Unification of classical nucleation theories via a unified Itô-Stratonovich stochastic equation

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Classical nucleation theory (CNT) is the most widely used framework to describe the early stage of first-order phase transitions. Unfortunately, the different points of view adopted to derive it yield different kinetic equations for the probability density function, e.g., Zeldovich-Frenkel or Becker-Döring-Tunitskii equations. Starting from a phenomenological stochastic differential equation, a unified equation is obtained in this work. In other words, CNT expressions are recovered by selecting one or another stochastic calculus. Moreover, it is shown that the unified CNT thus obtained produces the same Fokker-Planck equation as that from a recent update of CNT [J. F. Lutsko and M. A. Durán-Olivencia, J. Chem. Phys. **138**, 244908 (2013)] when mass transport is governed by diffusion. Finally, we derive a general induction-time expression along with specific approximations of it to be used under different scenarios, in particular, when the mass-transport mechanism is governed by direct impingement, volume diffusion, surface diffusion, or interface transfer.

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I. INTRODUCTION

Over the past century the classical approach to nucleation has reported an excellent ability to catch the essential rules underlying noise-induced phase transitions. The set of ideas that constitute this framework was developed over more than half a century. This development started with Gibbs's work [1–3] on near-equilibrium phase transitions. Several years later, Volmer and Weber [4,5] introduced kinetic aspects improving the purely thermodynamical picture given by Gibbs. This was further developed from a more atomistic point of view by Farkas [6], who developed Szilard's ideas, and by Becker and Döring [7], Tunitskii [8], Frenkel [9,10], and Zeldovich [11] within the context of liquid-vapor transitions. Finally, Turnbull and Fisher [12] extended such a formalism with the aim of describing solid nucleation first from liquid and then from solid phases. Besides being intuitively appealing, classical nucleation theory (CNT) has shown an overwhelming robustness. Not only is it able to generate a satisfactory estimation for the nucleation rate equation, which is good for practical purposes [13,14], but it also provides a natural mechanism for cluster formation, which turns out being more real than initially expected [15]. In more recent years, a massive number of studies have renovated, if not improved, CNT based on either phenomenological or fundamental grounds [7–11,16–33]. The primary goal of this paper is to describe a systematic method to derive the Fokker-Planck equation for the probability to find clusters of a given size within the general setting of CNT. This results in a surprising generalization of the usual form of the stationary distribution compared to what is usually assumed in the classical theory: Rather than a simple Boltzmann distribution depending on the work of formation of a cluster, there is a state-dependent prefactor that depends on the chosen stochastic calculus. For the particular choice of the Stratonovich calculus, the resulting expression reproduces the one recently derived from a more elaborate formalism based on fluctuating hydrodynamics [29,32]. Thus, one of the main contributions of this work is to provide a simpler route to that result based solely on CNT. From that, another important contribution results from the derivation of a general induction-time expression accompanied by specific approximations for it to be used in a variety of scenarios. Special attention is paid to those where the mass-transport mechanism is governed by direct impingement, volume diffusion, surface diffusion, or interface transfer. To do this we follow the scheme outlined below.

In Sec. II a stochastic differential equation (SDE) is proposed to model the time-evolution equation for the cluster size under a general stochastic calculus that is parametrized by α so that $\alpha = 0$, $\frac{1}{2}$, and 1 corresponds to Itô, Stratonovich, and backward Itô conventions [34,35], respectively. The state-dependent components of the postulated SDE are derived from a phenomenological point of view, following the CNT reasoning. The Fokker-Planck equation connected to such a SDE is then introduced in Sec. III, the similarities to the Zeldovich-Frenkel equation now being apparent, except for an additional term that affects the effective energy barrier. The effects of such a term are qualitatively explained in the same section. While the Zeldovich-Frenkel equation is recovered under backward Itô convention, the one derived by Lutsko [29,32] is obtained under Stratonovich calculus. The study of the Itô convention unveils the necessary condition for the different Fokker-Planck equations (FPEs) to converge. Section IV is devoted to the derivation of a generalized expression for the mean first-passage time as well as different approximations for the most common experimental conditions. Our results are summarized in Sec. V.

