dr, \qquad (4.36a)$$

and also as

$$V = \frac{1}{3}\pi R_{L}^{3}(2 - 3\cos(\theta_{c}) + \cos^{3}(\theta_{c}))$$
(4.36b)

The solid fluid interaction energy term $V_{sf}(z_0)$, derived for spherical solid substrate becomes the well-known 9-3 potential while considering $R_S \rightarrow \infty$ (see Eq.(4.8)) which is expressed as

$$V_{sf}(z_0) = 4\pi\varepsilon_{sf}\rho_S\sigma^3 \left[\frac{1}{45}\left(\frac{\sigma}{z_0}\right)^9 - \frac{1}{6}\left(\frac{\sigma}{z_0}\right)^3\right].$$
(4.37)

Equation (4.15) representing the Gibbs free energy of formation of a droplet of volume V_L on a spherical solid surface, within the framework of CNT, is then expressed as

$$\Delta G_{V_L}(\text{CNT}) = -V_L \rho_L \Delta \mu + 2\pi R_L^2 (1 - \cos(\theta_C)) \gamma_{LV} + 2\pi \Delta \rho \int_0^{\frac{\pi}{2}} \sin(\theta) d\theta \int_0^{R_L(\theta)} V_{sf}(z_0) r^2 dr,$$
(4.38)

which is actually the Gibbs free energy of heterogeneous nucleation of a droplet of volume V_L on a flat surface of solid substrate with 9-3 solid-fluid interaction energy potential for $V_{sf}(z_0)$. Equation (4.25) can be simplified due to the consequences of $R_S \rightarrow \infty$ as

$$I_2 = \frac{\pi K \Delta \rho^2}{4} \left(C + \frac{1}{2C} - \frac{1}{4C} \exp\left(-2C\right) \right) \int_0^{\pi/2} \sin(\theta) d\theta \left\{ R(\theta) + \frac{1}{R(\theta)} \left(\frac{dR(\theta)}{d\theta}\right)^2 \right\}.$$
 (4.39)

The free energy of heterogeneous nucleation on the solid substrate of infinite radius can be obtained from Eq.(4.29) which is written as

$$\Delta G_{V_{L}}(DFT) = -V_{L}\rho_{L}\Delta\mu + \frac{3}{2}\Delta\rho\Delta\mu V_{L}\left(\frac{1}{C} - \frac{2}{C^{2}} + \frac{2}{C^{3}} - \frac{2}{C^{3}}\exp(-C)\right) + \frac{\pi K\Delta\rho^{2}}{4}$$

$$\left(C + \frac{1}{2C} - \frac{1}{4C}\exp(-2C)\right)\int_{0}^{\pi/2}\sin(\theta)d\theta \left\{R(\theta) + \frac{1}{R(\theta)}\left(\frac{dR(\theta)}{d\theta}\right)^{2}\right\} + 2\pi\Delta\rho$$

$$\int_{0}^{\pi/2}\sin(\theta)d\theta \left[\int_{0}^{R(\theta)}V_{sf}(z_{0})r^{2}dr - \frac{1}{2}\int_{0}^{R(\theta)}V_{sf}(z_{0})\exp\left(C\left(\frac{r}{R_{L}(\theta)} - 1\right)\right)r^{2}dr\right]$$

$$+ \frac{1}{2}\int_{R(\theta)}^{\infty}V_{sf}(z_{0})\exp\left(-C\left(\frac{r}{R_{L}(\theta)} - 1\right)\right)r^{2}dr$$

$$\left(4.40\right)$$

The above equations (Eq.(4.38) and (4.40)), obtained from the general expressions are the same as the one obtained directly in the case of heterogeneous nucleation on flat solid substrate [see Chapter 3].

4.4 Results and discussions

The present formalism is applied to a model L-J system and the coexistence densities and spinodal densities which predict the extent of supersaturation and metastibility limit of the fluid have been obtained from the temperature-density diagram shown in section 2.6 of chapter 2.

The optimized density profile for a given volume of droplet on the solid surface can be obtained by evaluating the parameter C (in Eq.(4.17)) through minimization of the free

energy of heterogeneous nucleation (Eq.(4.29)) with respect to this parameter. This minimized quantity represents the free energy of formation of the droplet.

The free energy of formation of the droplets of different volumes at different conditions such as size of the seed and strength of the solid-fluid interaction has been obtained by using both CNT and present DFT methods. The results of the size effect of seed on nucleation and the heterogeneous nucleation on convex solid surface by applying CNT are available in the earlier work of Fletcher [11] and Qian et.al [12], but the results reported by them corresponds to the critical cluster and nucleation barrier only. The strong attraction between the solid and the liquid was introduced only by considering the contact angle zero, which is very nice and ideal approach but not quantitative to differentiate the cases of two different and strongly adsorbing liquid on the solid surface. In our work, the solid-fluid interaction can be tuned by the parameter ε_{sf} present in the expression of $V_{sf}(z_0)$ and therefore the free energy of formation of two different liquids can be quantitatively distinguished. In addition to this, the shape of the nucleus (i.e. the contact angle) of any arbitrary size (from subcritical to supercritical) during the course of nucleation has been obtained, which gives an idea of the shape profile with the variation of size of the liquid as well as the solid sphere. Our results on the effect of the size of the solid sphere (R_S) and strength of solid-fluid interaction (ε_{sf}) at supersaturation S=4 in the framework of CNT have been plotted in Fig.4.5 and the same obtained through the present DFT method have been shown in Fig.4.6. From Fig.4.5, one can see that the nucleation is favored by some intermediate contact angle ($\theta_C \approx 90^\circ$) when the solid-fluid strength is not high i.e. $\varepsilon_{sf} = 1$ to 2 in case of CNT, though the seeding effect $(\theta_{C}=0)$ becomes favorable at higher size (supercritical nucleus). The seeding effect is significant when the value of ε_{sf} is high. In Fig. 4.5g - 4.5i, one can see that the droplet

formation is initiated at higher contact angle and then the nucleation and growth is favored by the seeding effect. From the results of CNT (Fig.4.5), it is clear that the seeding is not favored even at higher value of \mathcal{E}_{sf} , if the volume of the liquid is less. This is obvious, because of the bulk density and sharp density profile approximations considered in CNT, so that if the small volume of liquid completely covers the solid, then the liquid-vapor surface area to volume (actual volume of the liquid only) ratio is high and therefore seeding is not favored for low volume liquid in CNT. This observation is different in the present DFT (see Fig.4.6) with the chosen values of the parameters (R_S and ε_{sf}), where a diffuse density model has been considered and the liquid is free to reconstruct its density profile (unlike a constrained step like density in CNT). Though the liquid-vapor surface area to volume ratio is still high when the volume of the liquid is less, but due to the diffuseness of the interface, the positive surface energy unlike CNT cannot lead over the total negative energy due to the volume as well as the solid-fluid interaction energy and therefore the seeding is favored even in case of small droplet also within the chosen range of the parameters R_S and ε_{sf} . The vapor-liquid interfacial energy considered in CNT is $\gamma_{LV} = 1.24\epsilon/\sigma^2$, which has been obtained from ref [14]. In case of CNT, (see Fig. 5c,5f and 5i), spinodal decomposition observed when the solid-fluid interaction is high enough (i.e. in case of $\varepsilon_{sf} = 4$, not at $\varepsilon_{sf} = 1$ or 2). Similarly in case of DFT also, the barrier has been vanished when the value of $\epsilon_{sf} > 2$ (see Fig. **6a,6d** and **6g**) and also there is no barrier for larger seed size even at low ε_{sf} value (i.e. $\varepsilon_{sf} = 1$ or 2).



