

# Nucleation. Thermodynamical and Stochastical Descriptions

A thesis submitted by Antonio Patrón Castro  
Supervised by Manuel Morillo Buzón



Department of Atomic, Molecular and Nuclear Physics  
University of Seville  
June, 2019

“The most merciful thing in the world, I think, is the inability of the human mind to correlate all its contents... some day the piecing together of dissociated knowledge will open up such terrifying vistas of reality, and of our frightful position therein, that we shall either go mad from the revelation or flee from the light into the peace and safety of a new dark age.”

-H.P. Lovecraft [11]

# Contents

<b>1</b>	<b>Abstract</b>	<b>1</b>
<b>2</b>	<b>First-Order Phase Transitions</b>	<b>2</b>
2.1	Van der Waals Fluid . . . . .	2
2.2	Thermodynamic Fluctuations . . . . .	6
<b>3</b>	<b>Classical Nucleation Theory</b>	<b>7</b>
3.1	Thermodynamics of Nucleation . . . . .	7
3.1.1	The Capillary Model . . . . .	9
3.1.2	Work for Cluster Formation . . . . .	10
3.2	Kinetic Theory of Nucleation . . . . .	13
3.2.1	Nucleation Stage and the BDT Model . . . . .	15
3.2.2	Equilibrium Approach . . . . .	17
3.2.3	Nucleation Rate in CNT . . . . .	20
3.3	Homogeneous Nucleation of Water . . . . .	22
3.3.1	Equilibrium Distribution and Critical Cluster . . . . .	23
3.3.2	The Cloud Chamber and Temperature Dependencies . . . . .	26
3.4	Deficiencies of the CNT . . . . .	28
<b>4</b>	<b>Density Functional Theory</b>	<b>30</b>
4.1	Density Functional and Variational Approach . . . . .	31
4.2	Approximations for the Free Energy . . . . .	33
4.2.1	Gradient Approximation . . . . .	33
4.2.2	Hard-Sphere Model . . . . .	34
4.3	N-Parameter Theories . . . . .	35
<b>5</b>	<b>Conclusion</b>	<b>36</b>

# 1 Abstract

Nucleation is a non-equilibrium process through which a system evolves from an old thermodynamic phase to a new (energetically stable) one in what we call a *first-order phase transition*. This process is widely spread in natural phenomena like condensation, sublimation, evaporation or crystal growth, and it is also of technological relevance [1].

In this work, the main theories behind nucleation developed throughout the last century by researchers like Gibbs, Zeldovich and Kashchiev will be reviewed. We will start with the study of the Van der Waals equation (VDWE), as it provides a general insight of the main conditions required for a phase transition to occur. Next, the *Classical Nucleation Theory* (CNT), the core of this work, with its central paradigm of well-defined clusters is introduced. With the aid of the capillary model and the assumption of large spherical clusters, a first approach to estimate the minimum work required for a cluster to form (also known as the potential or nucleation barrier) is obtained, with a general description of how the cluster grows depending on its initial size. Moreover, the CNT also provides a dynamical theory of cluster formation based on the attachment and detachment of n-mers (clusters formed by 'n' molecules), which leads to Fokker-Planck, Langevin, Kramers-Moyal and Master equations, due to the stochastic nature of the time-dependent concentration of n-mers in the system. With the help of the BDT (Becker-Döring-Tunitskii) model and the Zeldovich's ideas, an analytical expression for the nucleation rate is derived, which constitutes the main quantity that allows to corroborate the theoretical predictions experimentally.

With this framework, we will focus on the study of homogeneous nucleation of water droplets in condensate vapor phases, with the goal of obtaining the cluster size equilibrium distribution functions and the performance of a comparison between the theoretical and experimental nucleation rates measured in diffusion cloud chambers. This procedure will allow us to study the limitations and validity of the classical theory, and its study will conclude with a section where an oversight of its main controversies and deficiencies is provided.

Finally, following this, we will make a brief introduction presenting the framework and some fundamental approximations of the modern paradigm of the *Density Functional Theory*, which is based on variational calculus. This theory provides a completely new framework that improves the classical theory and opens the door to new models that, in concordance with the experiments, allows us to deepen in this field of study, helping us to uncover the mysteries of phase transitions and matter itself.

## 2 First-Order Phase Transitions

Let us consider a macroscopic system whose properties and time evolution will be studied. This system might have different thermodynamic phases. We define a phase as a spatial region of the system whose macroscopic properties remain homogeneous for a given set of variables, due to particular arrangements of its atoms and molecules and their interactions. Many instances of systems showing different phases are found in Nature. A most typical case is water, which can be found in three different phases (liquid, solid or gas) depending on the temperature and pressure. Other examples are ferromagnetic materials, which can present spontaneous magnetisation depending on its temperature, or crystalline solids, whose atoms may be arranged in different lattices depending again on the external parameters. A phase transition, from a thermodynamic point of view, is defined then as the process through which the system changes its macroscopic properties from the ones corresponding to the old phase to the new ones [1].

The first classification of possible types of phase transitions was proposed initially by Paul Ehrenfest (1933) [1]. According to Ehrenfest's proposal, phase transitions are classified depending on the behaviour of the Gibbs free energy at the transition point. It is said that we have an *n-order phase transition* if the *n*-th derivative of the Gibbs free energy at the transition point presents a discontinuity. Further experiments and investigations carried out by Onsager (1944), Gebhardt (1980) and others [1] showed that this classification does not include all possible cases. Here, we will focus on the study of first-order phase transitions, characterised by discontinuities of the internal energy  $U$ , the entropy  $S$  and the volume  $V$  of the system.

In order to illustrate the physical nature of first-order phase transitions, it is worth to analyze the behavior of a Van der Waals (VDW) fluid, as we do next.

### 2.1 Van der Waals Fluid

A VDW homogeneous fluid is characterised by the following equation of state

$$\left(p + \frac{N^2 a'}{V^2}\right) (V - Nb') = Nk_B T, \quad (2.1)$$

where  $p$  is the pressure,  $V$  the volume,  $N$  the number of particles,  $T$  the absolute temperature,  $k_B$  the Boltzmann's constant, and  $a'$  and  $b'$  are constants that account for the attraction between particles and their effective volume respectively. They depend on the material under study [1]. It is interesting to outline that this equation can be derived

from statistical-mechanical considerations, assuming a Hamiltonian including a dominant hard-sphere potential and a Lennard-Jones potential which is treated as a thermodynamic perturbation [6]. This allows us to visualize the connection between the material constants and the microscopic interactions between molecules. Moreover, these constants may be expressed in terms of the critical coordinates, which are obtained from the definition of a saddle point as

$$\left(\frac{\partial p}{\partial V}\right)_{T_c} = \left(\frac{\partial^2 p}{\partial V^2}\right)_{T_c} = 0.$$

These equations lead to

$$p_c = \frac{a'}{27b'^2}, \quad V_c = 3Nb', \quad T_c = \frac{8a'}{27k_B b'}.$$

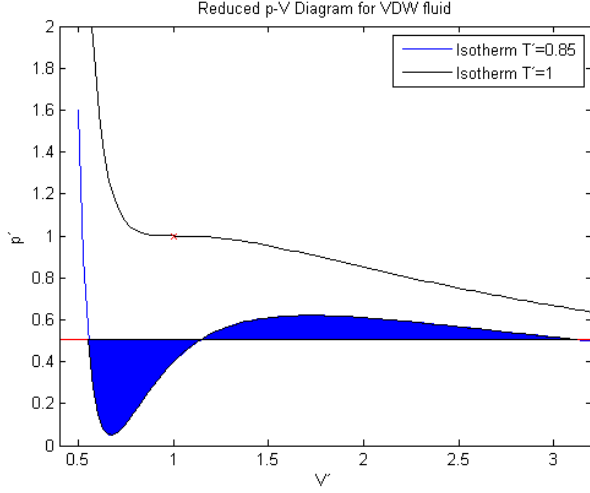
By substituting the reduced coordinates  $p' = p/p_c$ ,  $V' = V/V_c$  and  $T' = T/T_c$  into Eq.(2.1) we obtain the reduced VDW equation

$$\left(p' + \frac{3}{V'^2}\right)(3V' - 1) = 8T'. \quad (2.2)$$

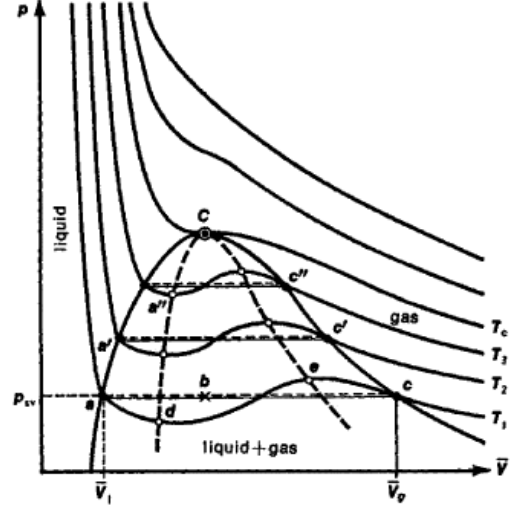
This last expression is universal as it does not depend on any particular material constants. Let us now discuss the thermodynamic potentials governing the behaviour of our fluid. Considering that our system is placed within a thermal bath of temperature  $T_B$  and constant pressure  $p_B$ , the fluid will be in stable thermodynamic equilibrium (TDE) when it occupies a volume for which the Gibbs free energy  $G = F - p_B V$  is minimum [7]. Knowing that the differential expression for the Helmholtz free energy  $F$  is given by  $dF = -SdT - pdV$ , we can obtain the conditions for obtaining a minimum of the Gibbs free energy,

$$\begin{aligned} \left(\frac{\partial G}{\partial V}\right)_T &= \left(\frac{\partial F}{\partial V}\right)_T + p_B = -p + p_B = 0 \quad \rightarrow \quad p = p_B, \\ \left(\frac{\partial^2 G}{\partial V^2}\right)_T &= \left(\frac{\partial^2 F}{\partial V^2}\right)_T = -\left(\frac{\partial p}{\partial V}\right)_T > 0 \quad \rightarrow \quad \left(\frac{\partial p}{\partial V}\right)_T < 0. \end{aligned}$$

On one hand, the first condition assures us that we can reach the stable TDE if our system's pressure is equal to the external pressure. This result makes physical sense, because a difference (gradient) of pressures would result in a force which would try to expand or contract our system until this difference vanishes. On the other hand, the second condition assures that the pressure of the fluid decreases if we expand its volume, a well known fact to be true for the majority of common fluids.



(a) 1a



(b) 1b

Figure 1: Reduced p-V diagrams for VDW fluid. Fig.(1a) shows the critical isotherm (black) and a  $T'=0.85$  isotherm with  $p'_B=0.505$  [1], where both blue regions have the same area, according to Maxwell's construction. Fig.(1b) [10] shows several isotherms in order to visualize the binodal (continuous line joining a, c and C points) and spinodal (dashed line joining d, e and C points).

Figure 1 shows two similar reduced p-V diagrams for different isotherms. On one hand, isotherms of temperature greater than the critical one  $T_c$  are known as supercriticals, where there is no distinction anymore between the liquid or gas phases of the fluid. Moreover, for even greater temperatures, the VDW fluid can be regarded as an ideal gas. On the other hand, those isotherms whose temperature is lower than the critical one are known as subcriticals. We will be interested in those isotherms, where there is a clear distinction between the liquid and gas phases of the fluid and thus, we can talk about a *phase transition* between them.

There are two key concepts that emerge by applying the TDE conditions for a subcritical isotherm [1]:

- **Spinodal Curve:** As it can be noticed in both graphs from Figure 1, for a subcritical isotherm, there is a region between the  $p'(V')$  local minimum and local maximum where the second stability condition breaks down. Namely, the region is *unstable*. As we increase the temperature, this region shrinks until the maximum and minimum coincide at the critical point. The curve obtained by joining local extremes for different subcritical isotherms is called spinodal.

- **Binodal Curve:** For a given external pressure  $p'_B$  at a subcritical temperature, Eq.(2.2) presents three solutions for the volume  $V$ , two of which are of physical interest while the third one lies within the spinodal region, which is unstable. They correspond to a liquid or gas in stable TDE. When both solutions correspond to the same minimum of the Gibbs free energy, then the liquid and gas are in *phase equilibrium*, that is, both phases coexist as separate phases at what is called the equilibrium pressure  $p'_B = p'_E$ <sup>1</sup> of the fluid. By joining the coexistence points for different subcritical temperatures, the binodal curve is obtained. Its maximum is located at the critical point, where both phases coexist, but their boundaries vanish, so there is no distinction anymore between both phases and then we have what is known as a *supercritical fluid*.