II. THEORY

Nucleation is a quite complex process that certainly requires a huge number of relevant variables (order parameters) to be fully described. However, as we commented in Sec. I, CNT is based on a manageable description of the process

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that considers a single order parameter, namely, the size of the emerging embryo (cluster) of the new phase within the old one. This is commonly assumed to be spherical and to have the same physical properties as those of the final stable state [13,14]. This apparently crude simplification is nevertheless more than efficient when it comes to predicting the functional dependence of the nucleation rate on the thermodynamic quantities involved [13,14]. That is why our study starts with a proposed SDE for the time evolution of the cluster size. There are two reasons we are motivated to propose such an equation. First, it is known that nucleation is a thermally activated process involving the escape from a metastable state via overcoming an energy barrier [13,14,36]. Thus, if the nucleation process is governed by a single order parameter it should undergo, at least to a good approximation, a Langevin equation as proposed by Kramers [37]. Second, recent studies [29,32,33] have shown a formal derivation of such SDEs when the mass transport is governed by diffusion. A general Langevin equation is assumed and their drift and diffusion terms will be deduced from phenomenological arguments and inspired by the ideas underlying CNT.

Stochastic dynamics

Let us consider a system that is set in a metastable state and direct our attention to an arbitrary spherical cluster of those randomly growing and shrinking. Let X be the size of such a cluster, accounting for the number of molecules inside it. Following Kramers' reasoning for thermally activated escape processes [37], we propose the model equation

$$dX(t) = \eta^{-1}(X,t)F(X,t)dt + \sqrt{2k_BT\eta^{-1}(X,t)} \star dB(t), \tag{1}$$

where η is an effective viscosity, F is the effective force acting on X, T is the temperature, k_B is the Boltzmann constant, and $dB(t)$ is a Wiener process. Intrinsic to this equation is the consideration of X as a continuous variable, an approach first introduced by Zeldovich [11,13,38–41]. Based on the work of Ree *et al.* [42], it was shown (see, e.g., Sec. 9.1 of Ref. [13]) that clusters of more than a few molecules can be fairly well described within the framework of the continuous approach and so will we consider it a sufficient paradigm. The star product was introduced to note that we are using a general stochastic calculus (hereafter called α calculus) defined by means of the definition of the stochastic integral [43–46]

$$I_\alpha[R(x,t)] = \int_{t_0}^{t} dB(t')R(x(t'),t') := \text{ms lim}_{n\to\infty} \sum_{i=0}^{n-1} R(x(t_i^*),t_i^*)\Delta B_i, \tag{2}$$

where $R(x,t)$ is a left-continuous function, i.e., a function that is continuous from the left at all the points where it is defined, the symbol := means definition, ms lim represents the mean square limit, i.e., a second moment convergence, $t_i^* = (1-\alpha)t_i + \alpha t_{i+1}$, and $\Delta B_i = B(t_{i+1}) - B(t_i)$. It can be shown [43–46] that by choosing $\alpha = 0, \frac{1}{2}$ or 1, one recovers the Itô, Stratonovich, or backward Itô definition. At the moment we will focus our effort on obtaining a good estimation of the drift term and later we will discuss the consequences of selecting one or another value of α.

As previously mentioned, our aim is providing an alternative route of derivation of CNT starting from the cluster-growth law. Based on CNT, we know that the effective force F is related to the work of cluster formation W through its derivative

$$F(X,t) = -\frac{\partial W(X,t)}{\partial X} \equiv -W'(X,t). \tag{3}$$

The work of cluster formation is usually expressed as the increment of free energy experienced by the system due to the emergence of a cluster of size X. Depending on the system under consideration, that work is specified in terms of either the Gibbs $\Delta\mathcal{G}$ or Helmholtz $\Delta\mathcal{F}$ free energy or the grand (Landau) potential $\Delta\Omega$. In spite of making the derivation as general as possible, we do not specify a given thermodynamic potential since knowing the functional dependence of F on W is more than sufficient.

