

DENSITY FUNCTIONAL THEORY STUDIES OF LIQUID-VAPOR NUCLEATION
AND INTERFACIAL PROPERTIES

by

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DISSERTATION TITLE

Density functional theory studies of liquid-vapor nucleation
and interfacial properties

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DENSITY FUNCTIONAL THEORY STUDIES OF LIQUID-VAPOR NUCLEATION AND INTERFACIAL PROPERTIES

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University of Nebraska, 2003

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This dissertation is focused on the study of thermodynamic properties of liquid-vapor interfaces. As a result of this study an improved theory of liquid-vapor nucleation has been developed. This theory is based on the classical thermodynamics as well as on the density functional theory (DFT). Several DFT approaches with different approximations for the radial correlation function of the system have been considered. The Lennard-Jones (LJ) fluid and a weak dipolar fluid have been investigated within these approaches. The important characteristics of these fluids such as surface tension, the Tolman length, disjoining pressure near 9-3 LJ wall and the chemical potential as a function of liquid film thickness have been obtained. The microscopic consideration has provided all the necessary parameters for the further development of nucleation theory. The theory of heterogeneous nucleation on mesoscopic wettable particles has been developed with account of curvature and compressibility corrections. The homogeneous nucleation at high supersaturation of vapor also has been studied. The behavior of the planar surface tension and the Tolman length in the frameworks of local density approximation (LDA), weighted density approximation (WDA), random phase approximation (RPA) and modified mean field approximation (MMF) has been studied.

The temperature dependencies for these quantities have been obtained. It has been found that the limiting value of the Tolman length for large droplets is very small, even less than a molecular size, and it becomes closer to zero with any improvement in the description of the radial correlation function of the system. Based on the nucleation theory developed, the most important characteristics of nucleation such as the chemical potential of the liquid condensate, its threshold value and formation free energy of the droplet have been obtained as well as other essential quantities for nucleation kinetics. Those include the nucleation barrier and the half-widths of formation free energy curve near equilibrium and the critical sizes of droplets.

PREVIEW

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Introduction

The first-order phase transition in the metastable phase usually proceeds with the nucleation process that is the formation of spherical droplets of a new phase. The nature of the phase change can be very different. In this work only the liquid-vapor nucleation will be considered. The most common example of such a process is the formation of liquid droplets in the supersaturated vapor. This phenomenon occurs for instance in clouds and results in rain droplets. However this is not the only example of nucleation. Liquid-vapor nucleation can be seen in many technological and scientific processes. Those involve painting the surfaces of different shape, spreading liquids and processes taking place in the cloud chambers to track the elementary particles, such as Wilson's chamber. All the nucleation processes can be further divided into homogeneous and heterogeneous nucleation.

To study homogeneous nucleation one has to assume that there are not any foreign particles in the system, because those particles can serve as formation centers for the droplets of the new phase. Thus the homogeneous nucleation process takes place only as a result of the appearance of the critical nucleus. These critical nuclei are essentially the spherical droplets of the new phase such that if the size of the droplets is larger than the critical size the droplets will grow into the new phase. On the other hand if the droplets have the size smaller than the critical one, they will turn into vapor again. Generally, the homogeneous nucleation takes place at relatively slow rate compared to that for heterogeneous nucleation.

Heterogeneous nucleation is the most common mechanism to initiate the first-order phase transition. It requires the existence of certain foreign particles in the system.

The process could proceed with the formation of a liquid-like film on the surface of foreign particles. Many kinds of particles can act as heterogeneous nucleation centers. These include ions, droplets of acid, soluble or insoluble sols and dust particles. It is known that thermodynamic properties of the liquid film formed on the surface of a particle strongly depend on the nature of the surface force. A general feature for heterogeneous nucleation is the existence of a threshold supersaturation beyond which the so-called barrierless nucleation can take place. In contrast, the homogeneous nucleation, which occurs only in an impurity-free environment, is much less common in nature. In fact the homogeneous nucleation process always requires a higher value of supersaturation than that for heterogeneous nucleation.

The classical nucleation theory was first introduced by Becker and Döring [1] and further developed by Frenkel [2], Zeldovich [3], Lifshitz and Slezov [4], Kuni [5], Kashchiev [6], Volmer [7]. According to these studies, homogeneous nucleation takes place as a transition from metastable state through energetic barrier to the formation of the stable phase. The nucleation rate (the number of droplets appearing per unit of time per unit of volume) is exponentially proportional to the height of activation barrier. This height is equal to the work of the formation of the unstable critical cluster. In the classical theory with the capillary approximation the cluster is considered to be a macroscopic droplet. Its work of formation is considered as the sum of volume and surface contributions. In this case the formation work of the critical droplet equal one third of its surface tension multiplied by the surface area.

