Fokker–Planck equations for nucleation processes revisited

David Reguera*, J.M. Rubí, A. Pérez-Madrid

Departament de Física Fonamental, Facultat de Física, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain

Abstract

We present a new approach to analyze homogeneous nucleation based on non-equilibrium thermodynamics. The starting point is the formulation of a Gibbs equation for the variations of the entropy of the system, whose state is characterized by an internal coordinate or degree of freedom. By applying the method of non-equilibrium thermodynamics we then obtain the entropy production corresponding to a diffusion process in the internal space. The linear laws together with the continuity equation lead to a kinetic equation of the Fokker–Planck type. By choosing properly the degree of freedom we are able to obtain a new kinetic equation for a global crystallization order parameter (used in recent simulations), and also we recover some of the existing equations. The consistency of the scheme we propose is proved in the quasi-stationary case. Finally, we also outline the way in which our formalism could be extended to more general situations. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The first step in many phase transformations of pure substances – for example, condensation of gases or solidification of melts – is the formation of small embryos of the new phase within the bulk metastable substance. This is an activated process: a free energy barrier must be overcome in order to form embryos of a critical size, beyond which the new phase grows spontaneously. This fundamental mechanism of phase transformation is known as homogeneous nucleation, and the rate at which critical-sized embryos are formed is the nucleation rate (for reviews on nucleation, see for example Refs. [1–5]).

To analyze the process, three different types of schemes have basically been proposed in the literature. The first one is referred to as the classic nucleation theory.

* Corresponding author.

In it, the process is usually described by means of a master equation that completely determines the evolution of the clusters size distribution. The fact that the size of the clusters vary in a discrete way (due to the loss or gain of a single monomer) causes difficulties in the treatment and resolution of this type of equation. For this reason there have been several trials to obtain a continuous diffusive equation as an approach to the master equation. The advantages that a continuous description may offer are mainly the computational efficiency and the possibility of transforming the Fokker–Planck equation into a Shrödinger-type equation, soluble by means of Quantum Mechanics' usual methods. The second type of description is centered on the construction of dynamic models of the cluster interface. By assuming that the molecules of the interface behave as Brownian particles, it is possible to arrive at the characterization of the clusters size distribution in terms of a Fokker–Planck equation. Finally, the last scheme is based on the theory of the density functional. In this approach to the problem, the kinetic description is carried out through the continuity equation for the probability density.

As we will see, the three points of view lead to express the nucleation rate by means of a diffusive equation. However, in spite of the great variety of proposed equations, till now none of them has turned out to be fully satisfactory.

In this paper we present an alternative approach that allows us to obtain kinetic equations applicable to homogeneous nucleation. Our method is based on the formalism of internal degrees of freedom [6–9], formulated in the framework of non-equilibrium thermodynamics, and applied successfully before to other problems like the adsorption kinetics of particles on surfaces [10], the description of chemical reactions [11] or the treatment of noise in interfaces of semiconductor devices [12]. This formalism allows us to derive Fokker–Planck equations from a Gibbs equation and not as a continuous approach to a master equation. Moreover, within this framework we recover directly the proper equilibrium distribution and we may derive explicit expressions for drift and diffusion coefficients.

The paper is structured as follows. In Section 2 we will discuss the different procedures proposed (inside the scope of homogeneous nucleation) to obtain Fokker–Planck equations. Section 3 presents our method to derive a general Fokker–Planck equation describing the kinetics of homogeneous nucleation. In Section 4, we will particularize for several different interpretations of the internal coordinate. We will derive a new kinetic equation in terms of an order parameter associated with the degree of crystallization of the system and we will reproduce some of the kinetic equations proposed in the literature. In Section 5, we will discuss the quasi-stationary case and show how in this case our approach overcomes some of the inherent difficulties of previous treatments. Finally, in the last section we will stress our main results.

2. A brief review of the previous treatments

In this section we will present a brief summary of the different Fokker–Planck equations that have been proposed to treat the problem of homogeneous nucleation. These

equations have been obtained mainly from three different ways: as continuous approaches to a master equation; starting from microscopic kinetic models by considering the separation of a molecule from the cluster surface like a problem of Brownian diffusion through a barrier; or as the consequence of imposing a continuity equation for the probability density in the framework of the density functional theory. We will discuss all of these in different subsections.