The derivation of an expression for η requires nonetheless a slightly longer discussion. According to CNT, the effective time a cluster will spend losing a molecule is given by the inverse of the difference between monomer attachment f and detachment g frequencies

$$\tau_{\leftarrow} = \frac{1}{g(X,t) - f(X,t)}. \tag{4}$$

Within the nucleation regime, clusters experience a stronger force to shrink than to grow due to their metastable nature. This results in a higher detachment rate than the corresponding attachment frequency (see Chap. 10 of Ref. [13]) with $\tau_{\leftarrow} \ll 1$ s, typically of order 10^{-7}–10^{-12} s as discussed by Kashchiev (Figs. 10.2, 10.4, and 10.6 of Ref. [13]).

On the other hand, from the definition of the Kramers-Moyal coefficients [34]

$$D^{(n)}(x,t) = \frac{1}{n!}\lim_{\tau\to 0}\frac{1}{\tau}\langle [X(t+\tau)-x]^n\rangle\Big|_{X(t)=x}, \tag{5}$$

it was argued [44,46] that the first Kramers-Moyal coefficient related to Eq. (1) is given by

$$D^{(1)}(X,t) = a(X,t) + \alpha\frac{\partial b(X,t)}{\partial X}b(X,t) = -\frac{1}{\beta\eta(X,t)}\left(\beta W'(X,t) + \alpha\frac{\partial}{\partial X}\ln\eta(X,t)\right), \tag{6}$$

with $a(X,t) = \eta^{-1}(X,t)F(X,t)$ and $b(X,t) = \sqrt{2k_BT\eta^{-1}(X,t)}$ the drift and diffusion forces, respectively, and $\beta = 1/k_BT$. Now we can use the fact that the time $\tau_{\leftarrow}$ is expected to be small compared to the typical time scale associated with a significant change of $\langle X(t)\rangle$ so that the limit in Eq. (5) can be approximated by evaluation at $\tau = \tau_{\leftarrow}$ for which $\langle X(t+\tau_{\leftarrow}) - X(t)\rangle = -1$, giving

$$D^{(1)}(X,t) = \left\langle\frac{dX}{dt}\right\rangle \sim f(X,t) - g(X,t), \tag{7}$$

which agrees with the cluster-growth law derived in CNT [14]

$$\left\langle\frac{dX}{dt}\right\rangle_{\text{CNT}} = f(X,t) - g(X,t). \tag{8}$$

As we know from CNT, whereas the analytical expression of $f(X,t)$ can be derived from collision theory [13,14], finding the frequency $g(X,t)$ is not a trivial task. This is so because monomer detachment depends on parameters characterizing the cluster that may differ appreciably from those of the bulk new phase. To get rid off this problematic quantity we follow the same reasoning as in CNT.

Let us assume that $f(X,t)$ is a well determined quantity. We can evaluate the difference $f(X,t) - g(X,t)$ in terms of $f(X,t)$, making use of the detailed balance equation

$$f(X-1,t)\widetilde{P}(X-1,t) = g(X,t)\widetilde{P}(X,t), \tag{9}$$

with $\widetilde{P}(X,t)$ being the quasiequilibrium probability density function [17]

$$\widetilde{P}(X,t) = P_0(t)\sigma(X,\alpha;t)e^{-\beta W(X,t)}, \tag{10}$$

where $P_0(t)$ is an instantaneous normalization constant and σ is some function of X, α, and t. To accomplish our goal, we follow Kashchiev [17] and approximate $f(X-1,t)\widetilde{P}(X-1,t)$ by the truncated Taylor expansion about point X,

$$\begin{aligned} &f(X-1,t)\widetilde{P}(X-1,t) \\ &\quad\sim f(X,t)\widetilde{P}(X,t) - \frac{\partial}{\partial X} f(X,t)\widetilde{P}(X,t), \end{aligned} \tag{11}$$

and hence

$$f(X,t) - g(X,t) \sim f(X,t)\frac{\partial}{\partial X}\ln f(X,t)\widetilde{P}(X,t). \tag{12}$$