(a)



















Fig4.5. Plot of the free energy of formation as obtained by CNT as a function of the volume of the liquid drop at a given solid-fluid strength (ε_{sf}) and at different sizes of the solid sphere R_s . The results at $\varepsilon_{sf} = 1$ and Rs = 1, 2 and 4 are plotted in **Figs. 4.5a, 4.5b and 4.5c** respectively. Figures **4.5d, 4.5e and 4.5f** are for $\varepsilon_{sf} = 2$ and Rs = 1, 2 and 4 respectively and the results at $\varepsilon_{sf} = 4$ and Rs = 1, 2 and 4 are plotted in **Figs. 4.5g, 4.5h and 4.5i** respectively.











(d)







Fig4.6. Plot of the free energy of formation as obtained by DFT as a function of the volume of the liquid drop at a given solid-fluid strength (ε_{sf}) and at different sizes of the solid sphere R_s . The results at $\varepsilon_{sf} = 1$ and $R_s = 1$, 2 and 4 are plotted in **Figs. 4.6**a, **4.6**b and **4.6**c respectively. Figures **4.6**d, **4.6**e and **4.6**f are for $\varepsilon_{sf} = 2$ and $R_s = 1$, 2 and 4 respectively and the results at $\varepsilon_{sf} = 4$ and $R_s = 1$, 2 and 4 are plotted in **Figs. 4.6**g, **4.6**h and **4.6**i respectively.

4.5 Conclusions

A general theory for the size effect of the seed on the vapor to liquid nucleation of L-J fluid using DFT with square gradient approximation for the free energy functional have been presented here. The present methodology, though not completely analytical, with the use of some simple numerical integration, has been made overall simple by proper modeling of density and Helmholtz free energy density. The results of homogeneous nucleation have been obtained at one end of the seed size (zero size limit) whereas the heterogeneous nucleation on the flat surface is obtained on the other side (when the radius of the seed is infinity). A variational minimization of the free energy expression with respect to the parameter present in the density profile as well as the contact angle leads to the free energy of formation of the drop on the surface of the substrate. This method can thus be used to predict the shape, density profile and free energy for a given volume of the droplet including critical droplet, which provides an idea about the kinetics of nucleation. Spinodal decomposition has been observed either by increasing the strength of the solid-fluid interaction or by changing the size of the seed. The change of shape (i.e. contact angle) of the nucleating particle at different solid-fluid interaction energy and different size of the seed particle have been observed, which gives an idea of the shape profile in the course of nucleation. The effect of constrained (CNT) and unconstrained (DFT) density profile on the seeding effect has been also observed.

CHAPTER 5

Interfacial properties of vapor-liquid planar interface: Application to model and real fluid

5.1 Introduction

Surface tension is one of the most important properties of a fluid from the viewpoint of scientific and technological interest. The interfaces play a crucial role in some of the very important phenomena such as nucleation and hence in the fabrication of nanostructured materials. Therefore, the determination (experimental) and calculation (theoretical) of the surface tension have been of interest for a long time. The topic of understanding surface tension and other interfacial properties of fluid systems have been extensively discussed in the literature from time to time [48-50]. Although different theories viz, statistical mechanical theory [51-52], density functional theory (DFT) [53-57] etc. and molecular simulations [58-62], have been used for the investigation of interfacial properties of vapor liquid planar interface, it is found that the most versatile theory for this purpose is the DFT.

In the present work, DFT with square gradient correction with a model density and Helmholtz free energy density has been applied to investigate the interfacial properties of the vapor-liquid interface at coexistence condition along the lines of van der Waals and Cahn and Hilliard density functional formalism of the interface [**81**, **108**]. The density at the planar interface has been modeled in a way similar to that used in the case of curved interface of liquid droplet-vapor system discussed in Chapter 2-4. A double well type model for the local part of the Helmholtz free energy density has been proposed here. The proposed method has

been applied to L-J fluid and various interfacial properties such as surface tension, density profile, width of the interface etc. have been predicted. The problem has also been solved numerically to obtain the exact density profile and surface tension for L-J fluid.

The knowledge of surface tension of real fluids (e.g. water) is very important from both scientific and industrial consideration and obtaining the experimental value at any arbitrary temperature is not always feasible. Therefore, an accurate theoretical prediction of surface tension of real fluids is important and useful. Limiting the discussion to the most versatile theory for interfacial phenomena, viz. DFT, a gradient theory of inhomogeneous fluids for the prediction of the surface tension of water was proposed by Guerrero and Davis [118] and an approximate closed-form solution to the DFT approach has been presented by Mon and Stroud to calculate the surface tension of simple liquids, which was applied to liquid metals [119]. Sanchez derived a new equation relating the surface tension to isothermal compressibility and mass density, which was based on a generalized square-gradient approximation for the free energy density of a nonuniform fluid and was applied to various organic compounds as well as elemental and simple polyatomic fluids [120]. An extended mean-field density-functional theory of the liquid-vapour interface of water has been described by Yang and coworkers [121], while an extended van der Waals theory along the lines of square gradient DFT has been proposed by Muhlbacher to calculate the interfacial properties of water [122]. Jackson and coworkers [123] and also Gross [124] proposed a statistical associating fluid theory based DFT to investigate the interfacial properties of vapor- liquid interface. Molecular dynamics simulation has been carried out by Dhir and coworkers [125] to calculate the density and surface tension of water. The accurate calculation of the surface tension of water or other real fluids by the methodologies discussed above, however, requires a detailed microscopic knowledge of the fluids and related

calculations. It is found to be difficult to arrive at a simple and general expression for the surface tension through these theories and simulations.

In the present work, a general method of calculating the surface tension of real fluids has been proposed with the use of some suitable approximations [112]. The method has been applied on two types of liquids, viz i) water and heavy water and ii) argon and the results are found to be quite accurate throughout the temperature range from triple point to the critical point. The densities of water and heavy water at different temperature have been collected from Refs. [126] and [127], which are found to be very close to the experimental values. The experimental results of surface tension of light water and heavy water have been taken from Refs. [128] and [127] respectively. The experimental densities and surface tension of argon are taken from the work of Lee and Barker [129] and Ref. [130]. The results obtained in the present work are found to be quite close to the experimental values.

5.2 Density functional theory of surface tension

A diffuse density model at the liquid - vapor interface (as used in Ref. [**109-111**] in our works on nucleation) with the density profile

$$\rho(z) = \rho_L - \frac{\left(\rho_L - \rho_V\right)}{2} \exp(az), \text{ for } -\infty \le z \le 0$$
(5.1a)

and

$$\rho(z) = \rho_V + \frac{\left(\rho_L - \rho_V\right)}{2} \exp(-az), \text{ for } 0 \le z \le \infty$$
(5.1b)

have been considered, where ρ_V is the density of the vapor phase, ρ_L is the density of the liquid phase and the parameter *a* in the density expression is a measure of the degree of

diffuseness which is determined by minimizing the surface free energy of the liquid-vapor interface with respect to this parameter variationaly. The density profile given by Eq. (5.1) is shown in Fig. 5.1 in arbitrary units. The present density profile is a continuous function of z and the expression for $\rho(z)$ and its first derivative with respect to z at z = 0 as obtained from either of Eqs. (5.1), are given, respectively, by

$$\rho(z) = \frac{\left(\rho_L + \rho_V\right)}{2} \text{ at } z = 0 \text{ and } \frac{d\rho(z)}{dz} = -\frac{\left(\rho_L - \rho_V\right)a}{2} \text{ at } z = 0.$$