The mechanism of heterogeneous nucleation is different. We only consider a simple situation that the heterogeneous nucleation occurs on spherical particles. In this

case, droplet formation on the particles can be developed in two ways, depending on the wettability of the liquid on the surface of the particle. The first possible way is the formation of a liquid film on the entire surface of the particle (complete wetting). The film then grows into a large liquid droplet with the foreign particle at the center. The second way is via forming microlenses of liquid on the surface of the particle with a nonzero contact angle. These separate microlenses then grow in size, collapse into a thick film, which covers the entire surface of the particle, and then develops into a large liquid droplet. Here we will only consider the first possibility. A sufficient condition for this possibility is that the liquid condensate can wet the surface of the particle completely as the radius approaches to infinity (or the coefficient of spreading of the condensate is positive in the planar limit [8]).

In any case, the thermodynamic properties of the liquid condensate are essential for the development of both homogeneous and heterogeneous nucleation theories. The classical theory requires the knowledge of properties such as bulk densities of both coexisting phases, chemical potential of the condensate, pressures in both phases. In heterogeneous case the nature of the surface forces is important and several additional parameters are needed to describe those forces. Since the structure of the liquid in general is not known, all these quantities can not be determined within the frameworks of classical thermodynamics. They should be treated as input parameters of the theory, which are generally taken either from experiments or from some other microscopic theories.

Another important issue is that typically the clusters or liquid films formed on the surface of the foreign particles, in the cases of interest to nucleation experiment, can

contain no more than several hundreds of molecules. So one may ask the question if the macroscopic thermodynamics could be applied to such small systems. It is even hard to distinguish between volume and surface contributions in such a case. On the other hand the majority of the experimental data [9] allows only measurements of the bulk liquid or vapor characteristics along with the data for planar liquid-vapor interface. The question how far these data can be extrapolated to microscopic clusters is open. In the homogeneous case this becomes practically important at high supersaturations of vapor, at which the critical size of the droplet becomes extremely small and some microscopic corrections to the predictions of macroscopic thermodynamics must be included. For instance, near the gas spinodal the surface tension of the droplet not only differs from the value in the planar limit but becomes zero altogether [10]. In the case of low supersaturations the classical nucleation theory can be improved systematically by including small curvature and compressibility corrections [11-13]. But those corrections themselves can hardly be determined without invoking additional microscopic theories.

In the case of small droplets as well as molecularly thin liquid films one has to take into account the effect of overlapping of the surface layers. Thus in this case the bulk liquid characteristics can not be used to describe properties at the center of such droplets or films. Even nonmonotonic behavior can occur for some thermodynamic characteristics such as the density, pressure or chemical potential of the liquid condensate as functions of the droplet size. The reason for this nonmonotonic behavior is the existence of the disjoining pressure [8,14], which is mainly responsible for the heterogeneous nucleation mechanism and also may play some role in homogeneous case. For instance, it will definitely affect the surface tension.

But even in the case of sufficiently large droplets, where the density at the center is nearly indistinguishable from the bulk value, the surface tension still depends on the curvature. This was first shown by Tolman [15] in 1949, who had introduced the curvature correction to the surface tension of the spherical droplet, which is now known as the Tolman length.

All the aforementioned curvature corrections, that are dependent on the droplet size, cannot be calculated without applying some microscopic theory. One of the main goals of the present study is to obtain the curvature corrections based on the Density Functional Theory (DFT), one of the widely used methods for inhomogeneous fluids [16]. The detailed description of this method will be given in Chapter 2. Along with DFT there are some other microscopic approaches based on direct molecular simulations of the system, such as Molecular Dynamics (MD) and Monte Carlo simulations (MC). Both approaches consider the liquid-vapor system as constructed from the finite number of particles interacting via some intermolecular potential. These approaches are extremely useful in the case of the small systems such as homogeneous liquid droplets at high supersaturations. The review of the historic development of MD and MC methods can be found in Ref. [17].