Substituting Eq. (10) into (12) we get

$$\begin{aligned} f(X,t) - g(X,t) = &- f(X,t)\frac{W'(X,t)}{k_B T} \\ &+ f(X,t)\frac{\partial}{\partial X}\ln[\sigma(X,\alpha;t)f(X,t)], \end{aligned} \tag{13}$$

where we replaced $\sim$by $=$, assuming that these approximations are accurate enough for all practical purposes. Finally, by substituting Eq. (13) into (7) and equating to Eq. (6) we eventually get

$$\begin{aligned} \eta^{-1}(X,t) &= \beta f(X,t), \\ \sigma(X,\alpha;t) &= f^{\alpha-1}(X,t). \end{aligned} \tag{14}$$

Having Eqs. (3) and (14), the Langevin equation proposed at the very beginning (1) can be finally rewritten

$$dX(t) = -f(X,t)\frac{\partial\beta W(X,t)}{\partial X}dt + \sqrt{2f(X,t)} \star dB(t). \tag{15}$$

This stochastic equation is equivalent to that derived by Lutsko [29,32] from fluctuating hydrodynamics for a single-order parameter, when we set $\alpha = \frac{1}{2}$ (i.e., Stratonovich calculus). Moreover, as it will be checked in Sec. III, this equation is statistically equivalent to the Zeldovich-Frenkel equation for $\alpha = 1$ (i.e., backward Itô calculus), given that it produces the same time-evolution equation for the probability density function. It is thus interesting to see how the hypotheses underlying Zeldovich's derivation are equivalent to choosing a specific stochastic calculus. Now the equilibrium with the thermal bath is always ensured regardless of the value of α, unlike the common belief that only the backward Itô convention is capable of guaranteeing equilibrium [45]. Actually, such a belief is reached after considering the equilibrium regime as equivalent to a Boltzmann distribution law. Nevertheless, from previous studies we know that this is not true for nucleation, where the equilibrium distribution derived from a fluctuating-hydrodynamic framework shows a state-dependent prefactor [29,32]. That is why we free the derivation herein presented of that restriction, assuming instead a local-equilibrium law (10) with a general state-dependent prefactor. This results in a general equilibrium distribution function [using Eqs. (10) and (14)], which yields a state-independent pre-exponential factor for $\alpha = 1$, as expected. Noteworthy in such a case is that the resulting theory cannot be covariant, as will be shown in Sec. III B.

Nevertheless, Eq. (15) differs from that produced by Tunitskii's equation [8,47]

$$dX(t) = [f(X,t) - g(X,t)]dt + \sqrt{f(X,t) + g(X,t)}dB(t), \tag{16}$$

which is interpreted under Itô's convention, i.e., $\alpha = 0$. In order to know under what circumstances both equations are equivalents, we follow the same reasoning as that which led us to Eq. (14), and so we arrive at

$$f(X,t) - g(X,t) = -W'(X,t)\eta^{-1}(X,t), \tag{17}$$

$$f(X,t) + g(X,t) = 2k_B T\eta^{-1}(X,t). \tag{18}$$

Then

$$\frac{g(X,t)}{f(X,t)} = 1 + \frac{1}{1 - W'(X,t)/2k_B T}\frac{W'(X,t)}{k_B T}. \tag{19}$$