Fig.5.1 Density profile at the liquid – vapour interface in arbitrary units

The surface tension of the planar interface (γ_{∞}) within the framework of density functional theory with square gradient approximation can be expressed as,

$$\gamma_{\infty} = \int_{-\infty}^{+\infty} f(\rho(z)) \, dz + \frac{1}{2} K \int_{-\infty}^{+\infty} (\nabla \rho(z))^2 \, dz - \int_{-\infty}^{0} f_L \, dz - \int_{0}^{+\infty} f_V \, dz \quad , \tag{5.2}$$

where $f(\rho(z))$ is the local Helmholtz free energy density of the nonuniform system and f_L and f_V are the free energy density of the uniform liquid and vapor phase respectively and *K* is the coefficient of the square gradient term. A double well type Helmholtz free energy density has been proposed here for the term $f(\rho(z))$ which is written as,

$$f(\rho(z)) = f_0 + \mu_0 (\rho(z) - \rho_0) - d_2 (\rho(z) - \rho_0)^2 + d_4 (\rho(z) - \rho_0)^4, (5.3)$$

where μ_0 is the chemical potential of any of the phases ($\mu_L = \mu_V = \mu_0$, at equilibrium) and the parameters ρ_0 , f_0 , d_2 and d_4 are evaluated from the thermodynamics of the fluid phase. The first derivative of $f(\rho(z))$ with respect to density is the chemical potential μ as given by

$$\mu = \mu_0 - 2d_2(\rho - \rho_0) + 4d_4(\rho - \rho_0)^3 \quad . \tag{5.4}$$

From the thermodynamics of two phase equilibrium system, μ should be equal to μ_0 at $\rho = \rho_V$ and $\rho = \rho_L$ which leads to the relations $\rho_0 = (\rho_L + \rho_V)/2$, i.e., the average density, ρ_{av} and a relation between d_2 and d_4 as

$$\frac{d_2}{d_4} = \frac{1}{2} \left(\rho_L - \rho_V \right)^2 \quad . \tag{5.5}$$

Similarly the Helmholtz free energy density $f(\rho(z))$ should satisfy the boundary conditions $f(\rho(z)) = f(\rho_L)$ at $\rho = \rho_L$ and $f(\rho(z)) = f(\rho_V)$ at $\rho = \rho_V$, which again leads to another relation between f_0 and d_4 given by

$$f_0 = \frac{d_4}{16} \left(\rho_L - \rho_V \right)^4 + f_{av} \qquad , \qquad (5.6)$$

where $f_{av} = (f(\rho_L) + f(\rho_V))/2$. The model free energy density of the two phase region has been shown in **Fig. 5.2** (in arbitrary unit).



Fig.5.2. The dashed curve corresponds to the model free energy density for the two phase region used in the present work. The solid line is a linear interpolation between $f_L \equiv f(\rho_L)$ and $f_V \equiv f(\rho_V)$ at densities ρ_L and ρ_V respectively.

From the above relations (Eqs. (5.5) and (5.6)), it is clear that there is only one unknown parameter in Eq. (5.3) which has to be obtained for the evaluation of free energy density of the two phase regions $f(\rho(z))$, with respect to that of the one phase regions (i.e., $f(\rho_L)$ and $f(\rho_V)$). This parameter can be chosen to be f_0 in Eq.(5.3), which represents the free energy density at the average density ρ_{av} , and is proposed to be obtain by evaluating the free energy density using suitable equation of state evaluated at ρ_{av} .

Using the model density profile (Eqs.(5.1)) and model free energy density functional (Eq.(5.3)) in the interfacial energy expression (Eq.(5.2)), Eq. (5.2) can be rewritten as

$$\gamma_{\infty} = \int_{-\infty}^{0} \left(f(\rho(z)) + \frac{1}{2} K(\nabla \rho(z))^{2} - f_{L} \right) dz + \int_{0}^{+\infty} \left(f(\rho(z)) + \frac{1}{2} K(\nabla \rho(z))^{2} - f_{V} \right) dz .$$
 (5.7)

Using the model density profile (Eqs.(5.1)), the model free energy density functional (Eq.(5.3)) and the relations obtained in Eqs. (5.5) and (5.6), in the above interfacial energy expression (Eq.(5.7)) and simplification, one can obtain the surface tension as

$$\gamma_{\infty} = \left(\frac{11}{96}\right) \frac{d_4 (\Delta \rho)^4}{a} + \frac{Ka(\Delta \rho)^2}{8} \quad , \tag{5.8}$$

where, $\Delta \rho = (\rho_L - \rho_V)$ and the parameter *a* can be obtained by minimizing Eq. (5.8) with respect to *a*, so that $d\gamma_{\infty}/da = 0$, and the expression for the parameter *a* is obtained as

$$a = \left(\frac{11}{12}\right)^{\frac{1}{2}} \left(\frac{d_4}{K}\right)^{\frac{1}{2}} \left(\Delta\rho\right) \quad . \tag{5.9}$$

Using Eq.(5.9) in Eq. (5.8) , the expression of surface tension is obtained as

$$\gamma_{\infty} = \frac{1}{24} \left(33 \ K d_{4} \right)^{\frac{1}{2}} \left(\Delta \rho \right)^{3} .$$
(5.10)

Equations (5.1)-(5.10) thus provide a scheme for obtaining the surface tension of a fluid provided the values of the coefficient of the square gradient term (*K*), the parameter d_4 and vapor-liquid coexistence densities are known. The coefficient of the square gradient term, K, in Eq. (5.10), can be approximately written as **[114,115**]

$$K = -\left(\frac{1}{6}\right) \int \Phi(r) r^2 d\mathbf{r}$$
(5.11)

where $\Phi(r)$ denotes the attractive potential, which for the L-J fluid system has been already mentioned in chapter 2.

The present formalism when applied to the L-J fluid, the parameter d_4 in the double well free energy density functional model has been calculated via Eq.(5.6) where the parameter f_0 is

obtained by evaluating the free energy density using the same equation of state (i.e, Carnahan- Starling) with L-J correction as $f(\rho) = f_h(\rho) - (1/2) \alpha \rho^2$ evaluated at ρ_{av} .

The thickness of the interface D, in 10-90 convention is the distance $D = R_V - R_L$, where R_V and R_L are distances from the centre of the drop to the poitns, where $\rho(R_V) = \rho_V + 0.1(\rho_L - \rho_V)$ and $\rho(R_L) = \rho_V + 0.9(\rho_L - \rho_V)$ respectively. In our present model, R_L and R_V are obtained from Eqs. (5.1a) and (5.1b) and are, $R_L = \ln(0.2)/a$ and $R_V = -\ln(0.2)/a$. The interface thickness thus can be written as

$$D = -\frac{2\ln(0.2)}{a}$$
(5.12)

While the discussion so far is based on the model density profile, we have also obtained the density profile as well as the surface tension numerically. For this purpose, the surface tension of the planar interface is first expressed in terms of the Helmholtz free energy as

$$\gamma_{\infty} = \int_{-\infty}^{+\infty} (f(z) - f^{L,V}) dz$$
(5.13)

where $f(z) = f(\rho(z)) + \frac{1}{2} K (\nabla \rho)^2$, is the Helmholtz free energy density of the liquid-vapor two phase system and $f^{L,V}$ is the Helmholtz free energy density on either side of the dividing surface (Superscript L stands for the liquid side and V for the vapor side). The local part of the free energy $f(\rho(z))$ is obtained from the present double well model (Eq.(5.3)). The density profile and surface tension have then been obtained by minimizing Eq.(5.13) and solving the resulting Euler-Lagrange equation numerically by using the suitable boundary conditions i.e, $\rho(-\infty) = \rho_L$ and $\rho(\infty) = \rho_V$ and the Lagarange multiplier which in this case is the chemical potential of the vapor- liquid system.

5.3 Calculation of surface tension of real fluids

The formalism discussed in section 5.2 has been further manipulated to obtain the surface tension of real fluids by applying some suitable approximations. Using Eq.(5.5), Eq.(5.10) can be alternatively written as

$$\gamma_{\infty} = \left(\frac{11}{96}\right)^{\frac{1}{2}} \left(d_2 \ \mathrm{K}\right)^{\frac{1}{2}} \left(\Delta\rho\right)^2 \quad . \tag{5.14}$$

Detailed calculations are, however, required to obtain K and d_2 , which is more difficult when the liquid is complex like water. The problem has been overcome in the present work with the use of some approximation and modeling as follows.