Now, the most interesting case of this section lies when we have an external pressure  $p'_B \neq p'_E$ , and between the  $p'(V')$  local maximum and minimum pressures. In this case, both liquid and gas phases would be in TDE, but corresponding to minima of the Gibbs free energy of different depth, that is, since the deepest one it is said to be in *truly stable* TDE, the second one corresponds to a *metastable* TDE. The metastable states lie within the two regions (metastable liquid and metastable gas) between the binodal and spinodal curves, and the transition from a metastable state to the truly stable state corresponds to a *first-order phase transition*. The process through which this transition takes place is the *nucleation* of the old (metastable) phase into the new (truly stable) one [1].

It is important to outline that the phase transition depends on the difference between the corresponding truly stable and metastable free energies  $\Delta g$  [1], or more explicit, the quotient  $S = p'_B/p'_E$ <sup>2</sup>[2]. Both quantities, for the case of nucleation of liquid droplets in condensed gas phases, are related by means of the Kelvin formula [1]

$$\Delta g = -\frac{k_B T}{v_0} \log S, \quad (2.3)$$

where  $v_0$  is the volume of a molecule from the system. The quantity  $S$  is known as the thermodynamic driving force or *supersaturation*. Physically, it represents the gain in free energy per particle associated with the transition from the old to the new phase, and it establishes both the direction and the strength of the transition. For  $\Delta g = 0$  (or  $p'_B/p'_E = 1$ ), there exists no preferred direction nor driving force for the transition, and hence, for

---

<sup>1</sup>The equilibrium pressure  $p'_E$  may be obtained by applying Maxwell's rule; the pressure for which the blue areas on Figure 1a have the same area. These areas represent the excess heat gained and transferred by the system in its metastable states, and whose balance must be null, so the total amount of heat involved in the transition is  $p'_E(V'_f - V'_i)$  [7].

<sup>2</sup>For sufficient diluted (weak) solutions and ideal gases, this ratio is approximately equal to the ratio of densities of the two states (metastable and truly stable), that is:  $p'_B/p'_E \approx \rho_{met}/\rho_E$  [2]



nucleation, and then the old phase is said to be *saturated*, while for  $\Delta g > 0$ , the transition is not possible in the desired direction. In this case the old phase is said to be *undersaturated* [1].

## 2.2 Thermodynamic Fluctuations

We have determined the necessary conditions for a phase transition to occur, but our analysis does not include the time needed for the transition to happen. Indeed, the supersaturated phase will remain a certain time on its metastable state due to the fact that there is an energy barrier between both TDE states. Moreover, this energy barrier will have a maximum of different heights depending on the path followed during the transition. Then our next problem would consist in determining the path through which the energy cost is minimized. One could think of a path corresponding to the uniform change of density from the old phase to the new one as the desired one. However, this path is not actually followed due to its high energy cost.

Another possibility proposed by Kashchiev [1], energetically much cheaper, consists in a non-uniform change of density due to thermodynamic fluctuations on the density. In this case, the energy barrier would be much lower due to the fact that in this case the number of particles involved in the transition is much less than in the uniform case, where all the particles would participate in the process. This approach can describe multiple everyday phenomena such as rains and snowfalls, where droplets and flakes are just the manifestation of density fluctuations. By following this path, nucleation can be defined, according to Kashchiev, as *the process of random generation of nanoscopically small formations of the new phase that have the ability for irreversible overgrowth to macroscopic sizes*. [1]

From Einstein's theory of thermal fluctuation [7], the probability of occurrence of those density fluctuations is exponentially proportional to the minimum work required for the process to occur,

$$P \propto \exp\left(-\frac{W_{min}}{k_B T}\right), \quad (2.4)$$

where  $T$  is the absolute temperature and  $k_B$  is the Boltzmann's constant. The estimation of the minimum work  $W_{min}$  is one of the main goals of both the Classical Nucleation Theory, developed mainly by Gibbs, and of the Density Functional Theory, based on variational calculus. This goal, together with the proposal of a kinetic model to describe the generation and time evolution of clusters, constitutes the core of every nucleation theory.

### 3 Classical Nucleation Theory

If we want to go further into the issue of nucleation, one has to start from Gibbs treatment of phase transitions. His work consisted mainly in the study of the reversible (near equilibrium) work required for creating a small formation of the new phase within the old one, commonly known as a *cluster*. By considering spherical symmetry, thermodynamic assumptions, and with the aid of the *capillary model*, Gibbs derives a formula that mainly depends on a negative volume and positive surface contributions, whose main consequence is that there exists a minimum work (which implies a minimum size) for a cluster to form and grow up. Otherwise it will shrink until it vanishes.

Furthermore, in order to get a first insight into the nucleation kinetics, one has to take into account Szilard's ideas, developed by Farkas [2], which are based on the assumption that a cluster is formed by the attachment and detachment of single particles or subsets of particles. With these ideas, a *master equation of nucleation* is formulated, and from there, by applying the Becker-Döring-Tunitskii model and the Zeldovich equilibrium approach, stochastic equations (such as Fokker-Planck and Kramers-Moyal ones) for describing the kinetics are obtained. Combining them with the thermodynamic assumptions, one can formulate an expression for the nucleation rate, the key magnitude of this theory. The combination of all of these ideas constitutes what it is known as the *Classical Nucleation Theory* (CNT) [2].

#### 3.1 Thermodynamics of Nucleation

In what follows we shall discuss the energy requirements for a set of molecules from a system in a metastable state to form a cluster in a small spatial region due to thermal fluctuations. This cluster will have a random size, and its time evolution will depend mainly on its initial size. The cluster will grow when its size is greater than a *critical size*, and it will shrink when it is not. Thus, this critical size is directly related to the minimum work for cluster formation.

Let us consider a homogeneous macroscopic system of volume  $V$  in a thermal and particle bath of temperature  $T$  and chemical potential  $\mu$ . The thermodynamic potential governing the behaviour of the system in equilibrium corresponds to the Gibbs free energy [6], whose differential equation is given by

$$dG = -SdT - Nd\mu - \sum_k Y_k dX_k, \quad (3.1)$$

where  $S$  is the entropy, and  $Y_k$  is the conjugate force (intensive variable) associated to the degree of freedom (extensive variable)  $X_k$ . For instance; the pairs pressure-volume,

magnetization-magnetic field, surface tension-area.

Let us consider that initially our system has an average density given by

$$\rho_{av} = \frac{\langle N \rangle}{V} > \rho_E(T) \quad \rightarrow \quad \frac{\rho_{av}}{\rho_E} > 1, \quad (3.2)$$

where  $\langle N \rangle = N = \left( \frac{\partial G}{\partial \mu} \right)_{T, X_k}$  according to the thermodynamic description [2, 6]. Due to the fact that the ratio of densities is greater than one, we are in a situation of supersaturation, that is, the transition from this metastable state to the truly stable one will take place. Considering that our system will only expand or contract its volume (not other extensive variables  $X_k$  are considered), and knowing that it is homogeneous (the chemical potential will remain constant), the Gibbs free energy of the initial state can be rewritten as follows

$$G_i = g(\rho_{av}, T)V = -pV, \quad (3.3)$$

where the sub index  $i$  denotes the initial state, and  $g(\rho_{av}, T)$  constitutes the Gibbs free energy per unit volume at constant temperature [1].<sup>3</sup> Sooner or later, a cluster of volume  $V'$  and density  $\rho_{cl}$  will spontaneously form within the old phase, as it is shown in Figure 2.

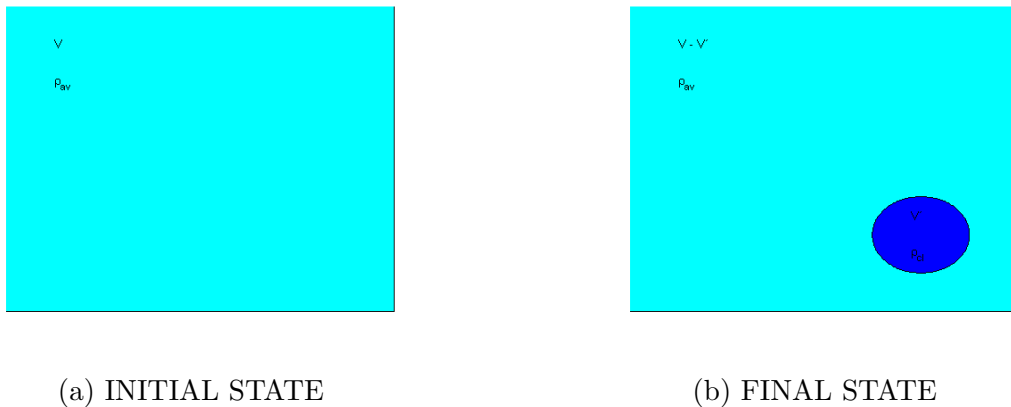


Figure 2: Illustrations of the thermodynamic system under study in its old phase before (a) and after (b) an homogeneous isotropic cluster is spontaneously formed [1].

The minimum work required for the cluster to form, at thermal and chemical equilibrium, is given by the change of Gibbs free energy  $\Delta G$  between the initial and final state [7]. At this point, in order to compute the free energy of the final state, one of the main assumptions of the CNT is introduced. The clusters are *well defined*, that is, there is a dividing surface

<sup>3</sup>With this notation, we do not intend to display the density as one of the intensive variables of the free energy, but as an additional parameter in order to make a distinction between the old and new phases through the transition.

between the cluster and the old phase with its own energy contribution. This surface is introduced as a mathematical device<sup>4</sup>. There is a difference between the cluster pressure and the pressure of the surrounding old phase, due to the density profile, preventing the system to reach equilibrium. This surface isolates the cluster from the environment by adding an *excess energy* [1], and due to this, the pressure will be the same for both the cluster and the old phase, and thus, the equilibrium conditions are fulfilled. This energy excess is given by the conjugate-pair contribution

$$G_S = \alpha_{st}A, \quad (3.4)$$

where  $\alpha_{st}$  is the surface tension (extensive variable), which generally depends on the surface area of the cluster, and  $A$  is the area of the dividing surface. With this assumption, the free energy of the final state will be given by

$$G_f = g(\rho_{av}, T)(V - V') + g(\rho_{cl}, T)V' + \alpha_{st}A. \quad (3.5)$$

Here the subindex  $f$  denotes the final state. Then, the required minimum work will be

$$W_{min} = \Delta G = G_f - G_i = (g(\rho_{cl}, T) - g(\rho_{av}, T))V' + \alpha_{st}A. \quad (3.6)$$

This last equation applies for any geometrical form that the cluster may adopt. But in order to obtain an analytical expression to work with, we are going to consider the clusters small enough so the gravitation effects that may deform their surfaces are neglected. Thus they will be regarded as spherical as a first approximation. Then  $V' = \frac{4\pi}{3}R^3$  and  $A = 4\pi R^2$ , so Eq.(3.6) can be rewritten as

$$W_{min} = -\frac{4\pi}{3}|\Delta g|R^3 + 4\pi\alpha_{st}(R)R^2, \quad (3.7)$$

where  $\Delta g = g(\rho_{cl}, T) - g(\rho_{av}, T)$ . This quantity is negative according to the definition of metastable and truly stable states. The first term of Eq.(3.7) is known as the volume term, while the second one as the surface term.