To get the usual approximation of $g(X,t)$ given in CNT [e.g., Eq. (10.90) of Ref. [13]], i.e.,

$$g(X,t) = f(X,t)\exp\left(\frac{\partial\beta W(X,t)}{\partial X}\right), \tag{20}$$

we need

$$\frac{\partial\beta W(X,t)}{\partial X} \ll 1, \tag{21}$$

given that in this limit one gets

$$\begin{aligned} \frac{g(X,t)}{f(X,t)} &\sim 1 + \frac{\partial\beta W(X,t)}{X} + \frac{1}{2}\left(\frac{\partial\beta W(X,t)}{\partial X}\right)^2 \\ &\sim \exp\left(\frac{\partial\beta W(X,t)}{\partial X}\right). \end{aligned} \tag{22}$$

That way, our proposed model will recover the Tunitskii equation under Itô's convention for slowly varying energy barriers, which indeed agrees with the hypotheses underlying CNT.

Thus far, we have derived heuristically a model (15) that seems to be in accord even with more rigorous and modern theories. In what follows we will study the dynamics of the probability distribution function (PDF) associated with Eq. (15) in order to discuss in terms of CNT. This will make it possible to get some important quantities such as the stationary distribution function (for undersaturated systems) or the nucleation (or induction) time.

III. FOKKER-PLANCK EQUATION

The time-evolution equation of the PDF $P(X,t)$ of the random variable X will be given by the Fokker-Planck equation [43–45]

$$\frac{\partial P(X,t)}{\partial t} = -\frac{\partial \mathfrak{J}(X,t)}{\partial X}, \tag{23}$$

where

$$\mathfrak{J}(X,t) = -\left\{ f(X,t)\frac{\partial}{\partial X}[\beta W(X,t) + (1-\alpha)\ln f(X,t)] + f(X,t)\frac{\partial}{\partial X}\right\} P(X,t) \tag{24}$$

$$= -\left(f(X,t)\frac{\partial \beta\Phi(X,t)}{\partial X} + f(X,t)\frac{\partial}{\partial X}\right) P(X,t), \tag{25}$$

with

$$\beta\Phi(X,t) = \beta W(X,t) + (1-\alpha)\ln f(X,t). \tag{26}$$

Now the similarities between this FPE and that obtained in CNT are apparent. Furthermore, the Zeldovich-Frenkel equation is recovered when the backward Itô convention is adopted. Surprisingly, this naive model also recovers the FPE given in more recent rederivations of CNT [29,32] when the Stratonovich calculus is considered.

A. Short-time propagators: Critical clusters with growing habits

Now we evaluate the impact of the extra logarithmic term. Since $0 \leqslant \alpha \leqslant 1$, it is evident that it entails an increase in the energy barrier with respect to the Zeldovich-Frenkel equation. However, there is another interesting effect of this additional term that has to do with the probability of a critical cluster [defined by $\beta W'(X_*,t) = 0$] to grow or shrink. While it is customarily accepted that these probabilities must be the same, this is only true under Itô's convention, as we will show. To this end, we will make use of short-time propagators [34].

It is known from collision theory that the analytical equation of $f(X,t)$ is size dependent and so is $\sqrt{2f(X,t)}$. Hence, their values will change from the initial to the final size during a unitary jump in the size axis X. This change implies that the cluster experiences different attachment rates in going from an initial size X_0 to another X. Here is where the choice of the stochastic calculus comes into play, since each of them corresponds to a different origin when evaluating the noise amplitude, which yields asymmetric probability distributions [43,44] for any $\alpha \neq 0$. Considering $\alpha \in [0,1]$, the short-time propagator [34] related to the FPE (22), and hence to the SDE (15), is given by

$$p_\alpha(X,t+\tau|X_0,t) = \exp\left(-\alpha\tau\frac{\partial D^{(1)}(\widetilde{X}_\alpha,t)}{\partial X} + \alpha^2\tau\frac{\partial^2 D^{(2)}(\widetilde{X}_\alpha,t)}{\partial X^2} - \frac{\{X - X_0 - [D^{(1)}(\widetilde{X}_\alpha,t) - 2\alpha(\partial D^{(2)}/\partial X)(\widetilde{X}_\alpha,t)]\tau\}^2}{4\tau D^{(2)}(\widetilde{X}_\alpha,t)}\right) \times [2\sqrt{\pi\tau D^{(2)}(\widetilde{X}_\alpha,t)}]^{-1}, \tag{27}$$