Molecular dynamics [18-22] has been used to investigate small spherical clusters and planar liquid-vapor interfaces as well as the dependence of the surface tension on the cluster's size. It has been shown that the surface tension approaches to zero as the droplet size goes to zero, which is in agreement with thermodynamic description of the surface layers [10]. The surface tension of the planar-liquid vapor interface decreases monotonically with the increasing of temperature [22]. The results of references [18-20]

confirmed the absence of the bulk liquid at the center of a small homogeneous droplet. Ref. [19] shows nonmonotonic behavior of the density at the droplet's center as its size changes. These works also include discussions of the behavior for the pressure tensor inside the droplet (different definitions of pressure tensor can be found in Ref. [23]). The components of the pressure tensor are important, because the mechanical definition of the surface tension is based on these components, and it is the mechanical surface tension that can be measured in most experiments. Some results of the previous MD simulations were however questionable, because the number of particles in the simulated system was too small. This makes almost impossible until recently to simulate the planar interface for the system with long range interactions without cutting the profile tail at large distances. On the other hand it seems that those long-range tails are responsible for the behavior of small parameters such as the Tolman length. This is why the controversy still exists in the literature regarding not only the absolute value, but even the sign of the Tolman length. For instance some authors found negative [22,24], while others [21,25] found positive values of the Tolman parameter. So it appears that it is more reasonable to consider the small microscopic systems in the frameworks of molecular simulations, while the mesoscopic to macroscopic systems using DFT. This is because DFT does not have any limitations on the number of particles.

Another example of molecular simulations is Monte Carlo (MC) [26,27]. Previous MC works were mainly concentrated on energetic characteristics of the droplets, such as formation work of the droplet rather than mechanical quantities, such as pressure tensor. Ref. [26] shows that the classical nucleation theory overestimates the barrier height of the homogeneous nucleation at high supersaturations. It will be shown later in this work (see

Chapter 6) that DFT can predict similar effect. The comparative analysis of MD and MC methods for homogeneous nucleation is given in Ref. 28. It seems that MC is more effective for small systems even with several tens of particles, while MD works better for systems having several hundreds or more.

Molecular simulations have been used extensively to explore various wetting phenomena on a planar solid surface [29-33]. Previous simulations have yielded important results such as the dependence of wetting temperature and the surface critical temperature on the surface force, as well as the density profiles of the liquid film near the solid surface.

Both DFT and molecular simulations have their own advantages and shortcomings. In molecular simulations, the number of molecules in the simulation cell is finite (typically, a few hundred to a few thousand), whereas a typical mesoscopic size of droplet possesses at least millions of molecules. We will discuss later in this work, that although DFT is free from such size limitation, it requires certain approximations in the correlation function and free energy functional, which render the calculation to be less accurate. However molecular simulations provide the basis to compare results with DFT. Since both DFT and molecular simulations can describe idealized systems with known intermolecular potential, it is much more reasonable to compare results of DFT with molecular simulations first rather directly with the real experiment. Another advantage of DFT is that it gives not only numerical but at least partially analytical results.

One topic, which was already mentioned above and will be one of the central issues of this work, is the Tolman length. This due to the fact that the Tolman length is responsible for the first curvature correction to the surface tension, while in both cases,

either homogeneous or heterogeneous nucleation, the liquid droplets are spherical objects. Even though the original definition of the Tolman length was given in Ref. [15], there is still no unique definition of this quantity in literature. A review of this controversial subject can be found in Ref. [34]. It will be considered in details in this work. Here we list some key problems. Originally the Tolman length was defined as the adsorption calculated for the Gibbs surface of tension divided by the difference of particle densities in the bulk phases. In the limit of the planar liquid-vapor interface, it follows that the Tolman length equals the distance between equimolar dividing surface and the surface of tension. It was taken for granted that the radius of the equimolar surface is larger than the radius of tension, so the parameter was thought to be positive and called a "length". However it has been often forgotten that such a definition is only valid in the case of the extremely large droplets, while for the smaller droplets the Tolman parameter is not a constant and will depend on the curvature of droplets. A related issue is the correct definition of the surface of tension (see for instance Ref. [35]). Another way to define the Tolman length is to consider the expansion of the surface tension of the spherical droplet over small curvature and find coefficients in this expansion. The results of this approach depend strongly on the approximation made to present the free energy of the system. For instance the simplest form of the free energy can be obtained by the so-called gradient expansion method [16, 36-42]. Even this method is very simple from the technical point of view, the results are not very useful, since the gradient expansion can be considered reliable only near the critical point and for the systems with short-range interactions. When this method is used beyond its limitations it brings on artifacts such as the exponential decay of density profile for any