The coefficient d_2 can in general be temperature dependent. Since the depth of the well of the free energy density (Eq.(5.2)) is maximum at the triple point (T_t), the values of d_2 and d_4 are maximum at the triple point. Further the difference in density of the liquid and vapor is zero at the critical point (T_c) i.e, $\Delta \rho = 0$ at $T = T_c$, and therefore it is clear from Eq.(5.5) that $d_2 = 0$ at $T = T_c$. Thus we propose here, a linear dependence of d_2 on the temperature in the range of triple point to critical point, as given by

$$d_{2} = C \frac{\left(T_{C} - T\right)}{\left(T_{C} - T_{t}\right)} , \qquad (5.15)$$

where C is the value of d_2 at T = T_t. The surface tension at the triple point ($\gamma_{\infty,t}$) is thus

$$\gamma_{\infty,t} = \left(\frac{11}{96}\right)^{\frac{1}{2}} \left(C \ \mathrm{K}\right)^{\frac{1}{2}} \left(\Delta \rho_t\right)^2 ,$$
 (5.16)

where, $\Delta \rho_t$ is the difference between the densities of the liquid and vapor at the triple point. The expression for C is thus given by

$$C = \left(\frac{96}{11}\right) \frac{1}{K} \frac{\gamma_{\infty,t}^{2}}{\left(\Delta\rho_{t}\right)^{4}}$$
(5.17)

Using Eqs. (5.15) and (5.17), Eq.(5.14) can be rewritten as

$$\gamma_{\infty} = \gamma_{\infty,t} \frac{\left(\Delta\rho\right)^2}{\left(\Delta\rho_t\right)^2} \left(\frac{\left(T_c - T\right)}{\left(T_c - T_t\right)}\right)^{\frac{1}{2}} \qquad (5.18)$$

Equation (5.18) is the general expression for calculating the surface tension of a liquid, using the available data on the surface tension at the triple point and coexistence densities, at different temperatures. It is clear from Eq.(5.18), that no microscopic knowledge and details calculations are required provided the surface tension at the triple point and coexistence densities are available.

It will also be of interest to consider the temperature scaling of γ_{∞} as given by Eq.(5.18), as the temperature approaches the critical point. Considering the explicit temperature dependence (Tc - T)^{1/2}, as well as an implicit temperature dependence of $(\Delta \rho)^2$ through the well know relation [49,115] $\Delta \rho = (\rho_L - \rho_V) \sim (Tc - T)^{1/2}$ near the critical point, one has the result $\gamma_{\infty} \sim (Tc - T)^{3/2}$, which is also predicted by the mean field theory.

5.4 Results and discussions

The formalism presented in section 5.2 is implemented here by considering application to a model L-J system. Equation (5.10) can be used to calculate the interfacial energy of vapor-liquid interface at coexistence condition. The coexistence densities are obtained from the temperature-density diagram shown in chapter 2. The surface tension of the planar

interface as obtained by using the model density (Eq.(5.10)) and by using the exact density profile obtained numerically, corresponding to minimization of Eq.(5.13), is found to be quite consistent for different temperature-ranges, as presented in Fig.5.3, and compared with the results of Monte-Carlo simulation and experiment [58] as well as with the prediction of Oxtoby [14]. As the WCA scheme has been used to calculate the coexistence densities, which predicts the critical temperature [14] to be higher than its actual value, the present calculated surface tension vanishes at a temperature which is higher than the experimental result (on real argon).



Fig.5.3 Surface tension of planar interface as a function of temperature. Present work (triangle), MF-DFT by Oxtoby [14] (dotted line), MC simulation from Ref [**58**] (open circle), Experimental results [58] (square) and exact numerical solution of the present work (open stars)
The optimized density profile obtained by implementing the optimized value of the parameter a (obtained from Eq. (5.9)) into Eqs. (5.1) is shown in **Fig. 5.4** at different values of temperature. The optimized model density and the exact numerically obtained density at reduced temperature T*=0.7 have also been plotted in **Fig. 5.5** and it is observed that the exact density is not much different from the model density for this particular choice of free energy density model. The thickness of the interface as calculated from Eq.(5.12) has been plotted in **Fig. 5.6**, where it is observed that the calculated thickness values based on different definitions of thickness are in good agreement with the predictions of the earlier theories and simulations. A very good agreement between the free energy density using the mean-field equation of state (EOS) (Carnahan-Starling form used for the hard sphere part in the present case) and same using the present optimized model free energy density is observed as shown in **Fig. 5.7** at reduced temperature T* = 0.7.



Fig 5.4 Density profile of planar interface at different values of reduced temperatures.



Fig.5.5 Model density profile and numerical density profile of planar interface at reduced temperature T*=0.7.



Fig.5.6 Thickness of the interface as a function of temperature. Present work for planar interface (open squares), for spherical interface (open triangles) and planar interface by Telo da Gama[**131**] (open circles) considering 10-90 convention of thickness measurement.

The thickness defined as $D = -(\rho_L - \rho_V)/[d\rho(z)/dz]_{z = z0}$ as reported by Chapela et al (Ref [59]) and compared with the present work (open diamonds), the results from MC and MD simulation are denoted by solid triangle (MC 255 molecules), stars (MD 255 molecules), solid circles (MD 1020 molecules) and hexagon (MD 4080 molecules).



Fig. 5.7 The Helmholtz free energy density as a function of density of two phases equilibrium system at reduced temperature $T^*=1.0$. The dotted line is the optimized result of the present work and the solid line is obtained from equation of state considered in the present work.

While considering the real fluids, Eq. (5.18) is implemented here by calculating the surface tension of ordinary water, heavy water and argon throughout the temperature range from triple point to the critical point. The surface tension at the triple point and the coexistence densities of vapor and liquid at any temperature are required for calculating the surface tension using the present prescription irrespective of the nature of the liquid. These values (i.e. surface tension at the triple point and the coexistence densities at any temperature) have been taken from the literature, viz. Refs.[126] and [128] for ordinary water and Ref.[127] for heavy water and Refs [129] and [130] for liquid Argon. The calculated surface tension of ordinary water as a function of temperature is shown in Fig. 5.8. The present calculated results have been compared with the experimentally measured surface tension (data from

Ref.[128]) and it is clear from the plot that the calculated surface tension is in very good agreement with the experimental results. The comparison between the calculated and experimental results on surface tension of heavy water is shown in Fig. 5.9. The experimental densities and surface tension of heavy water have been taken from Ref.[127]. The present approach is then applied to another type of fluid such as liquid argon and the results are plotted in Fig. 5.10. The experimental densities and surface tensions of argon have been taken from Refs. [129] and [130].



Fig.5.8 The surface tension of ordinary water as a function of temperature. The present calculated values are shown by square and the experimental values are denoted by the open circles.



Fig.5.9 The surface tension of heavy water as a function of temperature. The present calculated values are shown by open circles and the experimental values are denoted by the solid squares.



Fig. 5.10 The surface tension of argon as a function of temperature. The present calculated values are shown by solid sphere and the experimental values are denoted by the open squares.

5.5 Conclusion

The interfacial properties such as interfacial energy (surface tension), density profile, interface thickness for the vapor-liquid planar interface at coexistence condition have been investigated here based on DFT with square gradient approximation for the free energy functional, which is commonly used for the study of nonuniform fluids, interfaces etc. A double well type Helmholtz free energy functional for the local part and a diffuse density profile at the interface, which are considered to be the suitable free energy and the density model respectively for the two phase system (coexistence), have been used in this work. Since the model free energy density is very close to that obtained from EOS, the present modeling is useful for one-component two-phase system. We have also proposed here a scheme to calculate the surface tension of real fluids quite accurately at any arbitrary temperature ranging from the triple point to the critical point by using DFT with square gradient approximation which is very common for the study of interfaces. A double well type Helmholtz free energy functional for the local part and an exponential density profile at the interface, which are found to be suitable for two phase equilibrium system, have been used in this work. The work is completely analytical and a simple and general expression for the surface tension has been arrived at, which requires the coexistence densities of liquid and vapor at the temperature of interest and surface tension data at the triple point temperature as input. The present approach, however, has been applied on a few real fluids such as ordinary water, heavy water and argon in this work, but it can be extended to calculate the surface tension of any other fluid system with the available coexistence and triple point data. This work is able to calculate the surface tension of real fluids with a significant accuracy, without any detailed microscopic knowledge and calculations. Therefore, this approach can be a useful simple approach for calculating the surface tension of such fluids.