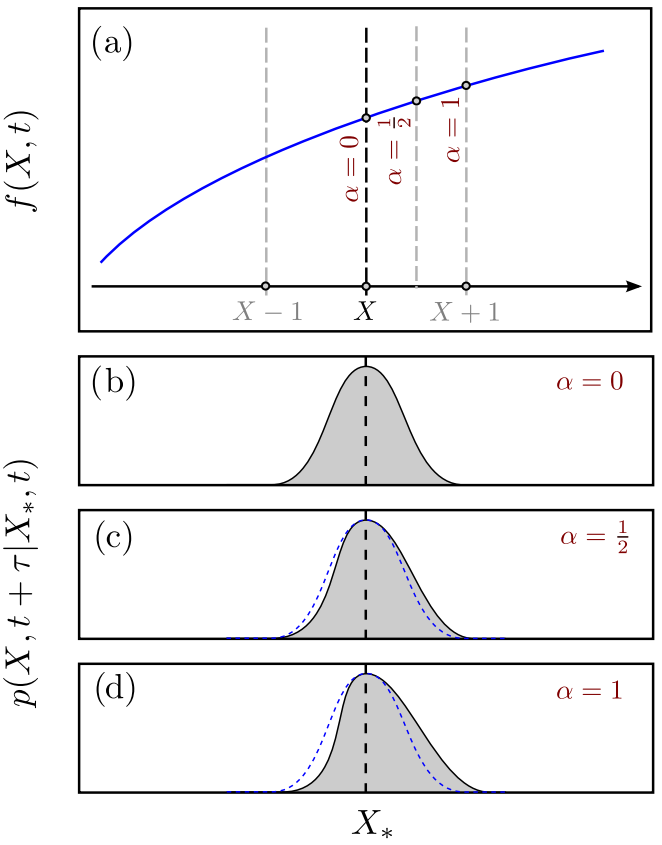

FIG. 1. (Color online) This figure is inspired by Fig. 4 of [44]. (a) Schematic representation of the dependence of the monomer attachment frequency on the cluster size. (b)–(d) Qualitative effect of the logarithmic term on the short-time propagators, in particular when the initial condition is the critical cluster. It can be readily observed how the symmetry of growing or shrinking is broken for all $\alpha \neq 0$.

where

$$\begin{aligned} D^{(1)}(\widetilde{X}_\alpha,t) &= -f(\widetilde{X}_\alpha,t)\beta W'(\widetilde{X}_\alpha,t) + \alpha f'(\widetilde{X}_\alpha,t), \\ D^{(2)}(\widetilde{X}_\alpha,t) &= f(\widetilde{X}_\alpha,t), \\ \widetilde{X}_\alpha &= \alpha X(t+\tau) + (1-\alpha)X(t) \\ &\equiv \alpha X + (1-\alpha)X_0. \end{aligned} \tag{28}$$

In the particular case of $X_0 = X_*$ we know by definition that $\beta W'(X_*) = 0$, i.e., the time evolution of the size for a critical cluster is purely stochastic (15). However, as we can observe in Fig. 1, the probability to grow only equals that to decrease for $\alpha = 0$, given that

$$p_{\alpha=0}(X,t+\tau|X_*,t) = \frac{1}{2\sqrt{\pi f(X_*,t)}}\exp\left(-\frac{(\Delta X_*)^2}{4f(X_*,t)\tau}\right), \tag{29}$$

where $\Delta X_* = X - X_*$. This is in line with the short-time propagator directly derived from Tunitskii's equation (16) when $f(X_*,t) = g(X_*,t)$, i.e., the probability to increase the cluster size by one unit must be equal to the probability to decrease by the same amount.