### 3.1.1 The Capillary Model

Eq.(3.7) provides a general insight of the required minimum work for a spherical cluster to form. However, the lack of knowledge of the quantities quantities  $\rho_{cl}$  and  $\alpha_{st}(R)$  does not allow us to continue our path. Within the CNT, the most important approximation is now introduced; the *capillary approximation* or *capillary model*, which is based on the following assumptions [1, 2]:

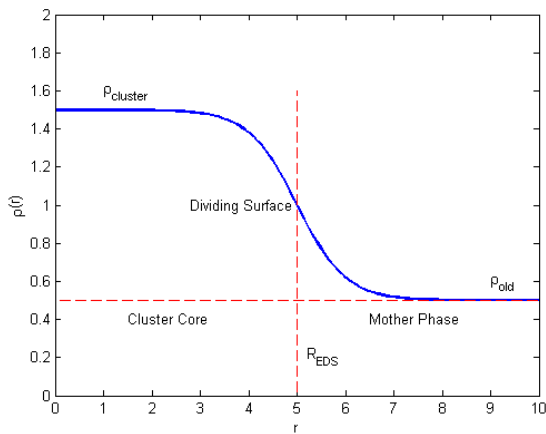
---

<sup>4</sup>There are many possibilities of choosing the position of this surface. The most convenient one for analysing the thermodynamics of homogeneous nucleation is the *equimolar dividing surface* (EDS), which satisfies the condition that the number of particles before and after the cluster appearance is conserved. [1]

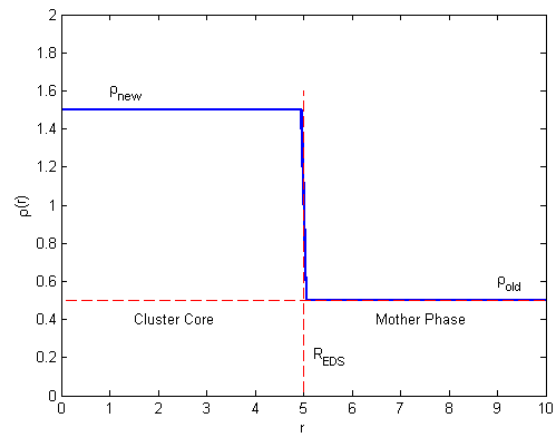
- The properties of the cluster are size independent, so in the end each cluster has the same properties as the resulting new phase, which implies that  $\rho_{cl} = \rho_{new}$ , where  $\rho_{new}$  is known from experimental measurements.
- The profile density function is given by the following piecewise function

$$\rho(r) = \begin{cases} \rho_{new} & r \leq R \\ \rho_{av} & r > R \end{cases} \quad (3.8)$$

- The surface tension is the same as the one for a planar interface between the new and old phases, that is, the clusters have a sharp boundary. Mathematically, this implies that  $\alpha_{st}(R) = \alpha_{st}(R \rightarrow \infty) = \alpha_{\infty}$ , which is size independent and thus constant.



(a) Generic Density Function



(b) Capillary Model

Figure 3: Representations of the local changes in the density profile due to the formation of a cluster as a function of the radius (in spherical coordinates) from its center [2],  $r$ , from a general approach (a) and from the capillary approximation (b). In both figures, the EDS establishes a distinction between the cluster (new phase) and the mother (old) phase. Within the capillary model, a sharp boundary at  $R = R_{EDS}$  separates both phases.

### 3.1.2 Work for Cluster Formation

With the assumptions presented in the capillary model, one can compute an analytical expression for the minimum work by rewriting Eq.(3.7) as follows

$$W_{min} = -\frac{4\pi}{3} |\Delta g| R^3 + 4\pi\alpha_{\infty} R^2, \quad (3.9)$$

where, in this case,  $\Delta g = g(\rho_{new}, T) - g(\rho_{av}, T) < 0$ . Figure 4 represents an illustration of the required minimum work as a function of the cluster radius. As it can be noticed, the

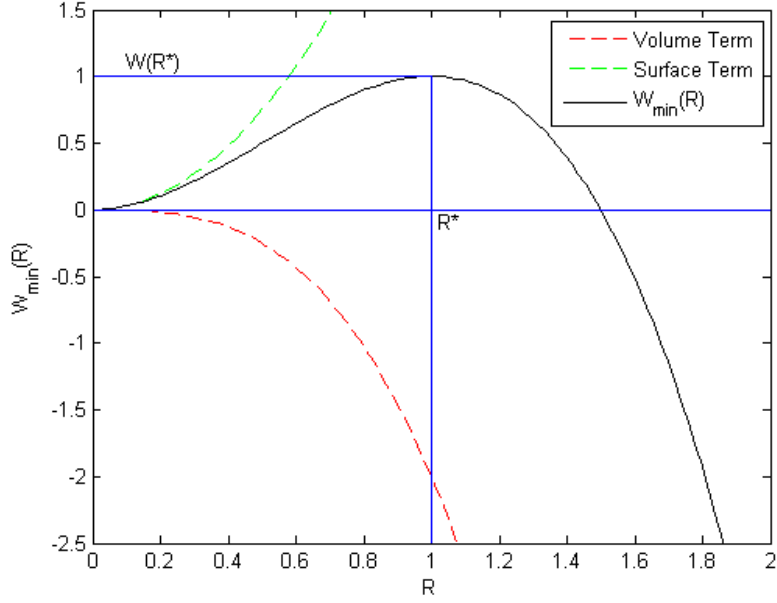


Figure 4: Representation of the required minimum work for a spherical cluster to form, within the approach of the capillary model, and described by Eq.(3.9) [2]. The volume term, the surface term, the maximum height  $W_{min}(R^*)$  and its associated radius  $R^*$  are represented.

energy barrier arises due to the energy compensation between the volume and surface terms. Moreover, Eq.(3.9) allows us to compute the critical radius  $R^*$

$$\frac{dW_{min}}{dR} = 0 \quad \longleftrightarrow \quad R^* = \frac{2\alpha_\infty}{|\Delta g|}, \quad (3.10)$$

which results in an energy barrier of height

$$W_{min}(R^*) = W^* = \frac{16\pi\alpha_\infty^3}{3(\Delta g)^2}. \quad (3.11)$$

It is interesting to mention that a cluster of radius  $R^*$  would be in unstable equilibrium with the old phase. This fact can be verified noticing in Eq.(3.10) that the equilibrium condition ( $\Delta g = 0$ ) is only satisfied when  $R$  tends to infinity, that is, when the new phase is finally formed.

$$\lim_{R \rightarrow \infty} \Delta g = \lim_{R \rightarrow \infty} -\frac{2\alpha_\infty}{R} = 0.$$

Due to the fact that this size is unstable, the cluster will tend to grow or shrink depending on its initial size (actually, thermal fluctuations may enlarge this critical size into a critical unstable region  $|W_{min}(R) - W^*| \leq k_B T$  [2]). On one hand, if it is smaller than the critical size,

its volume will not sustain the surface pressure and the cluster will collapse until it vanishes. On the other hand, if this size is greater than the critical size, the inner pressure will be enough to expand the clusters volume till infinity. Due to the nature of this phenomenon,  $W_{min}(R)$  can be understood as a potential energy, because the cluster size will tend (for a given initial size) to the state that minimizes this function [2]. Then one can also talk about a driving force which will contract or expand the cluster depending on the initial state. This force would be given by

$$F(R) = -\frac{dW_{min}}{dR} = 4\pi R (|\Delta g| R - 2\alpha_\infty). \quad (3.12)$$

Now that the energy barrier has been obtained with Eq.(3.11), the probability for density fluctuations to occur will be of the form

$$P \propto \exp\left(-\beta \frac{16\pi\alpha_\infty^3}{3(\Delta g)^2}\right). \quad (3.13)$$

We can rewrite the expression for the nucleation barrier in terms of the Kelvin formula (Eq.(2.3)),

$$W^* = \frac{16\pi v_0^2 \alpha_\infty^3}{3(k_B T)^2 (\log S)^2}, \quad (3.14)$$

and thus, the probability for density fluctuations,

$$P \propto \exp\left(-\beta \frac{16\pi v_0^2 \alpha_\infty^3}{3(k_B T)^2 (\log S)^2}\right), \quad (3.15)$$

so we can study their dependencies on the supersaturation  $S$ . On one hand, we observe that for high supersaturations ( $S \rightarrow \infty$ ), the nucleation barrier tends to vanish, while the probability tends to the unity. In this case, the system has reached the spinodal region, where no energy is required in order to evolve into the state of equilibrium, for the process is almost spontaneous, and thus, the probability for the density fluctuation to occur will be maximum. On the other hand, for low supersaturations ( $S \rightarrow 1$ ), the nucleation barrier tends to infinity, while at the same time the probability tends to zero. In this case the system is reaching the equilibrium state, where the two different phases coexist, and thus there is no such *driving force* that leads the direction of the process. However, this results in an unreal physical situation. What we actually have is a finite nucleation barrier, high enough to allow the coexistence between both phases, but that can be easily overcome if the system absorbs/emits enough amount of external heat. Indeed, this amount of heat is what we all know from thermodynamics as the *latent heat* [7].

With these results, the thermodynamics of nucleation developed by Gibbs has been completely discussed. Its main goal consisted in obtaining the maximum work the system would need in order to create a critical nuclei, which we derived to be the maximum height of the energy barrier, also known as nucleation barrier. It reflects that the energy balance of the cluster within the old phase depends mainly on two terms; the volume term, which is the energy cost of forming an spatially small new phase of different density within the initial phase, and the surface term, which takes into account the energy cost for creating a dividing surface between the cluster and the old phase.

In the following section we will obtain a kinetic constant that, together with the probability exponential provided by Eq.(3.13), allows us to formulate an analytical expression for the nucleation rate, which constitutes the second most important quantity to study on this work.

### 3.2 Kinetic Theory of Nucleation

Up to this point, we have discussed the energies involving the formation of a cluster with similar properties as the new, truly stable, phase within the old metastable one. However, now we must ask ourselves how actually this formation process takes place, that is, the nucleation dynamics. In the context of the CNT, we will follow what is known as the Szilard-Farkas model, which is based on the following assumptions [1]:

- Clusters are well defined entities formed by an arbitrary number of molecules  $n$ . This number constitutes the 'size' of the cluster. It fully characterizes the nucleation process. Then we say that this model is based on a *single order parameter* theory. A cluster containing  $n$  molecules is known as a  $n$ -mer. Thus, an unitary cluster would be a *monomer*, a cluster containing 2 molecules a *dimer*, then *trimer* and so on.
- Clusters grow or shrink by the attachment or detachment of  $m$ -mers. This growing or decaying process is characterized by the transition frequencies  $f_{nm}(t)$ , that take into account the number of transitions  $n \rightarrow m$  per unit time. Due to the fact that the clusters are fully determined by its size  $n$ , there is no need to describe molecular exchange between clusters of the same size.

With these assumptions, we define  $C_n(t)$  as the concentration of  $n$ -mers at a given instant  $t$  [2]. The time evolution of this quantity will depend on the possible outgoing and incoming transitions. We will call  $f_{nm}(t)C_n(t)$  the number of  $n \rightarrow m$  transitions per unit time and



volume. Thus, at a given instant of time  $t$ ,  $C_n(t)$  will increase at the rate

$$\sum_{m \neq n} f_{mn}(t)C_m(t), \quad (3.16)$$

while it will decrease with rate

$$\sum_{m \neq n} f_{nm}(t)C_n(t), \quad (3.17)$$

It is then clear that the time evolution of  $C_n(t)$  will be given by

$$\frac{dC_n(t)}{dt} = \sum_{m \neq n} [f_{mn}(t)C_m(t) - f_{nm}(t)C_n(t)], \quad (3.18)$$

which is known as the *Master Equation of Nucleation* (MEN) [2]. Actually, instead of a single equation, the MEN describes in principle, an infinite set of ordinary differential equations (ODEs). However, for practical and physical reasons, one typically sets a maximum size in order to get a finite set of ODEs. Eq.(3.18) is called the MEN because of the similarities with the master equations derived from Chapman-Kolmogorov equations in the discrete theory for Jump Markovian Processes [3]. However, this name is not completely well employed since the transition frequencies  $f_{nm}(t)$  generally depend on the concentration  $C_n(t)$  of  $n$ -mers, making Eq.(3.18) a non-linear equation [2].