type of intermolecular potential, divergence of the coefficients in the energy expansion, and the incorrect temperature dependence of the surface tension. It seems that more reliable approaches to calculate coefficients in the curvature expansion of the surface tension should be based on the full statistical-mechanics treatment in the spirit of works by Kirkwood-Buff [43] or Triezinberg-Zwanzig [44]. Such an approach to calculate the Tolman length has been developed by Blokhuis and Bedeaux [45,46]. They obtained the integral relations to calculate those coefficients, based on the knowledge of intermolecular potential and correlation function of the system. These equations were used in the MD simulations [21, 24, 25] as well as in the frameworks of DFT [46], and will be further discussed in this work. Some ideas to obtain approximate analytical expressions for the Tolman length were also reported in the literature, either based on approximations for the density profile [38,39,47] or just using thermodynamical expansions along with some symmetry principles [42,48-50].

Since density functional theory is the main method employed in this work, let me review the basic publications on the DFT applications to nucleation problems. The fundamentals of this method are described by R. Evans in Ref. [51]. The key idea behind the DFT is that thermodynamic potentials of the system can be presented as functionals of the its density profile (the number of particles per unit of volume as function of the position in space). The practical form of the functional depends on the assumptions made about intermolecular interactions in the system. Applying variational principle to the thermodynamic potential with respect to the density profile allows us to obtain the integral equation for the density profile in the equilibrium state.

The DFT method was first applied to homogeneous nucleation by D. Oxtoby and R. Evans for the Yukawa system [52] and by X. C. Zeng and D. Oxtoby for the Lennard-Jones system [53]. Such key characteristics of homogeneous nucleation as density profile and formation work of the critical cluster as well as temperature dependence of the nucleation rate were investigated in these works. The binary nucleation was studied thereafter in Ref. [54]. Aforementioned studies used the grand canonical ensemble in their treatment, however the method can be generalized [55] for the case of canonical ensemble. In later work [56] I. Hadjiagapiou showed that in the case of the Yukawa potential the DFT equation can be reduced to a nonlinear differential equation of the second order. He was probably the first who noticed nonmonotonic behavior of the density at the center of the droplet as the droplet size changes. He also studied the pressure tensor components inside of the spherical droplet. However his conclusions on the Tolman length have a problem. Even he found it was negative, but its absolute value is increasing continuously not reaching any finite limit in the case of the large droplets. The question of curvature dependence for the surface tension of the spherical droplet was further considered by V. Talnaquer and D. Oxtoby in [57], R. McGraw and A. Laaksonen [48, 58]. The curvature dependence of the Tolman length itself was studied in the frameworks of DFT in [57,59]. The temperature dependence for the limiting value of the Tolman length was first obtained in [46].

Heterogeneous nucleation and the behavior of the liquid near solid wall is another subject for DFT studies. Heterogeneous nucleation on ions was first investigated using DFT in Ref. [60]. All DFT studies mentioned so far were conducted in the frameworks of Local Density Approximation (LDA). This approximation assumes that short repulsive

forces between molecules (usually replaced in LDA/DFT by hard spheres) are of the local nature, while only weak long-range attractive interactions should be considered as nonlocal. It seems that such an approach should be effective at least in the case of liquid-vapor interfaces, but it is definitely not for the solid-liquid interface. This is why when the DFT was first employed to study behavior of a fluid near a solid surface [61-65], the so-called Weighted Density Approximation (WDA) developed by P. Tarazona [61,62] was used. Other attempts were made [66,67] to use oversimplified phenomenological or gradient expansion based methods. In the WDA framework, thermodynamic potentials of the system are considered to be functionals not of the usual density profile but of weighted density profile, averaged over local volume. The WDA has been shown to be quite accurate for describing highly nonuniform solid-liquid interfacial systems in comparison with molecular simulations [63,31,32]. A key feature of the WDA/DFT density profiles is the existence of density oscillations. These oscillations usually take place near hard walls, reflecting the local structure of the interface. But microscopic oscillations exist even in the absence of the wall. Evans and coworkers [68,69] noticed such a phenomenon, which takes place at low temperatures and high liquid densities. So the WDA can be an effective approximation not just for the heterogeneous case, but even for homogeneous nucleation.