CHAPTER 6

Density functional theory of size-dependent interfacial properties of Lennard-Jones fluids

6.1 Introduction

The importance of the knowledge of the interfacial properties of macroscopic and microscopic system in science and technology is well understood. In the context of the present thesis the interfacial properties play a crucial role in nucleation phenomena and thereby in the fabrication of nanostructured materials. Although the experiment can be performed for bulk sized system (i.e, for planar interface), in order to get an idea of the interfacial properties for small sized systems (i.e, for curved interfaces), theoretical predictions are of crucial importance. Different theories have been developed for the investigation of interfacial properties of vapor liquid planar interface (discussed in chapter 5). The idea of considering a planar interface no longer works when the system of interest is small in size. For such a system one has to consider a curved interface instead of a planar one and for liquid- vapor two phase system, it can be assumed that the interface is spherically curved. This curvature dependence of surface properties was first mentioned by Gibbs [63] and later developed by Tolman [64-66]. Tolman derived a simple relation between the surface tension γ and the radius R_s of the surface of tension and introduced a parameter δ which is the distance between this surface and the equimolar dividing surface with radius R_e, which divides the fluid into two homogeneous parts, the inner one with the liquid density and the outer one, with the vapor density. Density functional theory has been utilized time to time **[69-73]** for the investigation of interfacial properties of liquid droplet-vapor system. Many

molecular simulation (Monte Carlo as well as molecular dynamics) strategies had also been developed to investigate the size dependence of interfacial properties [74-77].

Although there have been a series of publications on the size-dependent surface tension, in the present work proposes a simple and analytical approach for evaluating the sizedependent interfacial properties and temperature density $(T-\rho)$ curve for a droplet-vapor equilibrium system. The methodology and the modeling of density profile (exponential density) and local Helmholtz free energy density (double well type) considered for the investigation of planar interface have been implemented here with suitable modification to obtain the surface tension of the stable droplet, i.e, at droplet-vapor coexistence and related coexistence densities of the liquid droplet and vapor phases. One of the conditions of the stable droplet is that, the system will obey Laplace relation as $\Delta P = 2 \gamma_s R_s$, (where ΔP is the pressure difference between the liquid and vapor phases, R_s is the radius of surface of tension and $\gamma_s = \gamma(R_s)$ is the associated surface tension. In the present work, we have considered zero value for the Tolman length (similar to ref [73,132]) so that the surface tension can be calculated at equimolar dividing surface R_e , and the associated surface tension is $\gamma_e = \gamma(R_e)$. The consideration of the large droplet gives an analytical expression for the surface tension (corresponding to planar interface) and related density profile. The present theory is then applied to the L-J fluid and the results obtained in this work for planar as well as spherical interfaces are shown to be consistent with the other earlier works.

6.2 Condition of liquid droplet-vapor equilibrium

The condition of mechanical stability of a drop of radius R (which can also be called as classical drop with well-defined radius R so that $\rho(r) = \rho_L$ for $0 \le r \le R$ and $\rho(r) = \rho_V$ for r >

R, where ρ_L and ρ_V are the densities of the bulk liquid and vapor respectively) is expressed by the Laplace law, i.e. $P_L(\rho_L) - P_V(\rho_V) = 2 \gamma/R$, where P stands for the pressure of liquid and vapor denoted by subscript L and V respectively and γ is the surface tension of the bulk system. Since in the present investigation, unlike a bulk liquid-vapor equilibrium system, a stable microscopic liquid drop suspended in its vapor, i.e. equilibrium between the tiny liquid droplet and its vapor phase has been considered, therefore the condition of the stability of the classical droplet may not work. In the case of a microscopic droplet, the definition of the drop radius (or the surface) is a difficult task because of the slowly decaying nature of the density at the interface and therefore different logic has been introduced for considering the surface of the droplet. Though the Laplace equation ($P_L(\rho_L) - P_V(\rho_V) = 2 \gamma/R$) is only valid for a macroscopic drop with well-defined radius, Gibbs introduced the idea of surface tension and the radius of the droplet in such a way that the Laplace equation retains its form for microscopic droplet as well, i.e. $P_L(\rho_L) - P_V(\rho_V) = 2 \gamma_S / R_S$, where R_S is the radius of the surface of tension and $\gamma_S = \gamma(R_S)$ is the associated surface tension.

The condition of equilibrium between a stable microscopic droplet and the vapor is therefore written as

$$\mu_L(\rho_L) = \mu_V(\rho_V) \tag{6.1a}$$

$$P_L(\rho_L) - P_V(\rho_V) = \frac{2\gamma_S}{R_S}$$
(6.1b)

where μ and *P* stand for the chemical potential and pressure respectively for the liquid (*L*) and vapor (*V*) phases at the corresponding densities ρ_L and ρ_V . As already mentioned, the Tolman length has been ignored here, and thus γ_s and R_s in Eq.(6.1b) can be replaced by the

corresponding terms which are related to equimolar dividing surface i.e, with γ_e and R_e and Eq.(6.1b) can be rewritten as

$$P_L(\rho_L) - P_V(\rho_V) = \frac{2\gamma_e}{R_e}$$
 (6.1c)

For the bulk system, the radius $R_e = \infty$, and the condition of equilibrium becomes $\mu_L(\rho_L) = \mu_V(\rho_V)$ and $P_L(\rho_L) = P_V(\rho_V)$.

6.3 Density model for the vapor-liquid spherical interface

The liquid (droplet)-vapor two phase (one component) system resembles the vaporliquid homogeneous nucleation discussed in chapter1 except that in this case the droplet is in equilibrium with the vapor whereas nucleation involves a non-equilibrium phenomenon with metastable vapor phase (supersaturated). The density profile of the present droplet-vapor two phase equilibrium system has therefore been modeled in a similar way as done in DFT of homogeneous nucleation (see Eqs. (2.1) in chapter 2), which is expressed as

$$\rho(r) = \rho_L - \frac{\left(\rho_L - \rho_V\right)}{2} \exp(a(r - R_{av})) , \text{ for } 0 \le r \le R_{av}$$
(6.2a)

and

$$\rho(r) = \rho_V + \frac{\left(\rho_L - \rho_V\right)}{2} \exp(-a(r - R_{av})) , \text{ for } r > R_{av}$$
(6.2b)

where ρ_V is the density of the vapor phase and ρ_L is the density of the liquid (droplet) phase at coexistence and R_{av} is the distance from the centre of the drop to the point where the density is the average of the liquid and vapor densities. The parameter *a* in the density expression which is a measure of the degree of diffuseness is determined by minimizing the surface free energy of the droplet-vapor interface with respect to the variation of this parameter. In **Fig. 6.1**, the density profile given by Eq.(6.2) is shown for specific value of the parameter *a* = 0.5

and $R_{av} = 5$. The density profile that we assume here is a continuous function of r and the expression for $\rho(r)$ and its first derivative with respect to r at $r = R_{av}$, as obtained from either of Eqs.(6.2), are given respectively by

$$\rho(r) = \frac{\left(\rho_L + \rho_V\right)}{2} \quad \text{and} \quad \frac{d\rho(r)}{dr} = -\frac{a\left(\rho_L - \rho_V\right)}{2} \quad at \ r = R_{av} \tag{6.3}$$



Fig. 6.1 Density profile $\rho(r)$ of a liquid droplet. The solid line represents the equimolar division of liquid and vapor phases with equimolar radius R_e and the dashed line is for the model used in the present work with $R_{av}=5$ and an arbitrary value of a = 0.5. Reduced units are used for the plot.