It is also interesting to develop a *continuity equation* from the MEN, which will be useful in the following sections. This can be carried out by defining the flux of clusters that grow from an arbitrary size  $m' \leq n$  up to a size  $m > n$ , which can be expressed as

$$j_{n,m}(t) = \sum_{m'=1}^n [f_{m'm}(t)C_{m'}(t) - f_{mm'}(t)C_m(t)]. \quad (3.19)$$

The net flux of clusters passing through the size  $n$  will be  $j_n(t) = \sum_{m \geq n+1} j_{n,m}(t)$ , that is, the addition of all the possible  $m$  fluxes. With these definitions, the MEN can be rewritten as

$$\frac{dC_n(t)}{dt} = -(j_n(t) - j_{n-1}(t)) = -\Delta_n j_n(t), \quad (3.20)$$

which has the form of a discrete continuity equation. Until now we have derived several expressions that imply summations over finite differences, due to the fact that the cluster size is defined as an integer number, for it represents the number of molecules in the cluster. However, in the context of the capillary model presented in the previous section, the order parameter employed was the cluster radius (considering spherical clusters, of course), which, in the end, is directly related to the cluster size  $n$ . In order to simplify the mathematics,

Zeldovich [1, 2] proposed that, if the radius is presented as a continuous variable, then the cluster size could be considered as a continuous variable too, so Eq.(3.18), (3.19) and (3.20) can be rewritten in terms of integrals as follows

$$\frac{dC(n, t)}{dt} = \int_1^M dm [f(m, n; t)C(m; t) - f(n, m; t)C(n; t)], \quad (3.21)$$

$$j(n, t) = \int_n^M dm \int_1^{M'} dm' [f(m', m; t)C(m'; t) - f(m, m'; t)C(m; t)], \quad (3.22)$$

$$\frac{dC(n, t)}{dt} = -\frac{\partial j(n; t)}{\partial n}. \quad (3.23)$$

The later expressions are only valid for large cluster sizes, for which the change between next neighbours clusters may be considered small enough.

### 3.2.1 Nucleation Stage and the BDT Model

The MEN provides a general insight of how clusters evolve through time depending on the attachment and detachment rates of  $m$ -mers. However, Eq.(3.18) and Eq.(3.20) imply the solution of ordinary differential equations with finite series and integrals with unknown coefficients and functions  $f_{nm}(t)$  and  $f(n, m; t)$  respectively. Further approximations are required in order to continue.

By taking into account that we are concerned with the initial processes occurring during the early stage of the phase transition, that is, the *nucleation stage*, then it is highly unlikely for clusters greater than monomers ( $m = 2, 3 \dots$  molecules) to play a significant role as their concentration is still low. Together with the fact that the chance of emitting dimers, trimers, etc. is also low, this means that the kinetics of nucleation may be governed mainly by the attachment and detachment of monomers as a first approximation [1]. Mathematically, this is given by the restriction

$$f_{nm}(t) = 0, \quad \forall n, m : |n - m| > 1, \quad (3.24)$$

Now, by imposing the above restriction into Eq.(3.18), we obtain the following equation

$$\frac{dC_n(t)}{dt} = f_{n-1, n}(t)C_{n-1}(t) - (f_{n, n-1}(t) + f_{n, n+1}(t))C_n(t) + f_{n+1, n}(t)C_{n+1}(t), \quad (3.25)$$

which basically means that the concentration of  $n$ -mers depends exclusively on the attachment and detachment of monomers. Or, in other words, it depends on the next-neighbour

interactions. Introducing the notation  $k_n^+ \equiv f_{n,n+1}$  and  $k_n^- \equiv f_{n,n-1}$  [2], and assuming that the transition frequencies are time independent, we arrive to the following expression

$$\frac{dC_n(t)}{dt} = k_{n-1}^+ C_{n-1}(t) - (k_n^- + k_n^+) C_n(t) + k_{n+1}^- C_{n+1}(t), \quad (3.26)$$

which is the core of the well known *Becker-Döring-Tunitskii Model* (BDT Model) [1, 2]. With the above equation, the flux of clusters defined in the previous subsection will be given by

$$j_n(t) = k_n^+ C_n(t) - k_{n+1}^- C_{n+1}(t). \quad (3.27)$$

Once Eq.(3.26) is obtained, we will focus on developing a similar equation for the case of treating the cluster size as a continuous variable. To do so, we will perform truncated Taylor expansions of the terms  $k_{n-1}^+ C_{n-1}(t)$  and  $k_{n+1}^- C_{n+1}(t)$  around the  $n$ -size

$$k_{n-1}^+ C_{n-1}(t) = k_n^+ C_n(t) - \epsilon \left( \frac{\partial(k_n^+ C_n(t))}{\partial n} \right) + \frac{1}{2} \epsilon^2 \left( \frac{\partial^2(k_n^+ C_n(t))}{\partial n^2} \right) + O(\epsilon^3), \quad (3.28)$$

$$k_{n+1}^- C_{n+1}(t) = k_n^- C_n(t) + \epsilon \left( \frac{\partial(k_n^- C_n(t))}{\partial n} \right) + \frac{1}{2} \epsilon^2 \left( \frac{\partial^2(k_n^- C_n(t))}{\partial n^2} \right) + O(\epsilon^3), \quad (3.29)$$

where  $\epsilon$  is a formal ordering parameter. Inserting these expressions into Eq.(3.26), setting  $\epsilon = 1$  and dropping the  $\epsilon^3$  and higher contributions of both expansions we arrive to the equation

$$\frac{\partial C(n, t)}{\partial t} = -\frac{\partial}{\partial n} \left( D^{(1)}(n, t) C(n, t) - \frac{1}{2} \frac{\partial}{\partial n} [D^{(2)}(n, t) C(n, t)] \right), \quad (3.30)$$

with,

$$D^{(1)}(n, t) = k^+(n, t) - k^-(n, t),$$

$$D^{(2)}(n, t) = k^+(n, t) + k^-(n, t).$$

Equation (3.30) is known as the *Tunitskii Equation* [2], and it has the similar form as the one for a general *Generation-Recombination* process (GR) <sup>5</sup> [2]. We may identify  $D^{(1)}(n, t)$  as the drift current of clusters along the size axis and  $D^{(2)}(n, t)$  as the diffusion current or white noise associated to the growth velocity and randomness. It is interesting to see where this nomenclature comes from; On one hand, if we neglect the second term from Eq.(3.30), a continuity-like equation is derived, for which  $D^{(1)}(n, t)$  represents the drift current, while on the other hand, if we neglect the first term, then the equation takes the form of a diffusion-like equation. However, the latter expression would only apply if  $C(n, t)$  was a probability function. Thus, we define then the probability of observing a  $n$ -mer as follows

$$P(n, t) = \frac{n(n, t)}{\sum_{n'} n(n', t)} = \frac{n(n, t)}{N_c(t)}, \quad (3.31)$$

---

<sup>5</sup>A common example for this kind of processes are the creation and destruction of electron-hole pairs between the valence and conduction bands within a semiconductor material.

where  $n(n, t)$  is the number of  $n$ -mers and  $N_c(t)$  the total number of clusters. Thus,  $C(n, t) = \frac{n(n, t)}{V} = C_{tot}(t)P(n, t)$ , with  $C_{tot}(t) = \frac{N_c(t)}{V}$ . If the total number of molecules is constant during the transition, that is,  $N_c$  and thus  $C_{tot}$  are constant, then Eq.(3.30) turns into

$$\frac{\partial P(n, t)}{\partial t} = -\frac{\partial}{\partial n} \left( D^{(1)}(n, t)P(n, t) - \frac{1}{2} \frac{\partial}{\partial n} [D^{(2)}(n, t)P(n, t)] \right). \quad (3.32)$$

This equation has the form of a *Fokker-Planck Equation* (FPE). The cluster size  $n$  is then considered a stochastic markovian process, whose first and second Markov moments are  $D^{(1)}(n, t)$  and  $D^{(2)}(n, t)$ . Thus, the differential equation that  $n$  must satisfy will have the form of a *Langevin Equation* [3]

$$n(t + dt) = n(t) + D^{(1)}(n, t)dt + N(0, 1)\sqrt{D^{(2)}(n, t)dt}, \quad (3.33)$$

where  $N(0,1)$  corresponds to a random number from the normal distribution. Although we have employed several approximations, Eq.(3.32) reflects the stochastic nature of the concentration of clusters, and thus the phase transition itself. For small clusters, the derived Fokker-Planck equation does not describe the same phenomenon as the BDT equation, Eq.(3.26), because higher order Markov moments become significant. In that case, by taking into account the whole Taylor expansions from Eq.(3.28) and Eq.(3.29), we arrive to the following expansion

$$\frac{\partial P(n, t)}{\partial t} = \sum_{j=1}^{\infty} \frac{(-1)^j}{j!} \frac{\partial^j}{\partial n^j} [D^{(j)}(n, t)P(n, t)], \quad (3.34)$$

with the Markov moments

$$D^{(j)}(n, t) = \epsilon^j [k^+(n, t) + (-1)^j k^-(n, t)]. \quad (3.35)$$

This equation constitutes a *Kramers-Moyal Equation* (KME) [3], which is a generalisation of the master equation for continuous variables. Despite being formally exact, the KME contains an infinite number of Markov moments, for which its numerical solution becomes even more difficult, and then truncation methods are required [3]. It is also interesting to outline that we can recover the FPE by considering from the KME just the first two moments of the expansion.

### 3.2.2 Equilibrium Approach

The KME and FPE allow us to compute the time evolution of the probability of finding a  $n$ -mer (and thus, concentration of  $n$ -mers) at any time, with the assumption of large clusters. Thus, we can use the tools of mathematical analysis and continuous calculus. However, in order to obtain  $P(n, t)$ , the statistical moments associated to the Markov process and thus

the attachment and detachment rates are required. On the one hand, the attachment rate will depend mainly on the mechanism governing the transport of particles within the old phase, that is, a mass transport problem [2], while on the other hand, the detachment rate depends on the physical properties of the cluster, which remain unknown.

Zeldovich proposed an idea in order to establish a relation between the monomer attachment and detachment frequencies [1, 2]. This relation comes from demanding that the flux of clusters defined by Eq.(3.27) to be zero under equilibrium conditions, that is, when the system is undersaturated. Mathematically, this demand is given by the condition

$$j_n^{eq}(t) = k_n^+ C_n^{eq}(t) - k_{n+1}^- C_{n+1}^{eq}(t) = 0, \quad (3.36)$$

where the superindex *eq* denotes the equilibrium conditions. This hypothesis is known as *detailed balance* or *constrained equilibrium condition* [2]. At quasi-equilibrium conditions, we can also consider the concentration of clusters being governed by a time-dependent Boltzmann distribution [1, 2], namely

$$C_n^{eq}(t) \propto \exp(-\beta \Delta G_n(t)), \quad (3.37)$$

where  $\Delta G_n(t)$  is the Gibbs free energy of the system containing an  $n$ -mer. For the sake of simplicity, we will consider that the temperature will remain constant throughout the process, so that  $\beta$  will be then time-independent. This assumption is known as the *isothermal condition* [1, 7]. By substituting this on Eq.(3.36) we obtain the following relation

$$k_{n+1}^-(t) = k_n^+ \exp[\beta(\Delta G_n(t) - \Delta G_{n+1}(t))], \quad (3.38)$$

which is the core of the Zeldovich approach. However, as we already mentioned, the detailed balance only holds for equilibrium conditions, so applying it for a nonequilibrium situation such as nucleation itself constitutes a huge assumption that we will discuss on further sections. Now, by expanding Eq.(3.38) in its continuous form, we obtain

$$\begin{aligned} k^-(n, t) &= k^+(n-1, t) \exp[\beta(\Delta G(n, t) - \Delta G(n-1, t))] \\ &\approx \left( k^+(n, t) - \epsilon \frac{\partial k^+(n, t)}{\partial n} \right) \left( 1 + \epsilon \beta \frac{\partial G(n, t)}{\partial n} \right) \\ &= k^+(n, t) - \epsilon \frac{\partial k^+(n, t)}{\partial n} + \epsilon \beta k^+(n, t) \frac{\partial G(n, t)}{\partial n}, \end{aligned} \quad (3.39)$$

where we have just considered the first-order terms of each expansion. By substituting the above expansion into the FPE equation provided by Eq.(3.32), we obtain the following expression

$$\frac{\partial P(n, t)}{\partial t} = \frac{\partial}{\partial n} \left[ k^+(n, t) \beta \frac{\partial G(n, t)}{\partial n} P(n, t) + k^+(n, t) \frac{\partial P(n, t)}{\partial n} \right], \quad (3.40)$$

which is known as the *Zeldovich Equation* (ZE) for the probability distribution function [2]. It will allow us to compute analytical estimations for both the cluster size distribution and the nucleation rate. We must discuss the following aspects regarding the ZE equation:

- **Cluster Size Limitations:** In order to derive Eq.(3.40) we have employed several assumptions. On one hand, we have neglected the  $\frac{\partial k^+(n,t)}{\partial n}$  contribution by considering that the attachment rate changes very little for large clusters, while on the other hand, we have just taken into consideration the first term of the expansion of the exponential in Eq.(3.39), which is only justified for  $\frac{\partial G(n,t)}{\partial n} \ll 1$ . Namely, we are limiting ourselves within the vicinity of the critical cluster, for which the Gibbs free energy reaches its maximum.
- **Equilibrium Solution:** We can impose the equilibrium situation by demanding a zero probability flux in the ZE [2, 7]

$$\beta \frac{dG(n)}{dn} P_{eq}(n) + \frac{dP_{eq}(n)}{dn} = 0. \quad (3.41)$$

By solving the above ordinary differential equation, we obtain

$$P_{eq}(n) = A \exp(-\beta \Delta G(n)) \quad \rightarrow \quad C_{eq}(n) \propto \exp(-\beta \Delta G(n)), \quad (3.42)$$

where the constant  $A$  is fixed by the normalization of the probability distribution function  $P_{eq}(n)$ . This last expression is useful in order to check the canonical form of the equilibrium distribution [2], as we firstly assumed with Eq.(3.37).