The WDA/DFT treatment of heterogeneous nucleation on mesoscopic wettable particles is going to be one of the main subjects for this study, since not too much work has been done on this subject yet. The planar surface can be considered as the limiting case for a mesoscopic particle when the diameter approaches to infinity. For the planar surface, the complete wetting may occur when the nucleating vapor is undersaturated.

Towards the complete wetting, the disjoining potential changes monotonically as a function of the thickness of the liquid film (see, for example, Fig. 1 in Ref. [63]), while it is nonmonotonic for the incomplete wetting. Thus far, most DFT studies about the heterogeneous nucleation focus mainly on systems involving partially wettable particles [70,71], namely, the second possible way of heterogeneous nucleation mentioned above. In that case, the line tension of the three-phase interface on the solid surface must be considered. The solid surface can be either planar [72] or curved [73,74]. DFT with a local gradient expansion was the basis for all those studies. However, I have already discussed that the LDA cannot qualitatively describe the structure of the density profile near the solid surface.

Recently DFT also received further development for the substances with more complicated intermolecular interactions. It is of great importance for consideration of more realistic fluids, such as polar fluids including water. The basis for this development formed by the Modified Mean Field (MMF) approximation introduced by P Teixeira and M. Telo da Gama [75] and further developed in Refs. [76-78]. The main aspect of those works is to develop better approximation for pair correlation function of the system beyond the Random Phase Approximation (RPA), when considering long-range intermolecular potential tail.

Based on this review, one can outline several open questions, which will become the key subjects for the this dissertation. These include:

- The influence of nonuniform structure of the small liquid droplet on the major characteristics of homogeneous and heterogeneous nucleation, such as chemical potential, pressure tensor, surface tension and others.

- Curvature dependence for the surface tension of spherical droplet.
- Attempt to resolve the uncertainty regarding the magnitude, sign and temperature dependence of the Tolman length.
- The influence of different approximations (MMF vs. RPA and WDA vs. LDA) within the frameworks of DFT on major interfacial properties of the fluid.
- The full description for the heterogeneous nucleation on the wettable particles in the frameworks of DFT.

These and some other subjects will be considered in the present dissertation based on the hybrid approach by combining DFT with classical nucleation thermodynamics. The latter yields general relations among thermodynamic and kinetic properties of the system while the DFT provides important microscopic properties of the liquid droplet. Outcomes of the hybrid theory include the threshold value of the chemical potential (or the threshold value of the supersaturation) for barrierless nucleation, the height of the activation barrier to nucleation, the half width of the barrier, as well as the position of the minimum and maximum on the curve of free energy of droplet formation versus the droplet size.

Chapter 1. Thermodynamics of nucleation

In this chapter the general aspects of the thermodynamics of nucleation will be considered. Even thermodynamic theory of nucleation has been developed for many years [1-13, 79,80], there are many open questions and misunderstandings especially regarding correct definitions of many parameters involved in this theory. In particular definitions of the surface tension, adsorption, disjoining pressure and dividing surfaces should be further discussed. Moreover the thermodynamics of nucleation will be presented in this chapter in a most convenient way for the sake of combining with the Density Functional theory, which is going to be the main method used in this dissertation. I shall start from the most general case of heterogeneous nucleation and then I will consider homogeneous nucleation as the limiting case of heterogeneous, that is when the size of the foreign particle inside of the liquid cluster is zero.

1.1. Heterogeneous nucleation

Several main thermodynamic equations such as Laplace equation and Gibbs-Duhem equation form the basis for the description of any droplet-like object in the classical nucleation theory [8] in heterogeneous as well as in homogeneous case. In this section I will formulate the generalized analogs of those equations in such a way that they will be appropriate for the description of heterogeneous nucleation on wettable particles. This will be done keeping in mind that DFT will be introduced in the next chapters as a useful tool for further investigation.

This problem has already been studied in the frameworks of classical thermodynamics [8,79], however several approximations were made in order to simplify the consideration. These approximations include (1) the fluid is incompressible, and (2)

the surface tension of the liquid-vapor, solid-liquid and solid-vapor interfaces does not depend on the curvature of interface and are equal to their values in the planar case. Those approximations may not be accurate when the liquid droplet is small. We will see in the later chapters that DFT shows that compressibility of the droplet is not negligible and the surface tension depends quite strongly on the curvature. Even though the modified classical nucleation theory allows accounting of compressibility and curvature corrections [11-13], but they only play the role of the input parameters. DFT on the other hand will provide a way to calculate these parameters. The compressibility can be measured in the real experiment, but the value of the Tolman parameter (the first order curvature correction), however, has been so far obtained only based on molecular simulations or DFT. This is due to the fact that the Tolman length is so small that it is difficult to measure this length using traditional experimental means. But even so, compressibility correction and the Tolman correction, having the same order of magnitude, provide the leading contribution to improve the classical capillary approximation in the case of the very large droplets.