2.1. Continuous approaches to a master equation

In the classical model of nucleation [3] one assumes that the size of a cluster can vary due to the loss or absorption of a single monomer. Hence the evolution of the clusters distribution is described by the set of discrete master equations

$$\frac{d\rho(n,t)}{dt} = \beta(n-1)\rho(n-1,t) + \alpha(n+1)\rho(n+1,t) - \rho(n,t)(\alpha(n)+\beta(n)),$$

$$(1)$$

where $\rho(n,t)$ represents the density of clusters containing n molecules and $\alpha(n)$ and $\beta(n)$ are the rates at which a cluster of size n loses or gains a single molecule, respectively.

To transform this master equation into a continuous equation, several different methods have been proposed in the literature. The most straightforward one consists of replacing the discrete variable n by a continuous variable x. After expanding in Taylor series we arrive at the well-known Kramers–Moyal expansion, which upon truncation in second order yields the diffusion-like equation

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial x}\left(D(x)\frac{\partial \rho}{\partial x} + A(x)\rho\right),$$

$$(2)$$

where $A(x)$ and $D(x)$ are the drift and diffusion coefficients, respectively.

This equation, however, has the serious inconvenience that it does not reproduce the equilibrium distribution of the original master equation. Additionally, it has also been proven that it overestimates the nucleation rate exponentially, with an error that grows unboundedly for large n [13].

The Fokker–Planck equations of Frenkel–Zeldovich [14], Goodrich [15] and Shizgal–Barret [16] try to solve these difficulties by imposing a relationship between drift and diffusion coefficients in order to ensure the correct equilibrium distribution. These three proposals differ in the expressions for those coefficients, chosen to improve the approximation. However, as pointed out by Gitterman and Weiss [17], none of them seem to be able to reproduce the correct deterministic behavior.

A variant of these equations is the one formulated by Rabin and Gitterman [18], where the innovation consists in considering that the coefficients of the Fokker–Planck equation cannot be fixed arbitrarily, but rather – in the vicinities of the critical point – they are determined by the critical dynamics of the system.

Van Kampen [19] proposed an alternative method, consisting in rescaling the rate constants α and β in terms of a parameter Ω (usually the system size) and to expand the result in powers of Ω^{-1}. In this way, one obtains an expansion similar to Kramers–Moyal that shares the same problems described previously.

The contribution of Grabert et al. [20] and later Hänggi et al. [21] is also based on a rescaling of the rate constants, but they obtain the coefficients (expressed in terms of the rates α and β) from non-linear transport theory. Their equation reproduces the equilibrium distribution appropriately, but it does not describe the short time behavior correctly and it gives an erroneous value of the variance of the distribution [17].

Finally, inside the scope of the Fokker–Planck equation obtained starting from the master equation, we can quote the essentially mathematical method of Wu [2,22] which proposes an index change and a mathematical optimization to minimize the error associated with approaching the master equation – discrete – by means of a continuous-diffusive-type expression.

2.2. Kinetic models

A different approach to obtain Fokker–Planck-type equations for homogenous nucleation, is based on the peculiar dynamics of a monomer near the surface of a cluster. Inside this scope we will consider the works of Lovett [23] and Ruckenstein and Narsimhan and Nowakowski [24–27].

Lovett uses thermodynamics to estimate the radius of the critical cluster and the height of the energy barrier that a monomer should surmount to leave the cluster surface. Considering that the monomer undergoes a Brownian movement, he uses the corresponding Fokker–Planck equation to study the probability of leaving the cluster. His model is only applicable to nucleation in gases, and he uses the macroscopic concept of interfacial tension which can doubtfully be applied to the description of small clusters.

Ruckenstein and coworkers [24–27] propose an alternative approach based on the calculation of the rate α. Their starting point is the estimation of the potential barrier that is generated at the surface of a spherical cluster of radius R from the interaction between monomers and the recount of the number of monomers that interact with a given one. They also consider that the movement of a molecule is Brownian. In the case of nucleation in liquids, they write a Smoluchowski equation in spherical coordinates for the distribution of probability $\rho(\boldsymbol{r}, t)$

$$\frac{\partial \rho(\boldsymbol{r}, t)}{\partial t} = \boldsymbol{\nabla}_{\boldsymbol{r}} \cdot \left(D \boldsymbol{\nabla}_{\boldsymbol{r}} \rho(\boldsymbol{r}, t) + \frac{D}{k_B T} \rho(\boldsymbol{r}, t) \boldsymbol{\nabla}_{\boldsymbol{r}} \phi(\boldsymbol{r}) \right). \tag{3}$$

Here D is the diffusion coefficient and $\phi(\boldsymbol{r})$ the interaction potential of a surface monomer. For gases, they use a diffusion equation in the energy space. These equations are just employed to obtain the rates α and β. The rates are introduced in the common Kramers–Moyal truncated expansion of the master equation to evaluate the nucleation rate.