- **Stationary Solution:** The physical situation underlying this solution is that the system reaches a steady state where the cluster production is constant. If a cluster reaches the supercritical size, it will grow indefinitely, so it will no longer be considered a stochastic process. In order to impose a stationary flux  $J_s$ , we can remove those clusters greater than the supercritical size ( $n_+ > n^*$ ) and reintroduce them in the form of monomers [2]. Mathematically, the restricted stationary flux is given by

$$J_s = - \left[ k^+(n) \beta \frac{\partial G(n)}{\partial n} P_s(n) + k^+(n) \frac{\partial P_s(n)}{\partial n} \right]; \quad P_s(n_+) = 0. \quad (3.43)$$

Solving the ordinary differential equation given by the above equation and applying the given initial condition, we obtain the stationary probability distribution function [2]

$$P_s(n) = J_s \exp(-\beta \Delta G(n)) \int_n^{n_+} \frac{dx}{k^+(x) \exp(-\beta \Delta G(x))}, \quad (3.44)$$

which will play a key role in the calculation of the nucleation rate.

### 3.2.3 Nucleation Rate in CNT

At this point, we have developed the theoretical background and all the mathematical tools that will allow us to compute an analytical value for the most important magnitude underlying the CNT; the nucleation rate, which measures the production of new clusters per unit volume. Its importance lies within the fact that the nucleation rate can be measured experimentally, thus establishing a first connection between the theory and the real world. It also allows us to check the validity of all the presented ideas by comparing them with the experimental results.

By taking into account that only supercritical clusters will take part in the nucleation process, the nucleation rate is defined by [2]

$$J(t) = \frac{dC_{n>n^*}(t)}{dt}, \quad (3.45)$$

where  $C_{n>n^*}(t)$  is the concentration of supercritical clusters, that is, those clusters whose sizes are greater than the critical one. Within the continuous approach,  $C_{n>n^*}(t)$  is given by

$$C_{n>n^*}(t) = \int_{n^*}^{\infty} C(n, t) dn = \int_{n^*}^{\infty} \frac{N_c(t)}{V} P(n, t) dn, \quad (3.46)$$

with

$$N_c(t) = \int_1^{\infty} n(n, t) dn, \quad (3.47)$$

being the total number of clusters [1, 2]. Now, by inserting Eq.(3.46) into Eq.(3.45), we obtain

$$J(t) = \frac{1}{V} \frac{dN_c(t)}{dt} \int_{n^*}^{\infty} P(n, t) dn + \frac{N_c(t)}{V} \int_{n^*}^{\infty} \frac{\partial P(n, t)}{\partial t} dn. \quad (3.48)$$

Using the Zeldovich Equation in the second term and imposing the steady state condition, we arrive to the following expression

$$J = -\frac{N_c}{V} \left[ k^+(n) \beta \frac{\partial G(n)}{\partial n} P_s(n) + k^+(n) \frac{\partial P_s(n)}{\partial n} \right] = \frac{N_c}{V} J_s, \quad (3.49)$$

which basically means that the nucleation rate depends mainly on the artificially imposed stationary flux  $J_s$  from the previous subsection. In order to go further, we need to develop an analytical expression for  $J_s$ . Zeldovich proposed a boundary condition in order to solve this problem [2]; monomers are indeed particles from the old phase, so their steady concentration must be equal to the initial average density

$$C_s(n = 1) = \rho_{av}. \quad (3.50)$$

Following this idea, the steady probability of finding monomers will be given by

$$P_s(1) = \frac{C_s(1)}{C_{tot}} = \frac{\rho_{av}V}{N_c}, \quad (3.51)$$

and thus, by substituting this into Eq.(3.43), we arrive to

$$J_s = \frac{\rho_{av}V}{N_c} \left( e^{-\beta\Delta G(1)} \int_1^{n^+} \frac{dx}{k^+(x) \exp(-\beta\Delta G(x))} \right)^{-1}. \quad (3.52)$$

The first exponential term comes from the fact that the system does not need to spend energy in forming monomers, as they already belong to the old phase. Now we will approximate the above integral by means of the Lagrange saddle-point method [8]. Knowing that the exponential term  $\exp(\beta\Delta G(n))$  must show a sharp maximum at the critical size  $n^*$ , we can use the following first order asymptotic expansion [1, 2]

$$\int_{I_x} \frac{\exp(\beta\Delta G(x))}{k^+(x)} dx \approx \frac{\exp(\beta\Delta G(n^*))}{k^+(n^*)} \left( -\frac{\beta}{2\pi} \frac{\partial^2 \Delta G(n)}{\partial n^2} \right)_{n=n^*}^{-\frac{1}{2}} + O(\beta^{-1}). \quad (3.53)$$

Finally, by applying these expressions on Eq.(3.49), we arrive to an analytical expression for the nucleation rate within the CNT context

$$J_{CNT} \approx z_d k^+(n^*) \rho_{av} \exp\left(-\frac{W^*}{k_B T}\right), \quad (3.54)$$

where  $W^*$  is the minimum work required for a critical cluster to form, and

$$z_d = \left( -\frac{\beta}{2\pi} \frac{\partial^2 \Delta G(n)}{\partial n^2} \right)_{n=n^*}^{-\frac{1}{2}}, \quad (3.55)$$

is the Zeldovich factor [2], which can be also expressed by means of the simplified formula

$$z_d = \left( \frac{\beta W^*}{3\pi(n^*)^2} \right)^{\frac{1}{2}}. \quad (3.56)$$

However, in our analysis we have not considered that the condition given by Eq.(3.50) implies that monomers already belonged to the old phase before the transition, so they do not contribute to the energy barrier  $W^*$ . In order to take this into account, we must redefine the energy barrier as

$$W_{SCCT}^* = W^* - W(n=1). \quad (3.57)$$

The sub-index SCCT comes from the *Self Consistent Classical Theory*, which provides an expression for the nucleation rate given by

$$J_{SCCT} \approx z_d k^+(n^*) \rho_{av} \exp\left(-\frac{W_{SCCT}^*}{k_B T}\right). \quad (3.58)$$



Let us briefly discuss the physical meaning underlying both Eq.(3.54) and Eq.(3.58). First, we must notice that this expression contains the same exponential term as the one we initially derived in previous sections from the thermodynamic approach. It is related to the probability for a critical cluster to form. Also, the initial average density  $\rho_{av}$  is related to the physical properties of the system in its old phase. In addition, we have the Zeldovich factor, which is directly related to the nucleation barrier, and the attachment constant  $k^+(n)$ , which provides us information about the mass transport phenomenon that is taking place in the system [1]. However, the dominant term of the expression is the exponential one, which tells us that, in the end, the nucleation rate is primarily governed by the nucleation barrier. This fact is corroborated by the theorem developed by Kashchiev [1] within the context of the CNT, known as the *Nucleation Theorem*, which relates the dependency of the nucleation rate with the supersaturation by means of the nucleation barrier and the critical nucleus. Mathematically, it is expressed by

$$\frac{\partial \log J}{\partial \log S} \approx -\frac{\partial \beta W^*}{\partial \log S} = n^*, \quad (3.59)$$

where  $J$  relates to the nucleation rate (in both the CNT and SCCT) and  $S$  is the supersaturation. Its importance lies in the fact that, given that the nucleation rate, the amount that allows us to make a connection between theory and experiments, it depends mostly on the physics behind the nucleation barrier, so a good step to begin in order to improve the classical theory would be to consider a new paradigm of nucleation from which corrections can be made to this barrier, and with this, the density functional theory would come into play.

In conclusion, the nucleation rate depends mainly on the nucleation barrier, and secondarily on the properties of the system before the transition occurs and the phenomenon through which particles within the system can diffuse and collide.

### 3.3 Homogeneous Nucleation of Water

Once we have developed the theoretical framework that allows a classical description of the nucleation process, we will use its main results in order to investigate the case of time-independent homogeneous nucleation of water droplets in the vapor phase. We have chosen water due to its importance in atmospheric processes, which play a key role in the development of life on Earth.

In this section we will study the equilibrium probability functions from both the thermodynamic and stochastic approaches, and we will compare them by means of the nucleus critical size. Also, we will obtain the nucleation rates of water droplets for different supersaturations

and temperatures, and we will compare them with experimental measurements carried out by Viisanen, Strey and Reiss in diffusion cloud chambers [4].

### 3.3.1 Equilibrium Distribution and Critical Cluster

In section 3.1 we derived the nucleation barrier and the critical radius of spherical clusters by computing the change of Gibbs free energy of the system before and after the cluster appearance, within the thermodynamic approach. However, it is expressed in terms of the critical radius  $R$ . As in the kinetic theory we worked with the nucleus size  $n$  as the stochastic variable, we can relate both quantities with the formula

$$n = \frac{4\pi R^3}{3v_0}. \quad (3.60)$$

Including this formula onto Eq.(3.9) results in a new expression for the Work for cluster formation (and thus the Gibbs free energy),

$$W(n) = -|\Delta g|v_0n + cv_0^{2/3}\alpha_\infty n^{2/3}, \quad (3.61)$$

where  $c = (36\pi)^{1/3}$ . By following the same procedure as in section 3.1, we arrive at the critical nucleus size

$$n^* = \frac{32\pi\alpha_\infty^3}{3|\Delta g|^3v_0}. \quad (3.62)$$

With the data provided by Table 1, a critical nucleus of  $n^* = 3.4372 \cdot 10^8$  molecules is obtained.

$\alpha_\infty(N/m)$	$T$ (K)	$S$	$m_0$ (kg)	$v_0$ (m <sup>3</sup> )	$p'_E$ (kPa)	$\gamma_1$
0.072	233	1.01	$3 \cdot 10^{-26}$	$3 \cdot 10^{-29}$	120	0.175

Table 1: Values of various quantities used for calculations regarding the nucleation of water droplets in vapours [1, 4].  $\alpha_\infty$  is the surface tension,  $T$  the nucleation temperature,  $S$  the supersaturation,  $m_0$  and  $v_0$  are the mass and volume of a monomer, and  $\gamma_1$  is the sticking coefficient of monomers onto the nucleus surface in vapours.