The relation between R_{av} and the equimolar radius R_e can be obtained from the conservation of density normalization, as given by

$$\int_{0}^{\infty} \rho(r)r^{2}dr = \int_{0}^{R_{e}} \rho_{L}r^{2}dr + \int_{R_{e}}^{\infty} \rho_{V}r^{2}dr .$$
(6.4)

For the given density profile $\rho(r)$ of Eqs.(6.2), the expression for R_e is given by

$$R_{e} = \left(3\left(\frac{2R_{av}}{a^{2}} + \frac{\exp(-aR_{av})}{a^{3}}\right) + R_{av}^{-3}\right)^{\frac{1}{3}},$$
(6.5)

and this radius R_e is used here as a measure of the size of the droplet.

6.4 Density functional theory of surface tension for vapor-liquid spherical interface

The total Helmholtz free energy of the nonuniform two phase system including the interface, F_{INT} , can be expressed by using DFT with square gradient approximation as

$$F_{INT} = \int f(\rho(r))d\mathbf{r} + \frac{1}{2}K\int (\nabla\rho(r))^2 d\mathbf{r}, \qquad (6.6)$$

where $f(\rho(r))$ in the first term, is the local Helmholtz free energy density, while the second term represents the square gradient correction. Equation (6.6) can be rewritten on the basis of the present density model as

$$F_{INT} = 4\pi \int_{0}^{R_{av}} f(\rho(r)) r^{2} dr + 2\pi K \int_{0}^{R_{av}} (\nabla \rho(r))^{2} r^{2} dr + 4\pi \int_{R_{av}}^{\infty} f(\rho(r)) r^{2} dr + 2\pi K \int_{R_{av}}^{\infty} (\nabla \rho(r))^{2} r^{2} dr \quad .$$
(6.7)

The total Helmholtz free energy (F_0) of the same system, without consideration of the interface, can be expressed by the consideration of the equimolar dividing surface as

$$F_{0} = 4\pi \int_{0}^{R_{e}} f(\rho_{L}) r^{2} dr + 4\pi \int_{R_{e}}^{\infty} f(\rho_{V}) r^{2} dr \quad .$$
(6.8)

The total interfacial Helmholtz free energy, arOmega , thus can be expressed as

$$\Omega = F_{INT} - F_0 . \tag{6.9}$$

Like planar interface (see chapter 5), a double well model for the local Helmholtz free energy density $f(\rho(r))$ has been proposed for using in Eq.(6.7), as

$$f(\rho(r)) = f_0 + \mu_0 (\rho(r) - \rho_0) - d_2 (\rho(r) - \rho_0)^2 + d_4 (\rho(r) - \rho_0)^4 , \qquad (6.10)$$

by considering an expansion around a density ρ_0 . Here μ_0 is the chemical potential of any of the phases ($\mu_L = \mu_V = \mu_0$ at equilibrium) and ρ_{av} is the average of the liquid density (at the centre) and the vapor density. The parameters ρ_0 , f_0 , d_2 and d_4 in Eq.(6.10) are evaluated from the thermodynamics of the fluid phase.

The derivative of $f(\rho(r))$ with respect to density is the chemical potential μ and is given by

$$\mu = \mu_0 - 2d_2(\rho - \rho_0) + 4d_4(\rho - \rho_0)^3 \quad . \tag{6.11}$$

From the thermodynamics of fluids, μ should be equal to μ_0 at $\rho = \rho_V$ and $\rho = \rho_L$ which leads to the relations $\rho_0 = (\rho_L + \rho_V)/2$, i.e the average density, and

$$\frac{d_2}{d_4} = \frac{1}{2} \left(\rho_L - \rho_V \right)^2 . \tag{6.12}$$

The Helmholtz free energy density $f(\rho(r))$ should satisfy the boundary conditions corresponding to the single phase region, viz $f(\rho(r)) = f(\rho_L)$ at $\rho = \rho_L$ and $f(\rho(r)) = f(\rho_V)$ at ρ = ρ_V , which again leads to another relation between f_0 and d_4 given by

$$f_0 = \frac{d_4}{16} \left(\rho_L - \rho_V\right)^4 + f_{av} \quad , \tag{6.13}$$

where $f_{av} = (f(\rho_L) + f(\rho_V))/2$. The model free energy density of the two phase region has been shown in **Fig.5.2** (chapter 5).From Eqs.(6.12) and (6.13), it is clear that there is only one unknown parameter in Eq.(6.10) for the evaluation of free energy density of the two phase regions $f(\rho(r))$, with respect to that of the one phase regions (i.e, $f(\rho_L)$ and $f(\rho_V)$). This parameter can be chosen to be f_0 in Eq.(6.10), which represents the free energy density at the

average density ρ_{av} , which we propose to obtain here by evaluating the free energy density using suitable equation of state evaluated at ρ_{av} .

The total interfacial energy Ω , is obtained by implementing the model densities Eq.(6.2) and the model double well type free energy Eq.(6.10) in Eq.(6.9) which can now be written as

$$\Omega = \left(\frac{4\pi}{3}\right) \mu \Delta \rho (R_{av}^{3} - R_{e}^{3}) -2\pi \mu \Delta \rho \left(\int_{0}^{R_{av}} \exp(a(r - R_{av}))r^{2}dr - \int_{R_{av}}^{\infty} \exp(-a(r - R_{av}))r^{2}dr\right) + \left(d_{4}(\Delta \rho)^{4}\pi + \frac{\pi(\Delta \rho)^{2}a^{2}K}{2}\right) \left(\int_{0}^{R_{av}} \exp(2a(r - R_{av}))r^{2}dr + \int_{R_{av}}^{\infty} \exp(-2a(r - R_{av}))r^{2}dr\right) - d_{4}(\Delta \rho)^{4}\pi \left(\int_{0}^{R_{av}} \exp(3a(r - R_{av}))r^{2}dr + \int_{R_{av}}^{\infty} \exp(-3a(r - R_{av}))r^{2}dr\right) + \frac{d_{4}(\Delta \rho)^{4}\pi}{4} \left(\int_{0}^{R_{av}} \exp(4a(r - R_{av}))r^{2}dr + \int_{R_{av}}^{\infty} \exp(-4a(r - R_{av}))r^{2}dr\right),$$
(6.14)

where $\Delta \rho = \rho_L - \rho_V$. On evaluation of the integrals, Eq.(6.14) can be rewritten as

$$\Omega = \left(\frac{4\pi}{3}\right) \mu \Delta \rho (R_{av}^{3} - R_{e}^{3}) - 2\pi \mu \Delta \rho \left(I_{1}(a, R_{av}) - I_{2}(a, R_{av})\right) + \left(d_{4}(\Delta \rho)^{4} \pi + \frac{\pi (\Delta \rho)^{2} a^{2} K}{2}\right) \left(I_{1}(2a, R_{av}) + I_{2}(2a, R_{av})\right) - d_{4}(\Delta \rho)^{4} \pi \left(I_{1}(3a, R_{av}) + I_{2}(3a, R_{av})\right) + \frac{d_{4}(\Delta \rho)^{4} \pi}{4} \left(I_{1}(4a, R_{av}) + I_{2}(4a, R_{av})\right)$$
(6.15)

where the integrals denoted by I_1 and I_2 are given by

$$I_1(a,R) = \int_0^R \exp(a(r-R))r^2 dr = \frac{R^2}{a} - \frac{2R}{a^2} + \frac{2}{a^3} - \frac{2\exp(-aR)}{a^3}$$
$$I_2(a,R) = \int_R^\infty \exp(-a(r-R))r^2 dr = \frac{R^2}{a} + \frac{2R}{a^2} + \frac{2}{a^3}.$$

After some algebra, Eq.(6.15) can be written in a simplified form and one can obtain the total interfacial energy as

$$\Omega = d_4 (\Delta \rho)^4 \pi \left(\left(\frac{11}{24} \right) - \frac{R_{av}^2}{a} + \left(\frac{635}{1728} \right) \frac{1}{a^3} - \frac{\exp(-2aR_{av})}{4a^3} + \frac{2\exp(-3aR_{av})}{27a^3} - \frac{\exp(-4aR_{av})}{128a^3} \right) + \frac{\pi(\Delta \rho)^2 a^2 K}{2} \left(\frac{R_{av}^2}{a} + \frac{1}{2a^3} - \frac{\exp(-2aR_{av})}{4a^3} \right) , \qquad (6.16)$$

which, on minimization with respect to the parameter a, provides $\Omega(R_e)$, the total interfacial free energy of a droplet (of radius R_e)-vapor interface and a_0 , the value of the parameter a for which Ω is minimum.