The main inconveniences of this formalism are that it considers (in the case of liquids) that the diffusion coefficient is constant, when in fact there are reasons to think that it is not totally true; moreover, the contribution of the bulk medium to the effective potential is not incorporated rigorously [5]. On the other hand, an important difficulty linked to this type of description arises from the fact that the nucleation rate is very sensitive to uncertainties in the interatomic potential [28].

2.3. Density functional theory

One of the main drawbacks of the classic theory is the assumption that the interface of the cluster is sharp, a hypothesis that – at least at the level of simulations – is not completely satisfactory.

Field models allow a treatment keeping in mind the possibility that the interface between the cluster and the original phase may be diffuse. The theory of the density functional [4,28] considers the free energy as a functional of the density and uses it to built a coarse-grained free energy. The free energy barrier can be taken out from variational principles. However, to be able to obtain kinetic information, hydrodynamic theory should be introduced.

The starting point of Cahn and Hilliard kinetic treatment [29,30] is the formulation of an equation of continuity for the current of probability density of a certain configuration of the system. Following the scheme of non-equilibrium thermodynamics, they postulate the following linear relationship:

$$J = -M\nabla\frac{\partial F}{\partial \rho},\tag{4}$$

where J is the current, M the atomic mobility (taken as constant), ρ the probability density and F the coarse-grained free energy. With these ingredients a Fokker–Planck equation is obtained.

The work of Langer [31–33] constitutes an extension of the previous treatments in the sense that it provides statistical mechanical basis where fluctuations are taken into account, in the sense that he considers diffusion in the phase space. He proposes the following equation:

$$\frac{\partial \rho(\{\eta\},t)}{\partial t} = \sum_{i,j}\frac{\partial}{\partial \eta_i}\left(M_{ij}\left(\frac{\partial \rho}{\partial \eta_j} + \frac{\partial G(\{\eta\})}{\partial \eta_j}\frac{\rho}{k_B T}\right)\right),\tag{5}$$

where $\{\eta\}$ is the set of all degrees of freedom that characterize a system configuration, $G(\{\eta\})$ the coarse-grained free energy functional, and M_{ij} a generalized mobility matrix.

The main inconveniences of these theories based on the functional density are that their correctness depends on the appropriate election of the free energy functional and that its range of application is restricted; concretely they are not easily applicable to time-dependent situations.

3. Non-equilibrium thermodynamics approach. Internal degrees of freedom

In our approach to the problem of homogeneous nucleation, we consider that the state of a system may be characterized by an internal coordinate or degree of freedom γ, which may for example represent the number of monomers of a cluster (conveniently normalized to become a continuous variable), its radius, or even an order parameter. The nucleation process can be viewed as a diffusion process through a barrier, in the space spanned by the values of the internal coordinate, from an initial value γ_1, corresponding to the metastable state, to γ_2, characterizing the new phase.

Our starting point will be to assume that the variations of the entropy, δS, due to the diffusion process are given by the Gibbs equation

$$\delta S = -\frac{1}{T} \int_{\gamma_1}^{\gamma_2} \mu(\gamma, t)\delta\rho(\gamma, t)\, d\gamma \,. \tag{6}$$

Here $\rho(\gamma, t)$ is the density in the internal space, $\mu(\gamma, t)$ its conjugated chemical potential and T the temperature of the system which is assumed constant.

In the absence of interactions among constituents of the system with different γ's, the chemical potential is the one for an ideal system [34]

$$\mu(\gamma, t) = k_B T \ln \rho(\gamma, t) + \Phi(\gamma), \tag{7}$$

where $\Phi(\gamma)$ is the potential and k_B the Boltzmann constant.