Now, from the kinetic theory, we will solve the *Langevin Equation* given by Eq.(3.33). But first, we need an analytical form for the monomer attachment frequencies  $k^+(n)$ . For the case of homogeneous nucleation in condensed vapours, according to the kinetic theory of gases [1], these frequencies are given by the expression

$$k^+(n) = \frac{\gamma_1 cv_0^{2/3} Sp'_E}{\sqrt{2\pi m_0 k_B T}} n^{2/3} = \gamma_1 I c v_0^{2/3} n^{2/3}, \quad (3.63)$$

where  $\gamma_1$  corresponds to the sticking coefficient of monomers onto the nucleus surface, which is given by the factor  $cv_0^{2/3}n^{2/3}$  (or  $4\pi R^2$ ), and  $I = Sp'_E/\sqrt{2\pi m_0 k_B T}$  is the Hertz-Knudsen impingement rate for an ideal gas [1]. Eq.(3.58), together with Eq.(3.56) and the Zeldovich equilibrium approach, they allow us to obtain an analytical expression for the monomer detachment frequencies  $k^-(n)$ , given by Eq.(3.36) with  $\epsilon = 1$ ,

$$\begin{aligned} k^-(n) &\approx k^+(n) - \frac{\partial k^+(n)}{\partial n} + \beta k^+(n) \frac{\partial G(n)}{\partial n} \\ &= \gamma_1 I c v_0^{2/3} n^{2/3} \left[ 1 - \frac{2}{3n} - \beta |\Delta g| v_0 + \frac{2}{3} \beta c v_0^{2/3} \alpha_\infty n^{-1/3} \right], \end{aligned} \quad (3.64)$$

and with this, both Markov moments  $D^{(1)}(n)$  and  $D^{(2)}(n)$  will be given by

$$\begin{aligned} D^{(1)}(n) &= k^+(n) - k^-(n) \\ &\approx \gamma_1 I c v_0^{2/3} n^{2/3} \left[ \frac{2}{3n} + \beta |\Delta g| v_0 - \frac{2}{3} \beta c v_0^{2/3} \alpha_\infty n^{-1/3} \right], \\ D^{(2)}(n) &= k^+(n) + k^-(n) \\ &\approx \gamma_1 I c v_0^{2/3} n^{2/3} \left[ 2 - \frac{2}{3n} - \beta |\Delta g| v_0 + \frac{2}{3} \beta c v_0^{2/3} \alpha_\infty n^{-1/3} \right]. \end{aligned} \quad (3.65)$$

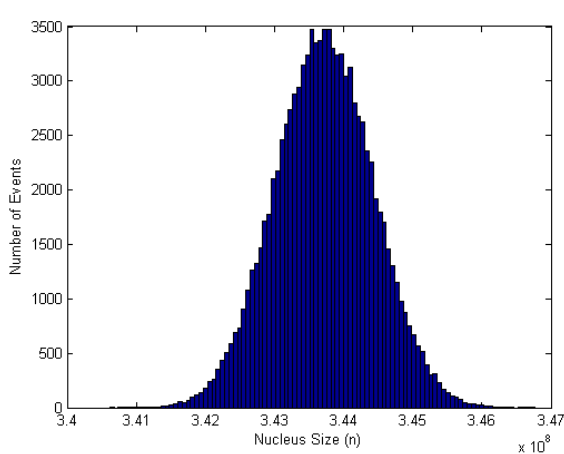
Now we can solve numerically the *Langevin Equation* with time-independent Markov moments. For that, we will employ what is known as the Euler-Maruyama approximation [3]: We will solve the *Langevin Equation* over a time interval of length  $T$ , which will be divided in  $M$  partitions of length  $\Delta t = T/M$ . Considering the initial condition  $X(0)$ , the time evolution of the stochastic variable  $X(t)$  can be approximated by the equation

$$X(t + \Delta t) = X(t) + D^{(1)}(X)\Delta t + N(0, 1)\sqrt{D^{(2)}(X)\Delta t}, \quad (3.66)$$

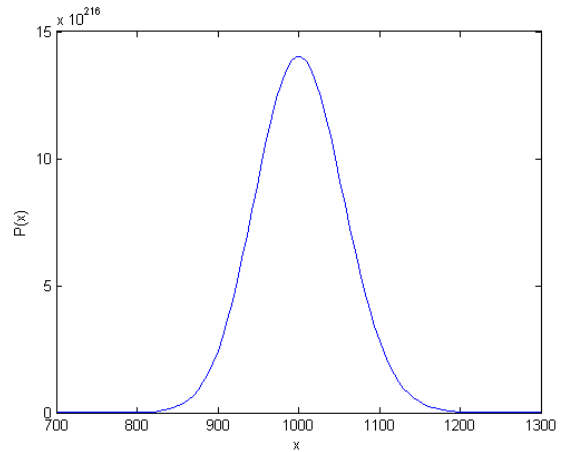
where  $N(0,1)$  corresponds to a random number from the normal distribution. This equation allows us to obtain stochastic trajectories of the Markov process  $X(t)$ . In Figure 5 the results of such calculation are shown. There, we can notice that the equilibrium distribution function obtained through the Euler-Maruyama algorithm coincides with the one derived from the thermodynamic approach. In fact, the critical size derived previously coincides with the maximum associated to the distribution function presented in Figure (5a).

However, despite this apparent success in our results, we must not forget the limitations under which we have worked with. We have assumed very low supersaturations and initial conditions of the cluster size near the critical size in order to perform our calculations. This is mainly due to two reasons:

- First of all, all of our assumptions are completely valid for equilibrium situations, despite we have been applying them for dynamical processes. Low supersaturations



(a) 5a



(b) 5b

Figure 5: Equilibrium distribution functions for the nucleus size. Fig.(5a) shows the histogram obtained by solving the *Langevin Equation* with the Euler-Maruyama method with parameters: Time interval  $T = 100000$ , Number of partitions  $M = 100000$ , and initial condition  $X(0) = 3.49 \cdot 10^8$ . Fig.(5b) shows a general distribution obtained with the function  $P(x) = \exp(G(x))$ , where  $G(x) = -A \cdot x + B \cdot x^{2/3}$  has the form of the Gibbs free energy presented in Eq.(3.61), with the parameters  $A = 1$ ,  $B = 15$ , in order to compare its form with the one obtained with the algorithm.

imply situations nearer the equilibrium than higher ones, where the nucleation barrier tends to the minimum, and thus the probability of forming a cluster increases. In practical terms, with higher supersaturations, the nucleation process requires less time for occurring, that is, it is faster than for lower supersaturations, where the process takes a bigger amount of time, and thus it can be approximated to a quasi-static process.

- Also, for low supersaturations, the critical nucleus size increases, and so does the nuclei found in the vicinity. This allows us to regard the nucleus size as a continuous variable, and thus the FPE may be applied. Moreover, In order to remain in the vicinity of the critical nucleus, the attachment frequencies  $k^+(n)$  must be some orders of magnitude smaller than the range of nucleus sizes we are working with (for the case of our concern,  $k^+(n) \sim 10^5$ ), otherwise, due to the diffusion term, our stochastic process would have abandoned the vicinity zone and thus our FPE would not be valid anymore.

### 3.3.2 The Cloud Chamber and Temperature Dependencies

We will continue our study of homogeneous nucleation of water by making a comparison between the theoretical predictions provided by the CNT with recent experimental measurements of the nucleation rate at different temperatures carried out in diffusion cloud chambers.

A diffusion cloud chamber is a device that allows nucleation studies in the steady state. It consists of a hot bottom and a cold top plates separated by a circular ring. The lower plate is covered by a thin film of water, while the rest of the volume is fulfilled with an inert carrier gas, with all the aerosol particles being removed. Vapor evaporates from the lower plate, diffuses through the carrier gas and condenses on the top plate. Since, as a first approximation, one can consider the temperature of the partial pressure of the vapor to decrease linearly with increasing height from the lower plate, while the equilibrium pressure varies exponentially with temperature, a supersaturated state appears within the chamber, whose maximum value is reached at about 2/3 of the distance from the lower to the higher plate [5].

With this apparatus, Viisanen, Strey and Reiss studied the formation of water droplets in supersaturated vapours at different temperatures and supersaturations with Ar as their carrier gas [4]. The analytical expression they employed for the nucleation rate can be obtained with the formulas we derived in previous sections. Let us start with the Zeldovich factor  $z_d$  that appeared in the expression of the nucleation, and that it is given by Eq.(3.56). Substituting the minimum work  $W^*$  provided by Eq.(3.61) and the monomer attachment frequencies  $k^+(n)$  given by Eq.(3.63) into Eq.(3.58), we obtain the expression

$$\begin{aligned}
 J &\approx z_d k^+(n^*) \rho_{av} \exp\left(-\frac{W_{SCCT}^*}{k_B T}\right) \\
 &= \left(\sqrt{\frac{W^*}{3\pi k_B T}} \frac{1}{n^*}\right) \left(\frac{\gamma_1 c v_0^{2/3} S p'_E}{\sqrt{2\pi m_0 k_B T}} (n^*)^{2/3}\right) \left(\frac{S p'_E}{k_B T}\right) \exp\left(-\frac{W^* - W(1)}{k_B T}\right) \\
 &= \gamma_1 \sqrt{\frac{c^3 \alpha_\infty}{18\pi^2 m_0}} \left(\frac{p'_E}{k_B T}\right)^2 v_0 S \exp\left(\frac{c v_0^{2/3} \alpha_\infty}{k_B T}\right) \exp\left(-\frac{4c^3 \alpha_\infty^3}{27(k_B T)^3 (\log S)^2}\right),
 \end{aligned} \tag{3.67}$$

where we have employed that

$$\exp\left(\frac{W(1)}{k_B T}\right) = \exp\left(\frac{-k_B T \log S + c v_0^{2/3} \alpha_\infty}{k_B T}\right) = \frac{1}{S} \exp\left(\frac{c v_0^{2/3} \alpha_\infty}{k_B T}\right).$$

As it can be noticed,  $J$  presents a double dependence on the supersaturation  $S$ ; a linear, and an exponential ones. It is obvious then to believe that the exponential will domain over the rest of the terms, as we pointed out in previous sections when we talked about the *Nucleation Theorem* [1].

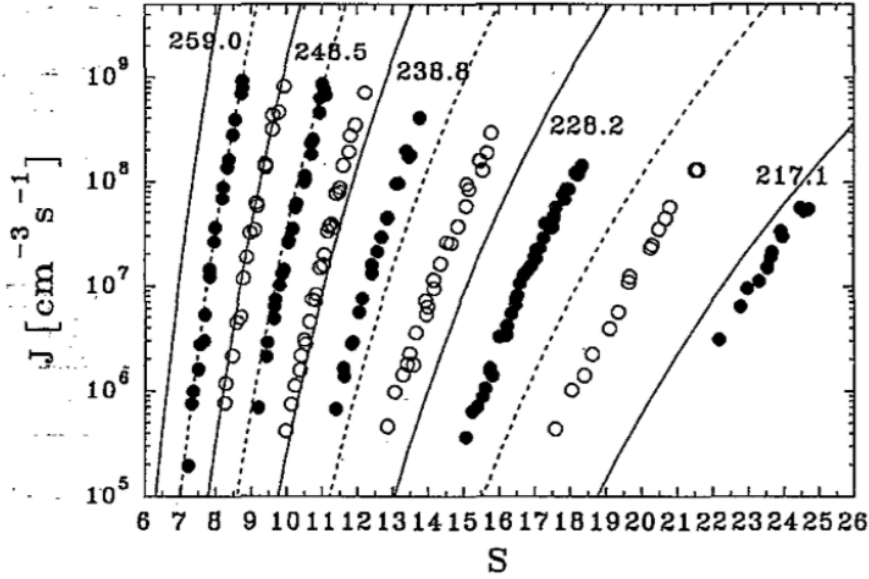


Figure 6: Comparison between the experimental measurements of the nucleation rate of water droplets in condensed vapour phases carried out in diffusion cloud chambers at different temperatures and the theoretical curves predicted from the CNT. The full lines correspond to the theoretical curves associated to the black dots, while the dashed ones correspond to the white dots. Both black and white dots correspond to experimental data [4].

Figure 6 shows both the experimental and theoretical nucleation rates for different temperatures. We can notice that there is a strong dependency on both the temperature and the supersaturation. However, since for low temperatures we find that the predictions of the CNT do not deviate too much from the experimental results, for higher temperatures we find deviations of even more than one order of magnitude, which leads to great relative errors in the measurements and thus, the general failure of the model. Apart from non-classical effect that may have played a role, there are two main aspects to outline that may explain the discrepancies between the theory and reality:

- First, the curves presented in Figure 6 are given for high values of the supersaturation  $S$ . As we commented on the previous subsection, higher supersaturations imply situations more dynamical, that is, situations way far from the equilibrium or quasi-equilibrium situations. This is again related to the fact that we developed our entire framework based on equilibrium (the thermodynamical approach) and quasi-equilibrium (detailed balance) assumptions, which are too coarse approximations for the non-equilibrium situation that we are trying to describe.
- Secondly, we should mention that the temperature is the key factor for this discrepancy. If we remember Figure 4 (Section 3.1.2), we mentioned that there was a critical unstable

region, temperature-dependent, from which clusters may play a role in the nucleation process. For high temperatures, this region may extend enough so smaller clusters may take part on the process, which is undesirable, because one of the main assumptions in both the thermodynamical and stochastic approaches of the CNT was to consider only large clusters. The description of the nucleation theory by means of small clusters is out of the scope of the classical theory [2].

Apart from these deficiencies, we must outline that, despite the limitations presented on the initial conditions that we had when we solved the *Langevin Equation*, we did not find actually any restraints in those theoretical curves that did corroborate the experimental data. Furthermore, those curves are given between way higher values than the one we used in order to perform our simulation. This paradox reflects once more the need to develop a consistent kinetic theory of nucleation that allows to erase these inconsistencies that emerge from the CNT.