The surface tension at the equimolar dividing surface γ_e , can be obtained by dividing Eq.(6.16) by the interfacial area $(4\pi R_e^2)$, i.e.

$$\gamma_e = \frac{\Omega(R_e)}{4\pi R_e^2} \tag{6.17}$$

In order to obtain γ_{e} , one has to find the densities of the liquid droplet of radius R_{e} and its vapor at coexistence. These coexistence densities can be obtained by solving two simultaneous equations (Eqs.(6.1a) and (6.1b)), which again requires the knowledge of γ_{e} . The surface tension and coexistence densities for such a system can thus be obtained by solving these two equations self-consistently along with Eq.(6.17).

In order to obtain the surface tension of the spherical droplet with an exact density profile using the free energy model, however, one has to solve Eq.(6.6) numerically. The

density profile and surface tension have thus been obtained here by minimizing Eq.(6.6) and solving the resulting Euler-Lagrange equation numerically by using the suitable boundary condition i.e, $d\rho(0)/dr = 0$ and $\rho(\infty) = \rho_V$ and a suitable value for the Lagrange multiplier representing the size-dependent chemical potential of the concerned vapor-liquid system. In analogy to the planar interface (chapter 5), the thickness of the interface D, within 10-90 convention is the distance $D = R_V - R_L$, where R_V and R_L are the distances from the centre of the drop to the points, where $\rho(R_V) = \rho_V + 0.1(\rho_L - \rho_V)$ and $\rho(R_L) = \rho_V + 0.9(\rho_L - \rho_V)$ respectively. In our present model, R_L and R_V are obtained from Eqs.(2a) and (2b) and are, $R_L = R_{av} + \ln(0.2)/a$ and $R_V = R_{av} - \ln(0.2)/a$. The interface thickness thus can be written as

$$D = -\frac{2\ln(0.2)}{a},$$
(6.18)

which is identical with that of the planar interface in the present density model.

6.5 Surface tension of the planar interface: A large radius limit of the drop

The expressions for the total interfacial energy (Eq.(6.16)) and the surface tension (Eq.(6.17)) obtained in section 6.4 are valid for a droplet of any arbitrary size ranging from $R_e = 0$ to ∞ . The interface of an infinitely large liquid drop-vapor interface can be considered to be a planar interface, which results from the bulk liquid- vapor equilibrium condition obtained by dropping the term $(2\gamma_e/R_e)$ in Eq.(6.1b). i.e, $\mu_L(\rho_L) = \mu_V(\rho_V)$ and $P_L(\rho_L) = P_V(\rho_V)$, where ρ_L and ρ_V are the equilibrium bulk densities of the liquid and vapor respectively. In the case of a planar interface, the problem becomes one dimensional as the density varies along the perpendicular axis (say, z). For simplicity, we consider that the equimolar dividing surface is located at z = 0 with the negative side of the z axis as the liquid region and the

positive side as the vapor phase (see **Fig.5.1**, chapter 5) and the present model of density profile for this planar case can be expressed as (identical to Eqs.5.1, chapter 5)

$$\rho(z) = \rho_L - \frac{\left(\rho_L - \rho_V\right)}{2} \exp(az), \text{ for } -\infty \le z \le 0$$
(6.19a)

and

$$\rho(z) = \rho_V + \frac{\left(\rho_L - \rho_V\right)}{2} \exp(-az), \text{ for } 0 \le z \le \infty$$
(6.19b)

The equimolar dividing surface and the surface of average density for such density profile can be obtained from the following equations as $\int_{0}^{\infty} \rho(z)dz = \int_{0}^{z_{e}} \rho_{L}dz + \int_{z_{e}}^{\infty} \rho_{V}dz \text{ and } \rho(z)|_{z=z_{av}} = \frac{(\rho_{L} + \rho_{V})}{2}, \text{ where, both the equimolar}$

dividing surface and the average density are located at z = 0. In the context of the analogy of the planar interface with the spherical interface with infinitely large value of R_e , one can consider that the location of the equimolar dividing surface and the surface of average density is the same, i.e, $R_e = R_{av}$ in the present model, which is also clear from Eq.(6.5).

The surface tension of a planar interface can now be obtained by dividing Eq.(6.16) by the interfacial area $(4\pi R_e^2)$ and considering the limit of R_e being infinitely large. This leads to the surface tension of the planar interface γ_{∞} , analytically expressed as

$$\gamma_{\infty} = \left(\frac{11}{96}\right) \frac{d_4 (\Delta \rho)^4}{a} + \frac{Ka(\Delta \rho)^2}{8} \quad , \tag{6.20}$$

where the parameter *a* can be obtained by minimizing Eq.(6.20) i.e, by considering $d\gamma_{\infty}/da$ = 0, which leads to an expression for the parameter *a*, given by

$$a = \left(\frac{11}{12}\right)^{\frac{1}{2}} \left(\frac{d_4}{K}\right)^{\frac{1}{2}} (\Delta \rho)$$
(6.21)

This expression of a is then used in Eqs.(6.19) to obtain the density profile of the vaporliquid planar interface .

The final expression for the surface tension of planar interface can thus be obtained from Eqs.(6.20) and (6.21), leading to the result

$$\gamma_{\infty} = \frac{1}{24} (33 \, d_4 K)^{\frac{1}{2}} \, (\Delta \rho)^3 \, . \tag{6.22}$$

Equations (6.20), 6.21) and (6.22) related to the interfacial properties of the planar interface as derived by considering the large size limit of the drop of the DFT results for the surface tension of droplet are exactly identical (as it should be) with Eqs. (5.8), (5.9) and (5.10) in chapter 5 exclusively obtained for the surface tension of planar interface.

6.6 Results and discussions

The present formalism is applied to the L-J fluid, with the parameter d_4 in the double well free energy density functional model calculated via Eq.(6.13) where the parameter f_0 is obtained by evaluating the free energy density using the same equation of state (i.e, Carnahan- starling) with L-J correction as $f(\rho) = f_h(\rho) - (1/2) \alpha \rho^2$ evaluated at ρ_{av} . In order to obtain the temperature-density diagram of the droplet-vapor equilibrium, the conventional Weeks, Chandler and Anderson (WCA) perturbation scheme, to calculate the pressure and chemical potential of the fluid (see section 2.6, chapter 2) has been employed and the coexistence densities are obtained by solving two simultaneous equations (Eqs.(6.1a) and

(6.1b)) self-consistently along with Eq.(6.17). The coefficient of the square gradient term, K, in Eq. (6.6) is calculated by using Eq.(2.25), chapter 2.

In **Fig.6.2**, we have plotted the temperature-density curve for both bulk liquid-vapor equilibrium (planar interface) and spherical liquid drop ($R_{av}=5\sigma$)-vapor (spherical interface) equilibrium and it is found that the coexistence densities are higher for the spherical case which is consistent with the earlier observation of Osman [**70**].