Quite generally, the evolution of the density in the internal space is governed by the continuity equation

$$\frac{\partial \rho}{\partial t} = -\frac{\partial J}{\partial \gamma} \tag{8}$$

which introduces the diffusion current in the internal space $J(\gamma, t)$. The expression for the entropy production related to the diffusion process can be obtained from Eq. (6) by using Eq. (8). One then arrives at

$$\sigma = -\frac{1}{T} \int J(\gamma)\frac{\partial \mu(\gamma)}{\partial \gamma}\, d\gamma \tag{9}$$

where a partial integration has been performed, with the assumption that the diffusion current vanishes at the initial and final states of the process.

Assuming locality in the internal space, for which only fluxes and forces with the same value of the internal coordinate are coupled, one then derives from expression (9) the linear law

$$J(\gamma) = -\frac{L(\gamma)}{T}\frac{\partial \mu(\gamma)}{\partial \gamma} \tag{10}$$

where $L(\gamma)$ is a phenomenological coefficient, which may in general depend on the internal coordinate. This expression can be used in the continuity Eq. (8) thus arriving at the Fokker–Planck equation

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial \gamma}\left(D(\gamma,t)\frac{\partial \rho}{\partial \gamma} + b(\gamma,t)\frac{\partial \Phi}{\partial \gamma}\rho\right), \tag{11}$$

where

$$b(\gamma,t) = \frac{L(\gamma)}{\rho(\gamma,t)T} \tag{12}$$

is the mobility in the internal space and

$$D(\gamma,t) = k_B T b(\gamma,t) \tag{13}$$

the corresponding diffusion coefficient.

In order to fully determine our Fokker–Planck equation we need to specify the form of the diffusion coefficient in the internal space and the potential. To obtain a microscopic explicit expression for the phenomenological coefficient $L(\gamma)$, we will apply fluctuating hydrodynamics in the internal space, in a similar way as in Ref. [11]. Adopting this framework, the presence of fluctuations in the diffusion process along the internal coordinate can be taken into account by adding a random contribution $J^r(\gamma,t)$ to the systematic contribution $J^s(\gamma,t)$ in the diffusion current

$$J(\gamma,t) = J^s(\gamma,t) + J^r(\gamma,t). \tag{14}$$

Considering that $J^r(\gamma,t)$ has zero mean and satisfies the fluctuation–dissipation theorem

$$\langle J^r(\gamma,t)J^r(\gamma',t')\rangle = 2k_B L(\gamma)\delta(\gamma - \gamma')\delta(t - t') \tag{15}$$

one can obtain the following Green–Kubo expression for $L(\gamma)$

$$L(\gamma) = \frac{1}{k_B}\int_{\gamma_1}^{\gamma_2} d\gamma' \int_0^\infty dt\,\langle J^r(\gamma,0)J^r(\gamma',t)\rangle. \tag{16}$$

Hence, in view of Eqs. (12) and (13) the diffusion coefficient $D(\gamma,t)$ is given by

$$D(\gamma,t) = \frac{1}{\rho(\gamma,t)}\int_{\gamma_1}^{\gamma_2} d\gamma' \int_0^\infty dt\,\langle J^r(\gamma,0)J^r(\gamma',t)\rangle. \tag{17}$$

This equation offers an explicit expression to determine the diffusion coefficient in the internal space. For each interpretation of the degree of freedom, the later equation could be transformed in order to be evaluated by means of simulations. For instance, the way to calculate the diffusion coefficient when the internal coordinate represents a global order parameter will be extendedly explained in a future paper.

Additionally, the nucleation barrier $\Phi(\gamma)$ can be estimated by means of simulations in the way proposed by van Duijneveldt and Frenkel in Ref. [35]. Consequently, our scheme becomes in this way completely soluble at least at the simulation level.

Finally, it is worth pointing out that our formalism recover in a natural and direct way (without additional impositions) the correct equilibrium distribution. Since at equilibrium, the current in the internal space J_{eq} vanishes, from Eq. (10); this condition is accomplished when the chemical potential is constant. Using Eq. (7) we then obtain the proper equilibrium distribution

$$\rho^{eq}(\gamma) \propto e^{-\Phi(\gamma)/k_B T} . \tag{18}$$

4. Particular expressions of the Fokker–Planck equations

The formalism we have proposed enables us to formulate a general Fokker–Planck equation in terms of an arbitrary internal coordinate γ specifying the state of the system. Thus, one of its inherent advantages comes from the fact that it is not necessarily restricted to give a vision of the nucleation only focused on the kinetics of clusters. Contrarily, a suitable choice of the internal coordinate will lead to the Fokker–Planck equation corresponding to a different description of the nucleation process.