Here I shall consider an open system, which consists of a wettable solid particle and a metastable vapor at a fixed temperature. Upon condensation, a liquid film with a uniform thickness will form on the surface of particle (complete wetting). Assuming the system has spherical symmetry, the density profile of the system is given by $\rho(r)$, where r is the distance from the center of the solid particle. Hereafter we shall refer the metastable vapor as phase 1, the liquid film as phase 2, and the solid particle as phase 3.

To Describe thermodynamics of this nonuniform system, I will use the Gibbs method of dividing surfaces to replace $\rho(r)$ by a step-like density profile, similar to the

sharp-kink model introduced by Getta and Dietrich [72]. This new density profile consists of the solid particle with density ρ_3 , the liquid film with density ρ_2 , which equals to the bulk density of liquid at the current supersaturation, and the vapor with density of ρ_1 . The solid particle has a radius \tilde{R}_n . We use \tilde{R}_n to represent its physical radius and R_n for the radius of the solid-liquid dividing surface. Radius R_n may differ from radius \tilde{R}_n by a few molecular diameters, depending on the thickness of solid-liquid interface. Following Ref. 72, let us set zero density between \tilde{R}_n and R_n . The radius of the liquid-vapor dividing surface is denoted by R . Thus, the thickness of the liquid film is given by $h = R - R_n$ (see Fig. 1). Finally, L denotes the outmost radius of the entire system. Parameter L can be chosen in such a way that beyond size L the physical density of vapor is nearly uniform (i.e. ρ_1).

The vapor's supersaturation is characterized by the chemical potential μ . At the fixed temperature, the vapor density ρ_1 is solely determined by μ , and so is the density of the bulk liquid ρ_2 . For the open system, the grand thermodynamic potential is

$$\Omega = -p_2 \frac{4\pi}{3} (R^3 - R_n^3) - p_1 \frac{4\pi}{3} (L^3 - R^3) + 4\pi R_n^2 \sigma_{32}(R_n) + 4\pi R^2 \sigma_{21}(R) + \tilde{\Omega}(h), \quad (1.1)$$

where p_2 is the normal pressure of the uniform liquid film (with the density ρ_2), p_1 is the pressure of the vapor (with the density ρ_1), $\sigma_{32}(R_n)$ is the surface tension of the solid-liquid interface, which depends on the curvature and the choice of the dividing surface R_n , and $\sigma_{21}(R)$ is the surface tension of the liquid-vapor interface, which also

Fig.1

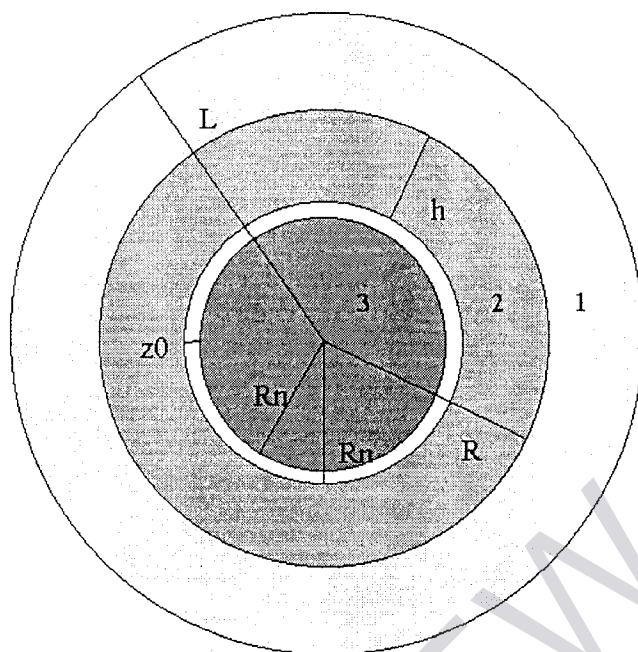


Fig.1. A schematic plot of a liquid droplet forming on the wettable solid particle.