Fig.6.2 Coexistence curve for planar (triangle) and spherical (stars) interface.

The size-dependent surface tension, γ_e , obtained in this work by using Eq.(6.17) has been presented in Fig.6.3 as the ratio γ_e/γ_{∞} and it is found that the surface tension of the small droplet is lower than that for the bulk phase, becomes larger at intermediate droplet size and asymptotically reaches unity (corresponding to the bulk value of surface tension) which agrees with the results of earlier works [**72,77**].



Fig.6.3 Size-dependent surface tension of spherical droplets. Surface tension predicted by using model density (solid circle) and using numerically obtained exact density (open circle).



Fig.6.4 Density profile of spherical interface ($R_{av} = 5\sigma$) at different reduced temperatures.

In **Figs. 6.4**, the density profiles obtained by the present work using the model density profile, for the spherical interface ($R_{av} = 5\sigma$) have been plotted for different values of the reduced temperatures. The calculated thickness of the interface for the same value of R_{av} has also been plotted in **Fig. 6.5**, where it is observed that the calculated thickness based on different definitions of thickness is in good agreement with the predictions of the earlier theories and simulations.

The vapor and liquid densities of the droplet-vapor equilibrium system are different from that of the bulk values and it has been found that there is an increase in the densities of both the liquid and vapor phases with decrease of the droplet size. The vapor and liquid densities have been plotted as a function of the droplet size in **Fig. 6.6a** and **Fig. 6.6b** respectively and compared with the molecular dynamical simulation results reported in [**74**].

In **Figs.6.7**, the optimized model density and the exact numerically obtained density at reduced temperature $T^*=0.7$ have been plotted and it is observed that the exact density is not much different from the model density for this particular choice of free energy density model and the agreement between the two density profiles becomes better with increase in size.



Fig.6.5 Thickness of the spherical interface ($R_{av} = 5\sigma$) as a function of temperature. Present work for planar interface (open squares), for spherical interface (open triangles) and planar interface by Telo da Gama [131] (open circles) considering 10-90 convention of thickness measurement .

The thickness defined as $D = -(\rho_L - \rho_V)/[d\rho(z)/dz]_{z = z0}$ as reported by Chapela et al (Ref (**59**)) and compared with the present work (open diamonds), the results from MC and MD simulation are denoted by solid triangle (MC 255 molecules), stars (MD 255 molecules), solid circles (MD 1020 molecules) and hexagon (MD 4080 molecules).



Fig.6.6(a): Vapour density vs radius of the equimolar dividing surface R_e (b): Liquid density vs radius of the equimolar dividing surface R_e . Solid squares (present work at T*=0.7) and solid circles (MD simulation results from Ref [74]) .Horizontal lines are the coexistence vapour densities for the planar surface in (a) and coexistence liquid densities for the planar surface in (b)



Fig.6.7 Model density profile and numerical density profile at reduced temperature T*=0.7. for Spherical interface of $R_{av} = 5 \sigma$, 10 σ and 20 σ .

6.7 Conclusions

We have investigated here the size-dependent interfacial properties such as interfacial energy (surface tension), density profile, interface thickness and temperature-density relationship for the vapor-liquid droplet coexistence condition based on DFT with square gradient approximation for the free energy functional, which is quite appropriate for problem with slowly decaying densities at interfaces. A double well type Helmholtz free energy functional for the local part and a diffuse density profile at the interface, which are supposed to be the suitable free energy and the density model respectively for the two phase system (coexistence), have been considered in this work. The size-dependent interfacial properties mentioned above have been obtained analytically in the present prescription and the results are quite similar to those from other theories and simulations. The consideration of the large

sized droplet corresponding to the planar interface are shown to predict the surface properties of the planar interface of the bulk system. The present prescription can be further extended to investigate the same for supersaturated vapor-liquid system so that a size- and supersaturation- dependent surface tension can be obtained and the outcome will be helpful to modify the result of CNT by retaining its simplicity.

CHAPTER 7

Conclusion

This thesis mainly deals with modeling of the vapor-liquid interface in terms of both density profile as well as the Helmholtz free energy density functional in a more realistic fashion and in such a way that the problem of vapor to liquid nucleation and interfacial properties have been solved analytically using classical density functional theory (DFT). As a result of this study a new and improved theory compared to the conventional classical nucleation theory (CNT) of vapor - liquid transition has been developed. This proposed methodology of obtaining the vapor to liquid nucleation and interfacial phenomena is based on the classical thermodynamics as well as density functional theory with square gradient correction for slowly varying density at interface. An exponential density at the interface which is found to be realistic and a perturbative approach to express the Helmholtz free energy density as Taylor series expansion with respect to the uniform fluid for the problem of nucleation and a double well type Helmholtz free energy density for the problem of interfacial phenomena have been proposed and are shown to be suitable for obtaining a simple theory. A modified form of CNT has been arrived at by considering the sharp density model of CNT into the result obtained by the proposed DFT. In order to investigate the heterogeneous nucleation on flat as well as spherical solid surface, single spherical cap and double spherical cap model have been introduced. The well-known 9-3 interaction model for the solid (wall)-fluid interaction corresponding to Lennard-Jones fluid has been considered for the heterogeneous nucleation on flat solid surface and the solid-fluid interaction for heterogeneous nucleation on spherical solid surface has been derived in this work. Therefore, the vapor to liquid nucleation has been thoroughly

investigated in the present thesis. The free energy of formation of the droplet, nucleation barrier, critical size, density profile of nucleating droplet, shape of the droplet, effect of various parameters on the shape, size and nucleation barrier etc. have been obtained in the present work and are found to lead to quite good results in comparison to the conventional CNT and several other earlier works.

Further extension and generalization of the work presented here is also possible. For example, the formulation of nucleation can be applied for the investigation of the reverse phenomena i.e. cavitation in liquid to vapor phase transition. The real system like water also can be investigated by the proposed methodology with the proper choice of local Helmholtz free energy density and the interaction potential. More appropriate free energy functional for inhomogeneous system can be proposed. The liquid-solid transition, precipitation etc. can also be studied.

The proposed theory when applied to the problem of interfacial phenomena, an analytical solution of the various interfacial properties such as surface tension, density profile, thickness of the interface etc. have been obtained for a model L-J fluid. The proposed theory has been applied to the problem of real fluid as well by incorporating some suitable approximations and the expression of surface tension has been obtained. The surface tension of a few real fluid systems have been obtained over a wide range of temperature from triple point to critical point, using the knowledge of the bulk densities along with a triple point surface tension data. The theory is applied to the real fluids like water, heavy water and argon and the resulting surface tension is fairly accurate, which is a significant achievement in the present work. The analytical solution to the problem of the size- dependent interfacial properties is another important achievement of this work.

droplet is a very difficult task, one has to depend on the theory of the size-dependent surface properties and therefore the present attempt is very significant for calculating the different properties of the interface like surface tension, density profile, thickness of the interface etc. analytically. The numerical solution with the exact density also supports the modeling of the present density profile. In the context of nucleation, the theory can be further developed to calculate the supersaturation dependent surface tension in addition to the size dependence.

The work in the present thesis is mainly based on DFT, and therefore it is a microscopic theory retaining the physical picture of the phenomena. Due to the incorporation of suitable and realistic approximations, the solution is however, mostly analytical and simple in nature.

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LIST OF PUBLICATIONS

 Homogeneous nucleation in vapor-liquid phase transition of Lennard-Jones fluids: A density functional theory approach.

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2. Density functional theory of size-dependent surface tension of Lennard-Jones fluid droplets using a double well type Helmholtz free energy functional.

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3. Density functional theory of surface tension of real fluids using a double well type Helmholtz free energy functional: application to water and heavy water.

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