Our purpose in this section will be to particularize this equation for different interpretations of the internal degree of freedom. In this way, we will see how we can propose a new Fokker–Planck equation for a global crystallization order parameter Q and also how to reproduce the already existing ones.

4.1. γ represents an order parameter

A possible way of characterizing the nucleation process, which has recently been used in computer simulations (see Refs. [36,37]), is by means of an order parameter Q that describes the global degree of crystallization of the system. In these simulations, the nucleation rate is calculated from a phenomenological rate equation using linear response theory. According to our theory, the underlying Fokker–Planck equation describing the kinetics of this process in terms of the variable Q, considered as the internal degree of freedom, is given by

$$\frac{\partial \rho}{\partial t} = \frac{\partial}{\partial Q} \left(D(Q,t) \frac{\partial \rho}{\partial Q} + A(Q,t)\rho \right), \tag{19}$$

where, from Eqs. (11)–(13), the expressions of the drift and diffusion coefficients are

$$A(Q,t) = \frac{L(Q)}{T\rho(Q,t)} \frac{\partial \Phi(Q)}{\partial Q}, \tag{20}$$

$$D(Q,t) = \frac{k_B L(Q)}{\rho(Q,t)} . \tag{21}$$

If the internal coordinate represents an order parameter associated with the whole crystalinity, the interpretation of ρ is slightly different. Now Q is a variable that characterizes the global state of the system. Therefore, the internal space associated with this

variable would be the set of all feasible replicas of the system in a given "macrostate". From this point of view, ρ would represent the non-equilibrium distribution of this ensemble whose meaning would be the fraction of systems with the value of the internal coordinate equal to Q at time t. The quantity $\rho \, dQ$ would then be interpreted as the probability that the order parameter of our system (a single realization of this non-equilibrium ensemble) has a value in the interval $(Q, Q + dQ)$ at time t. Since in this case, we work with system replicas that obviously do not interact with each other, the system is ideal and Eq. (7) for the chemical potential holds.

4.2. γ related with the number of molecules in a cluster

Let us assume that we choose as internal coordinate the number of monomers that constitute a cluster, n, or in a more convenient way, the dimensionless quantity $x = n/N$, with N being the total number of monomers. In this case ρ would represent the (time-dependent) clusters size distribution, and $\Phi(x)$ would be the free energy needed to form a cluster of size x. Assuming that x varies in a continuous way, we would recover the Fokker–Planck equation (2) obtained as continuous extrapolation to a master equation, with drift and diffusion coefficients formally analogous to expressions (20) and (21). In this case, Eq. (7) for the chemical potential will be valid only if clusters do not interact. This lack of interaction is also implicitly assumed in previous treatments.

4.3. γ is the cluster radius

If we consider the coordinate $\boldsymbol{r}$, corresponding to the position of a monomer in a cluster of radius R, as the internal degree of freedom and we work in spherical coordinates, we immediately recover the Smoluchowski equation proposed by Ruckenstein and co-workers [24–27]

$$\frac{\partial \rho(\boldsymbol{r}, t)}{\partial t} = \boldsymbol{\nabla}_r \cdot \left(D(\boldsymbol{r}, t) \boldsymbol{\nabla}_r \rho(\boldsymbol{r}, t) + \frac{D(\boldsymbol{r}, t)}{k_B T} \rho(\boldsymbol{r}, t) \boldsymbol{\nabla}_r \Phi(\boldsymbol{r}) \right). \tag{22}$$

Note that now, since the phenomenological coefficient defined in Eq. (10) is in general a function of the internal coordinate, the diffusion coefficient will depend on the radial distance $\boldsymbol{r}$. In this case ρ would represent the number density of monomers at $\boldsymbol{r}$, and ϕ the energy barrier to overcome in order to leave the cluster.

4.4. γ is the set of all system's degrees of freedom

If instead of using a single coordinate we carry out a complete description in terms of all the system's degrees of freedom $\{\eta\}$, characterizing a given configuration, we recover the form of the Fokker–Planck equation proposed by Langer [31–33]

$$\frac{\partial \rho(\{\eta\}, t)}{\partial t} = \sum_{i,j} \frac{\partial}{\partial \eta_i} \left(D_{ij} \left(\frac{\partial \rho}{\partial \eta_j} + \frac{\partial \Phi}{\partial \eta_j} \frac{\rho}{k_B T} \right) \right), \tag{23}$$

where now $D_{ij} = k_B L_{ij}(\{\eta\})/\rho(\{\eta\}, t)$. In this case, $\rho(\{\eta\}, t)$ corresponds to the probability density associated with the $\{\eta\}$ configuration and $\Phi(\{\eta\})$ is the functional free energy.