### 3.4 Deficiencies of the CNT

In the previous sections we have managed to develop the entire theoretical framework under which the CNT is built, leading to the derivation of the nucleation rate, which is the main bridge between reality and theory, and we have applied the obtained results to the particular case of the homogeneous nucleation of water droplets in condensed vapour. However, as it has been commented, we have used numerous assumptions that limit the range of validity of the results and expressions obtained, not to mention, some of those that give rise to unreal physical situations. Despite this, the CNT constitutes a solid base on which new theories can be developed with more realistic corrections. Therefore, in order to conclude with the study of Classical Nucleation Theory, we will briefly comment on its main defects [2].

- **The Capillary Model:** One of the most important assumptions we employed through the development of the CNT was indeed the capillary model, not only because it allows us to formulate in a simple way the work required for cluster formation from a thermodynamic approach, but also because it *defines* the cluster. In order to understand this, we must recover the density profile presented in Eq.(3.8) by means of the Heaviside function  $\Theta(x)$

$$\rho_{cap}(r) = \rho_{new}\Theta(R - r) + \rho_{av}\Theta(r - R). \quad (3.68)$$

With this approach, we can clearly make a distinction between two regions: The cluster ( $r < R$ ), for which we also imposed that it must have the same properties as the new phase (that is,  $\rho_{cl} = \rho_{new}$ ), and the surrounding environment ( $r > R$ ), which constitutes the old phase, due to the fact that there is a sharp interface between these two regions.

Despite being a simple model, it does not represent a real physical situation. In order to improve the model, we shall introduce what are known as *n-parameter theories* [2], for which clusters are completely defined by a set of  $n$  different parameters (the radius, width of surface, etc), and thus, the density profile adopts a more realistic form, such as in Figure 3(a). Another more sophisticated possibility that we will discuss in further sections is the *Density Functional Theory* (DFT), which will allow us to obtain the density profile by means of calculus of variations [1]. The only difficulty that arises from those approaches is that we would need to reformulate the entire kinetic theory of nucleation, because it is based mainly on the assumption of well defined clusters that provides the capillary model.

- **Large Clusters Assumption:** The thermodynamic approach introduced in section 3.1 in order to develop an expression for the nucleation barrier are only valid for a large number of molecules compounding the cluster, that is, in the *thermodynamic limit* [7]. Also, in order to derive the Fokker – Planck and Krammers – Moyal equations, we considered that the cluster size was large enough so it may be treated as a continuous variable. Indeed, together with the restriction imposed by the equilibrium approach, for which the range of validity of the nucleation rate lies within the vicinity of the critical size, it is though true to confirm that the description and contribution of small clusters to the nucleation process is outside the scope of the CNT. A self-consistent theory of nucleation must be able to describe both kinetics and energy balance of clusters within the old phase no matter their size [2].
- **Equilibrium Approach:** With the Zeldovich approach we were able to solve the problem of the detachment rate of clusters by imposing equilibrium conditions on the undersaturated system, resulting in an expression that relates this detachment rate with the attachment rate, which is a more suitable magnitude to compute. However, this argument leads to unphysical situations, because we are imposing that the new phase is in equilibrium with the old metastable phase during the transition, where actually the nucleation itself consists in a non-equilibrium process [1]. Moreover, the derived equilibrium probability distribution functions are only normalizable when the system is undersaturated [2], which, again, it is a nonphysical situation in our case.
- **Lack of Covariance:** In previous sections we used two different parameters for the description of the clusters size: the number  $n$  of molecules and the radius  $R$  of the associated spherical cluster. Although both descriptions are unequivocal, the interchange is not symmetric when we are dealing with the equilibrium probability distribution functions  $P(n)$  and  $P(R)$  respectively [2].



On one hand, with the Zeldovich approach, under equilibrium conditions, we derived a distribution function proportional to the Boltzmann factor

$$P(n) \propto \exp(-\beta\Delta G(n)). \quad (3.69)$$

While on the other hand, within the framework of the thermodynamic approach, we also derived an expression for the minimum work required for a cluster to form, which is directly related to the amount of Gibbs free energy required for the process to occur. The problem arises when we want to switch between distribution functions, because they are actually related by the transformation relation

$$P(n)dn = P(R)dR, \quad (3.70)$$

which means basically that the probability of finding clusters with a certain size must not depend on the chosen variable for its description. Using the above equations, we can estimate the probability distribution function for the spherical radius

$$P(R) \propto \exp\left(-\beta\left(\Delta G(R) + k_B T \ln \frac{dn(R)}{dR}\right)\right), \quad (3.71)$$

which is similar to the ones used in previous sections but for the Jacobian term. For large clusters, this contribution can be neglected in comparison with the volume and surface terms, but again, we are limiting ourselves to a certain range of validity for the cluster size.

## 4 Density Functional Theory

In the previous section we developed the *Classical Nucleation Theory*, which is fundamentally based on the definition of a cluster as a portion of the new phase formed within the old one during the phase transition. This cluster will grow or sink through the attachment and detachment of monomers, depending mainly on its initial size. With these ideas, all the theoretical background underlying the theory was developed. However, as it was already discussed, some physical issues emerge from the main assumptions employed in the development of our theory, one of the most important ones being the definition of a cluster. Within the context of the *Capillary Model* the answer is simple; all the molecules belonging to the region lower than the *equimolar dividing surface* form a cluster, while the rest of them conform the environment, that is, the old phase, as depicted in Figure 3b. However, we already pointed out the abruptness and simplicity of this model. A more realistic density profile for the cluster corresponds to the one shown in Figure 3a, where the change in density

is continuous. Thus, the density will depend on the spatial coordinates, that is,  $\rho = \rho(\mathbf{r})$ . A completely new theoretical approach is then necessary in order to obtain better estimations for the nucleation barrier.

Limiting our considerations to one-component homogeneous nucleation under isothermal and isobaric conditions, we introduce the *Density Functional Theory* (DFT) of nucleation, based entirely on the density functional approach [1].

## 4.1 Density Functional and Variational Approach

As it can be seen in Figure 3a, instead of a dividing surface between the molecules of the new and old phases, we have a continuous change of the molecular density through a transition region known as the *surface layer* [1]. Let  $\rho(\mathbf{r})$  be the molecular density at point  $\mathbf{r} = (x, y, z)$  in cartesian coordinates. This density is related to the average density  $\rho_{av}$  through the expression [2]

$$\rho_{av} = \frac{1}{V} \int_V \rho(\mathbf{r}) d\mathbf{r}. \quad (4.1)$$

Due to the fact that  $\rho(\mathbf{r})$  is non-homogeneous, other quantities related to it will present dependence with spatial coordinates too. Such is the case of the Helmholtz free energy per molecule  $f$ , which becomes a function of  $\mathbf{r}$ ,  $\rho$  and its derivatives. That is the main reason why thermodynamics, which operates with homogeneous quantities, is not adequate for determining the nucleation work  $W^*$ . Hence, we must reformulate the Gibbs free energy for both initial and final states of the system (Figure 2) as a function of the molecular density function. We will define the total free energy as a *functional* of the density given by

$$G[\rho] = \int_V g(\rho(\mathbf{r}), T) d\mathbf{r} = \int_V (f(\rho(\mathbf{r})) - \mu\rho(\mathbf{r})) d\mathbf{r}, \quad (4.2)$$

where  $g(\rho(\mathbf{r}))$  constitutes the Gibbs free energy per unit volume at constant temperature and  $\mu$  is the chemical potential. According to the definition presented in previous sections, the minimum work for a density fluctuation within the old phase will be given by

$$W[\rho] = \Delta G[\rho] = G_f[\rho] - G_i[\rho] = \int_V ((f(\rho(\mathbf{r})) - \mu\rho(\mathbf{r})) + p) d\mathbf{r}, \quad (4.3)$$

where we have taken into account that  $G_i[\rho] = - \int_V p d\mathbf{r}$ , approaching Eq.(3.3) in the thermodynamic limit. The resulting expression is valid for any arbitrary density profile. Similar to how we proceeded with the thermodynamic approach, we will focus our attention into the critical fluctuation (so called nucleus [2]), that is, the one required for triggering the phase

transition. It can be defined as a saddle point in functional space. To obtain the density profile  $\rho^*(\mathbf{r})$  characterizing the critical fluctuation, we must solve the following variational problem

$$(\delta W[\rho])_{\rho=\rho^*} \equiv \delta \left( \int_V ((f(\rho(\mathbf{r})) - \mu\rho(\mathbf{r})) + p) d\mathbf{r} \right)_{\rho=\rho^*} = 0, \quad (4.4)$$

whose solution will allow us to determine the nucleation barrier

$$W^* \equiv W[\rho^*(\mathbf{r})]. \quad (4.5)$$

The procedure presented above allowed us to obtain the variational equations required for the nucleation barrier without the need of introducing neither a dividing surface nor a capillary model in order to distinguish between the nucleus (cluster) and the old phase. In this case, the first stage of nucleation is treated as a density fluctuation of the old phase. This is in contrast with our previous analysis, where the cluster formed within the old phase already presented the same properties as the new phase and it was treated as a macroscopic independent system.

The only problem regarding Eq.(4.4) is that we need the exact form of  $f(\rho(\mathbf{r}))$  in order to obtain a solution for the density profile. However, even without having this information, we can derive a partial differential equation from this equation by considering the Helmholtz free energy as an exclusive function of  $\rho$  and  $\nabla\rho$ . In that case, the condition of extremal  $W[\rho]$  only applies if the Euler-Lagrange equation is satisfied [1, 2]

$$\left( \frac{\partial}{\partial\rho}(f(\rho, \nabla\rho) - \mu\rho) - \sum_{i=1}^3 \frac{\partial^2}{\partial x_i \partial \rho_{x_i}}(f(\rho, \nabla\rho) - \mu\rho) \right)_{\rho=\rho^*} = 0. \quad (4.6)$$

Here  $x_i$  are the cartesian coordinates, components of  $\mathbf{r}$ , and  $\rho_{x_i} = (\nabla\rho)_{x_i}$ . We can transform the obtained equation into the following one

$$\left( \frac{\partial}{\partial\rho}f(\rho, \nabla\rho) - \sum_{i=1}^3 \frac{\partial^2}{\partial x_i \partial \rho_{x_i}}f(\rho, \nabla\rho) \right)_{\rho=\rho^*} = \mu, \quad (4.7)$$

which can be interpreted as the chemical equilibrium between the fluctuation and the old phase [2]. The equation corresponds to a second order differential equation. Its physically acceptable solution must fulfill certain boundary conditions at the surface of the volume  $V$  of the system. In the case of spherical symmetry, it is interesting to outline the following boundary conditions commonly employed

$$\lim_{r \rightarrow \infty} \rho^*(r) = \rho_{av}, \quad \left. \frac{d\rho^*(r)}{dr} \right|_{r=0} = 0, \quad (4.8)$$

which apply for the two density profiles showed in Figure 3. Once we have the exact solution (or a good approximation) for the Helmholtz free energy, the determination of the critical fluctuation  $\rho^*(\mathbf{r})$  and the nucleation barrier  $W^*$  are guaranteed.

## 4.2 Approximations for the Free Energy

We have seen previously that the equations describing the critical fluctuation depend mainly on the modelling of the Helmholtz free energy. This modelling must take into account the non-local effects; the interaction between molecules at  $\mathbf{r}$  and  $\mathbf{r}'$  respectively. One way of doing that is considering  $f$  not only as a function of the unary density (i.e  $\rho^{(1)} \equiv \rho$ ), but also the binary  $\rho^{(2)}$ , ternary  $\rho^{(3)}$ , etc [1]<sup>6</sup>. However, this procedure implies several mathematical difficulties due to its complexity, so it is necessary to apply certain approximations.

In this work we will focus our attention on two approximations; the *Gradient Approximation* (GA) and the *Hard-Sphere Model* (HSM), which, despite their simplicity, they will allow us to recover results from previous sections regarding the CNT and the VDW fluid.