Nevertheless, for all $\alpha \in (0,1]$ the short-time propagator gradually becomes an asymmetric distribution reaching the

maximum deformation for [44] $\alpha = 1$,

$$p_{\alpha=1}(X,t+\tau|X_*,t) = \exp\left[\tau\frac{\partial}{\partial x}\left(f(x,t)\frac{\partial\beta W'(x,t)}{\partial x}\right)\Big|_{x=X} - \frac{\{\Delta X_* + [f(X,t)\beta W'(X,t) + f'(X,t)]\tau\}^2}{4\tau f(X,t)}\right]\Big/ 2\sqrt{\pi f(X,t)}. \quad (30)$$

Given that $f(X,t)$ is a monotonically increasing function of X (see, e.g., Chap. 10 of Ref. [13]), it can be shown that such an asymmetry favors the growth, instead of the shrinking. This fact has already been reported by Brettschneider *et al.* [44] in a different scenario but with similar conditions. Inspired by their discussion, this result has been schematically represented in Fig. 1. While this is a very interesting result that underlies the different derivations of CNT, it is true that for very large critical clusters $X_* \gg 1$, the general short-time propagator becomes

$$p_{\rm CNT}(X,t+\tau|X_*,t) = \lim_{X_*\gg 1} p_\alpha(X,t+\tau|X_*,t) \sim \frac{\exp[-(\Delta/X_*)^2 4 f(X_*,t)\tau]}{2\sqrt{\pi f(X_*,t)}}, \quad (31)$$

where we have considered the Szilard limit [6] in order to approximate $f(X,t) \sim f(X_*,t)$. Thus, we see that the different α calculi yield the same results only for very large critical clusters, which is equivalent to saying for near-equilibrium systems. It is worth mentioning that a recent rederivation of CNT (DCNT) from fluctuating hydrodynamics [29,32,33] has formally shown that the right FPE is that given for $\alpha = \frac{1}{2}$; otherwise this will not be a covariant theory. Hence, from the above discussion, the critical cluster will experience a slightly higher tendency to grow, unlike what would be initially expected from CNT.

B. Equilibrium and stationary distributions

In this section we explore the solutions of the general FPE given by Eqs. (22) and (25). It is widely known that finding the exact solution is a highly difficult problem, even potentially impossible. However, as discussed by Hänggi *et al.* [37], an exact solution can be obtained by assuming a stationary system with constant flux $\mathfrak{J}_s$, which is ensured by removing clusters once they reach a given size $X = X_{\rm max} > X_*$ (see also Refs. [13,48]). Then the steady-state distribution must satisfy $P_s(X_{\rm max}) = 0$. Let us consider $f(X,t) \equiv f(X)$ and $\Phi(X,t) \equiv \Phi(X)$. Returning to Eq. (25),

$$\mathfrak{J}_s = -\left(f(X)\frac{\partial\beta\Phi(X)}{\partial X} + f(X)\frac{\partial}{\partial X}\right)P(X), \quad (32)$$

which readily produces [34]

$$P_s(X) = Ae^{-\beta\Phi(X)} - \mathfrak{J}_s e^{-\beta\Phi(X)}\int^X \frac{e^{\beta\Phi(Y)}}{f(Y)}dY, \quad (33)$$

with A being a normalization constant. When the boundary condition on $P_s(X_{\rm max}) = 0$ is imposed, Eq. (33) becomes

$$P_s(X) = \mathfrak{J}_s e^{-\beta\Phi(X)}\int_X^{X_{\rm max}} \frac{e^{\beta\Phi(Y)}}{f(Y)}dY. \quad (34)$$

We note that for some change of variable $X \to Y(X)$, the stationary probability should fulfill

$$\widetilde{P}_s(Y) = P_s(X)\left(\frac{dX}{dY}\right), \quad (35)$$

which imposes the following condition on $f(X)$:

$$\widetilde{f}(Y) = f(X(Y))\left(\frac{dX}{dY}\right)^{1/(\alpha-1)}. \quad (36)$$

Therefore, as we can check, the classical Zeldovich-Frenkel equation cannot be covariant [32] given the singularity occurring for $\alpha = 1$. For all other values, whether the theory presents general covariance or not is conditioned by the definition of the attachment frequency. Thus far, the only derivation satisfying such a requirement has been DCNT within the context of diffusion-controlled mass transport [32]. As results from such a study, the effects related to the noncovariant character of CNT are subdominant.