5. The quasi-stationary case

In the previous section we have seen how to reproduce some different forms of the Fokker–Planck equations proposed in the literature. Our task now will be to ascertain if the equations we have obtained not only have the appropriate form, but are also physically consistent. To this purpose, we will focus our attention on the clusters size distribution equation.

Most of the proposed Fokker–Planck equations are just different continuous diffusive approximations to a discrete master equation. Thus, the rightness of these kinds of equations is evaluated in terms of the accuracy of the approximation. In particular, the two main requirements that a Fokker–Planck equation must satisfy is that it reproduces the equilibrium distribution and the deterministic growth rate $\dot{n}$ [21]; in other words, it must describe nucleation and growth appropriately.

The Fokker–Planck equation we present has been derived directly and not as a continuous approach to a master equation. Therefore, in general we do not have an underlying master equation model to which our expression should be adjusted and that serve us as a criterion to judge its accuracy.

However, we have shown that by construction our equation always guarantees the correct equilibrium distribution. Moreover, a case exists in which we can build a master equation to evaluate the correctness of our results. It is the quasi-stationary case, corresponding to high nucleation barriers.

When the height of the nucleation barrier is large enough as compared with the thermal energy, the system achieves a quasi-stationary state characterized by the current

$$J(n, t) = J(t)\{\theta(n - n_1) - \theta(n - n_2)\}. \tag{24}$$

This form implies that equilibrium is reached independently at each barrier side; consequently the chemical potential will be uniform

$$\mu(n, t) = \mu(n_1, t)\theta(n_0 - n) + \mu(n_2, t)\theta(n - n_0). \tag{25}$$

Here n_0 specifies the size of the critical cluster.

Substituting these two equations in Eq. (10) and integrating with respect to the coordinate n, we obtain

$$J(t) = \frac{D(n_0)}{n_2 - n_1} \left(\rho(n_1, t) \exp\left(-\frac{\Phi(n_0) - \Phi(n_1)}{k_B T} \right) \right.$$
$$\left. - \rho(n_2, t) \exp\left(-\frac{\Phi(n_0) - \Phi(n_2)}{k_B T} \right) \right). \tag{26}$$

If the nucleation barrier is high enough in such a way that a quasi-stationary state is reached, the clusters distribution of intermediate sizes does not vary in time, so that only the states corresponding to $\rho(n_1, t)$ and $\rho(n_2, t)$ matter. The value n_1 represents the smaller cluster distinguishable from equilibrium fluctuations in the metastable phase and n_2 corresponds to a postcritical stable cluster. Cluster sizes n_1 and n_2 (where $n_1 < n_0 < n_2$) are chosen such that for $n < n_1$, $\rho(n) = \rho_{eq}(n)$ and for $n > n_2$, $\rho(n) = 0$. These boundary conditions are habitual in classical treatments [1] and the final results do not strongly depend on the values of n_1 and n_2 [38]. If the intermediate sizes distribution is constant, it implies that the loss of one n_1 cluster supposes, after jumping the energy barrier, the formation of one postcritical nucleus. Conversely, the gain of a n_1 cluster is due to the disappearance of a postcritical cluster.

Accordingly, the master equation for this quasi-stationary situation has the following form:

$$\frac{d\rho(n_1, t)}{dt} = k^- \rho(n_2, t) - k^+ \rho(n_1, t) = -J(t), \tag{27}$$

$$\frac{d\rho(n, t)}{dt} = 0, \quad n_1 < n < n_2, \tag{28}$$

$$\frac{d\rho(n_2, t)}{dt} = k^+ \rho(n_1, t) - k^- \rho(n_2, t) = J(t), \tag{29}$$

where k^+ and k^- are the forward and backward rates. The forward rate k^+ is simply the probability that a cluster n_1 disappears, or equivalently, that it surpasses the nucleation barrier. Therefore, k^+ will be proportional to the Boltzmann factor associated with the height of the barrier

$$k^+ = \lambda \exp\left(-\frac{\Phi(n_0) - \Phi(n_1)}{k_B T}\right). \tag{30}$$

Similarly, for the rate k^- one has

$$k^- = \lambda \exp\left(-\frac{\Phi(n_0) - \Phi(n_2)}{k_B T}\right). \tag{31}$$

Note that the constant λ enters both expressions of k^+ and k^- in order to guarantee that in equilibrium the flow J_{eq} vanishes. This is the requirement to fulfill detailed balance.