### 4.2.1 Gradient Approximation

This first approximation consists in considering the free energy as an exclusive function of  $\rho$  and its first derivatives. Its general form is given by

$$f(\mathbf{r}) = f_u[\rho(\mathbf{r})] + K[\rho(\mathbf{r})](\nabla\rho)^2, \quad K[\rho(\mathbf{r})] > 0, \quad (4.9)$$

which corresponds to a truncated expansion of  $f(\mathbf{r})$  in terms of the density gradient  $\nabla\rho$ . In the above equation,  $f_u$  would correspond to the zeroth order term of the expansion, which is the global Helmholtz free energy per molecule, namely, the one the system would have if local effects were not involved, while the second term would correspond to the second order term of the expansion, accounting on the interactions between molecules at  $\mathbf{r}$  and the rest of the environment, making  $f(\mathbf{r})$  a non local function of  $\mathbf{r}$  [2]. The dependence of the functions  $f_u$  and  $K$  on  $\rho(\mathbf{r})$  can be determined by means of the regular solution theory of mixtures, as pointed out by Kashchiev [1].

By substituting Eq.(4.9) into Eq.(4.7), we are led to the *Cahn-Hilliard Equation* (CHE)

$$\left( \frac{\partial}{\partial\rho}(f_u(\rho)) - (\nabla\rho)^2 \frac{\partial}{\partial\rho}(K(\rho)) - 2K(\rho)(\nabla^2\rho) \right)_{\rho=\rho^*} = \mu. \quad (4.10)$$

This last equation can be simplified for the case of a spherical nucleus, as the critical fluctuation will only depend on the radial distance  $r$ ,  $\rho^*(\mathbf{r}) = \rho^*(r)$ . Considering that in spherical coordinates the following expressions apply

$$(\nabla\rho)^2 = \left( \frac{d\rho}{dr} \right)^2, \quad \nabla^2\rho = \frac{d^2\rho}{dr^2} + \frac{2}{r} \frac{d\rho}{dr}, \quad (4.11)$$

---

<sup>6</sup>It is defined the  $n$ -density  $\rho^{(n)}(\mathbf{r}^{(n)})$  as the density that takes into account the effect of an  $n$ -wise potential over the system. In case that  $n = 1$ , we recover the density for an ideal solution [6]

the CHE adopts the following form

$$\left( \frac{d}{d\rho}(f_u(\rho)) - 2K(\rho)\frac{d^2\rho}{dr^2} - \frac{4K(\rho)}{r}\frac{d\rho}{dr} - \left(\frac{d\rho}{dr}\right)^2 \frac{d}{d\rho}(K(\rho)) \right)_{\rho=\rho^*} = \mu, \quad (4.12)$$

By applying the boundary conditions presented in Eq.(4.8) to the above expression, the critical fluctuation can be computed numerically, and thus, the nucleation barrier can also be determined by solving Eq.(4.3), considering that  $d\mathbf{r} = 4\pi r^2 dr$  due to the spherical symmetry.

It is interesting to outline three results coming from the numerical simulations carried out by Cahn and Hilliard [1] using this model for low supersaturations:

- The density at the centre of the nucleus ( $\rho^*(0)$ ) approaches the one characterising the new phase ( $\rho_{new}$ ).
- The specific surface energy associated to the surface layer of the nucleus reaches the planar surface one.
- The appropriately defined mean radius approaches the one defined by the *equimolar dividing surface*.

Summarising, these aspects confirm the validity of the model for low supersaturations, as it leads to the same results as those predicted within the context of the CNT. However, the behaviour of both theories differs significantly for high supersaturations.

#### 4.2.2 Hard-Sphere Model

This model was first introduced in order to avoid the GA, which is only valid for smooth variations of the density profile [1]. The HSM is based mainly on the proposal of an expression for the free energy analogous to the one derived for the VDW fluid within the thermodynamic context

$$f_{VDW} = f_0 + k_B T \ln \left( \frac{b'\rho_u}{1 - b'\rho_u} \right) - a'\rho_u, \quad (4.13)$$

where  $f_0$  and  $\rho_u$  are reference energy and density respectively, and  $a'$  and  $b'$  are the same material constants presented in Eq.(2.1).  $b'$  accounts for the harsh short-range repulsion between molecules when they are closer than a radial distance  $d_0$ , and  $a'$  considers the weak long-range attraction between them, and it is generally given by the expression

$$a' = -2\pi \int_{d_0}^{\infty} r^2 u(r) dr, \quad (4.14)$$

where  $u(\mathbf{r})$  is the pairwise interaction potential [1]. For our case, a non-homogeneous density profile  $\rho(\mathbf{r})$ , the VDW-like expression for the Helmholtz free energy will be given by

$$f(\mathbf{r}) = f_{HS}[\rho(\mathbf{r})] + \frac{1}{2} \int_{V'} \rho(\mathbf{r}') u(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}', \quad (4.15)$$

where the first term corresponds to the free energy associated to a hard-sphere potential, while the second one accounts for the attraction between molecules at the point  $\mathbf{r}$  with the rest of the molecules of the system. By substituting the above expression in Eq.(4.7), we obtain the following equation

$$\left( \mu_{HS}[\rho(\mathbf{r})] + \int_{V'} \rho(\mathbf{r}') u(|\mathbf{r} - \mathbf{r}'|) d\mathbf{r}' \right)_{\rho=\rho^*} = \mu, \quad (4.16)$$

where  $\mu_{HS}[\rho(\mathbf{r})] = \frac{\partial}{\partial \rho}(f_{HS}(\rho))$ . Solving this equation with the previous boundary conditions, the critical fluctuation and the nucleation barrier can be computed. But in order to compute such quantities, we need a concrete form of the mean field pairwise potential  $u(|\mathbf{r} - \mathbf{r}'|)$ , like the Yukawa or Lennard-Jones potentials [1]. In comparison with Eq.(4.12), Eq.(4.16) is an integral equation that does not include  $\nabla\rho$ , but it allows us to obtain nearly-step solutions for the density profile, so that comparisons with the *capillary model* already presented with the CNT may be carried out.

### 4.3 N-Parameter Theories

In previous sections we have obtained differential equations that allow us to compute the critical density profile that minimizes the nucleation barrier, depending on the physical situation we are dealing with, for which we must specify different functions such as the Helmholtz free energy or the chemical potential. However, despite its usefulness, in most cases only numerical results will be obtained, while it is more suitable for physicists to work with analytical functions. These functions, provided by theoretical models, will depend on a set of parameters that will be adjustable in order to fit the experimental measurements.

We will assume that the density profile has already a certain analytical form, which depends on a set of  $n$  parameters  $\mathbf{X} = X_1, X_2, \dots, X_n$  such as follows,

$$\rho = \rho(\mathbf{r}, \mathbf{X}) = \rho(\mathbf{r}, X_1, X_2, \dots, X_n). \quad (4.17)$$

In this case, due to the fact that we already set a model density function, our goal now consists in determining the critical parameters  $\mathbf{X}' = X'_1, X'_2, \dots, X'_n$  that minimize the nucleation barrier, and then it can be proved that the variational problem presented in Eq.(4.4) transforms into

$$(\nabla_{\mathbf{X}} W(\mathbf{X}))_{\mathbf{X}=\mathbf{X}'} = 0, \quad (4.18)$$

where we have used the notation  $\nabla_X = \sum_i \mathbf{u}_i \partial_X$  [2]. This method is widely used because of the reduction of the computational cost needed to perform numerical calculations. The analytical models for nucleation based on this methodology are known as *n-parameter theories*.

We have already studied an example of this kind of model; the *capillary model* constitutes itself a clear example of an *one-parameter theory*, for it assumes a density profile that only depends on the radius of the spherical cluster. Thus, the radius  $R$  of the cluster constitutes the order parameter of the model<sup>7</sup>. With this, the nucleation barrier was obtained with Eq.(3.10), which is analogous to Eq.(4.18). Furthermore, the entire CNT constitutes an *one-parameter theory*, due to the fact that we assumed that the clusters are completely determined by one parameter; the nucleus size (or the radius for spherical nuclei). Another example of these models is given by the piecewise density profile

$$\rho(r) = \begin{cases} \rho_{new} & r \leq R - w \\ \rho_{new} + (\rho_{new} - \rho_{av}) \frac{r - (R - w)}{w} & R - w \leq r \leq R \\ \rho_{av} & r \geq R \end{cases} \quad (4.19)$$

which takes into account a gradual linear variation of the density through the surface of the spherical cluster, which has a width  $w$ . In this case, both the spherical radius  $R$  and the surface width  $w$  would be order parameters, and thus we would encounter a *two-parameter theory*.

## 5 Conclusion

Finally, we have arrived to the end of our journey. In this last section we will summarize the aspects that we have developed throughout this work, pointing out the main ideas and results.

We first started with the basis of first-order phase transitions. We used the Van Der Waals fluid as our key example in order to understand vapor-liquid transitions, and with this, the equilibrium conditions needed for the coexistence between phases, and the concepts of metastability, spinodal and binodal curves and supersaturation were introduced. Gathering all of these with a brief introduction to thermal fluctuations, we arrived to the definition of

---

<sup>7</sup>Despite that the density profile given by Eq.(3.8) also depends on the parameters  $\rho_{new}$  and  $\rho_{av}$ , these parameters do not count as order parameters, for they are initial conditions that can be obtained experimentally, and are, in principle, independent from the nucleation process.

the nucleation process itself.

From here, we focused our analysis into the *Classical Nucleation Theory*. Starting with Gibbs ideas, we defined a cluster as a thermodynamic system surrounded by a greater one, and with the help of the *capillary model* and the assumption of spherical clusters, we derived an expression for the nucleation barrier, and thus also for the probability for a density fluctuation to occur.

Then we studied the kinetic model provided by the CNT. Starting with the definition of the cluster and the transition frequencies, we arrived to the *Master Equation of Nucleation*. From here, with the aid of the BDT Model and Zeldovich's ideas, we derived Fokker-Planck, Langevin and Kramers-Moyal equations that allow a stochastic description of the nucleation process. Following this, considering the steady state, we arrived to an analytical expression for the nucleation rate, a quantity that can be measured experimentally, and thus, it links the theory and reality. In order to apply the previous results, we analysed the homogeneous nucleation of water droplets in condensed vapours. We first solved the Langevin Equation with the aid of the Euler-Maruyama approximation, leading to the equilibrium histograms. Then, we compared the theoretical nucleation rates with experimental ones measured in diffusion cloud chambers, leading to several inconsistencies of the theory. All of this analysis was useful for us to link with a last section of the CNT where its main deficiencies were commented.

Following the CNT, the *Density Functional Theory* was introduced as an alternative paradigm for the determination of the nucleation barrier and the definition of clusters themselves. Variational principles were used for deriving the nucleation barrier, and two approximations for the free energy as a functional of the density were introduced. These approximations also allowed us to recover previous aspects provided by the CNT and the VDW fluid. Finally, the concept of *n-parameter theory* was introduced as an analytical alternative to the numerical calculation, which allowed to present theoretical models depending on the process under study.

In conclusion, the field of nucleation is still an open field to study, where there are many unanswered questions yet, and which still holds many mysteries of matter and the world itself. The classical theory is the cornerstone from which we start, while the functional density paradigm is the current path that researchers travel in their eagerness to unravel reality.



## References

- [1] Dimo Kashchiev, *Nucleation: Basic Theory with Applications*, Butterworth-Heinemann, Elsevier Science, 2000.
- [2] Miguel Ángel Durán Olivencia, *Non-classical Nucleation Theories; a new stochastic paradigm*, CSIC-UGR, 2014.
- [3] Daniel T. Gillespie, *Markov processes: An Introduction for physical scientists*, Elsevier Science, 1991.
- [4] Y. Viisanen, R. Strey, and H. Reiss, *Homogeneous nucleation rates for water*, J. Chem. Phys. 99, 4680, 1993.
- [5] Peter P. Wegener and Philippe Mirabel, *Homogeneous Nucleation in Supersaturated Vapors*, Naturwissenschaften, 1987.
- [6] Donald A. McQuarrie, *Statistical Mechanics*, Harper Row, Harper's Chemistry Series, 1976.
- [7] Frederick Reif, *Fundamentals of statistical and thermal physics*, McGraw-Hill Science/Engineering/Math, 1965.
- [8] Nicolaas Govert de Bruijn, *Asymptotic Methods in Analysis*, North Holland, 1998.
- [9] Jean-Pierre Hansen, I.R. McDonald, *Theory of simple liquids*, Elsevier Academic Press, 2006.
- [10] A. A. Lopatkin, *Van der Waals Equation*, The Great Soviet Encyclopedia, 3rd Edition, Moscow, (1970-1979).
- [11] H.P. Lovecraft, *The Call of Cthulhu*, Weird Tales, New York, 1928.