Therefore, the nucleation rate $J(t)$ obtained from the master equation is given by

$$J(t) = \lambda \left(\rho(n_1, t) \exp\left(-\frac{\Phi(n_0) - \Phi(n_1)}{k_B T}\right) \right.$$
$$\left. - \rho(n_2, t) \exp\left(-\frac{\Phi(n_0) - \Phi(n_2)}{k_B T}\right) \right). \tag{32}$$

Identifying λ with the factor $D(n_0)/(n_2 - n_1)$ in Eq. (26), we see that at least in the case of high nucleation barriers, our diffusive equation reproduces the steady-state

nucleation rate. Moreover, we are going to prove that our formalism also recovers all the distribution moments of the master equation model.

By introducing Eq. (24) into the continuity Eq. (8) we obtain the following expression:

$$\frac{\partial \rho(n,t)}{\partial t} = -J(t)\{\delta(n - n_1) - \delta(n - n_2)\} \tag{33}$$

which yields the evolution equation for the r-moment $(r = 1, 2, 3 \ldots)$

$$\frac{d\langle n^r \rangle}{dt} = (n_2^r - n_1^r)J(t). \tag{34}$$

It is immediately realized that this expression agrees with the corresponding one evaluated from the set of master Eqs. (27)–(29).

Therefore, we have proved the validity of our equation in the quasi-stationary case, in the sense that it satisfies the two rightness criteria required to make our approach consistent, and moreover reproduces the same results obtained from a master equation. If the height of the barrier is low, the quasi-stationary hypothesis is no longer valid. This feature invalidates the considerations we have made in this section.

6. Conclusions

In this paper we have reviewed the different Fokker–Planck equations proposed in the literature to treat the problem of homogeneous nucleation. We have seen that the equations obtained as continuous approximation to a master equation have the main drawback of not being able to reproduce some of the master equation characteristics (as the equilibrium distribution, the deterministic growth, the variance of the distribution or the short time behavior). Moreover, in all of them (except in the vicinities of the critical point) the coefficients are not fully determined, but rather their expressions are postulated, or they are left in terms of the unspecified rates α and β. To estimate these rates an appropriate microscopic kinetic model is required.

On the other hand, equations obtained from kinetic models base their validity on the correction of the microscopic model proposed for the dynamics of the cluster interface. They do not give a complete and correct explicit expression for drift and diffusion coefficients. Finally, the field-theory approach is restricted to the vicinity of the critical point and to situations where temporal dependencies do not exist.

We have proposed a new method based upon non-equilibrium thermodynamics in the space of an internal coordinate characterizing the state of the system. This method allows us to easily obtain a set of general kinetic equations of the Fokker–Planck type that not only reproduce the ones which have been proposed, centered on the evolution of clusters size distribution, but they allow alternative descriptions of the nucleation process. In this context, we have derived a new Fokker–Planck equation in terms of the crystallinity parameter Q used by Frenkel et al. [36,37] in recent simulations.

We have verified that the Fokker–Planck equation we have obtained, apart from having the appropriate form, fulfills the two validity criteria required for these types of equations, at least in the quasi-stationary case. In fact, the quasi-stationary case corresponds to low supersaturations (and slow rates), that are the typical experimentally affordable conditions.

Our expression also keeps in mind all the possible dependencies (as much in n as in t), and it is able to propose a microscopic expression to calculate (by means simulations) the drift and diffusion coefficients.

Our model allows one to treat time-dependent nucleation and also effects of a pre-existent clusters distribution. Moreover, this new proposed formalism not only reproduces and overcomes some of the main drawbacks of the previous homogeneous nucleation treatments, but rather it constitutes an appropriate framework to treat nucleation processes from a wider perspective. In this context, we could take into account the possible interactions among clusters just by introducing an activity factor in the expression of the chemical potential (7). Moreover, the formalism could easily be extended to the case of heterogeneous nucleation and even to analyze hydrodynamic effects in the nucleation process by simply introducing additional variables in the Gibbs equation characterizing the liquid phase [8,9].

Acknowledgements

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