If we consider an initial equilibrium (undersaturated) state, the stationary PDF becomes the equilibrium distribution by identifying it with a zero flux regime. Then, imposing $\mathfrak{J}_s = 0$ in Eq. (33), we arrive at

$$P_{\rm eq}(X) = Af^{(\alpha-1)}(X)e^{-\beta W(X)} = Ae^{-\beta\Phi(X)}. \quad (37)$$

The results introduced in this section will be important for the derivation of the induction times, characterized by the mean first-passage time (MFPT). A detailed discussion on the estimation of the MFPT is introduced in Sec. IV.

C. Semiadiabatic limit

Real experiments could involve time-dependent coefficients. Following Weidlich and Haag [49], we will assume that such a dependence of both f and Φ on time is controlled via a certain control function $\kappa(t)$. Under this assumption we get

$$D^{(1)}(X,\kappa(t)) = -f(X,\kappa(t))\frac{\partial\beta W(X,\kappa(t))}{\partial X} + \alpha\frac{\partial f(X,\kappa(t))}{\partial X},$$
$$D^{(2)}(X,\kappa(t)) = f(X,\kappa(t)). \quad (38)$$

As is evident, if κ is time independent we recover the previous results. In most cases, the control function will be either the average density of the metastable state $\kappa(t) = \rho_{\rm av}(t)$ or the temperature of the system $\kappa(t) = T(t)$. In those cases in which $\kappa(t)$ is a slowly varying function of time, with respect to a typical time scale, one expects that the stationary solution follows adiabatically the motion of $\kappa(t)$, i.e., the system reaches a stationary state almost instantaneously. This hypothesis is also known as semiadiabatic limit [49]. The time scale that characterizes this limit can be interpreted as the relaxation time toward the initial metastable state, as pointed out by Talkner and Łuczka [50]. Under these circumstances, the zeroth-order approximation for the quasistationary PDF is

$$P_{\rm qs}(X;t) \sim A(t)e^{-\beta\Phi(X,\kappa(t))} - \mathfrak{J}_s e^{-\beta\Phi(X,\kappa(t))}\int^X \frac{e^{\beta\Phi(Y,\kappa(t))}}{f(Y,\kappa(t))}dY \quad (39)$$

and so the quasiequilibrium PDF for undersaturated conditions, for which the flux necessarily vanishes ($\mathfrak{J}_s = 0$), is

$$P_{\rm qe}(X;t) \sim A(t)e^{-\beta\Phi(X,\kappa(t))}. \tag{40}$$

The semiadiabatic approach is quite useful in order to make a first approximation of the MFPT under nonstationary conditions. Nonetheless, for a more accurate approximation of induction times the path-integral formalism developed by Getfert and Reimann [51] should be considered.

IV. ESTIMATION OF INDUCTION TIMES AND NUCLEATION RATES

In this section an approximation for the MFPT and so for the nucleation rate will be provided for most typical mechanisms governing mass transport, i.e., the attachment rate. To do that, we first get an approximation of the MFPT and then particularize it by using the most used expressions for $f(X)$ in the literature [13]. The reason why we focus on obtaining an approximation for the MFPT (hereafter denoted by τ) is that this quantity is closely linked to the nucleation rate J. Indeed, within the range of applicability of CNT one expects [e.g., Sec. 10.6 and Eq. (72) of Ref. [52]]

$$J_\alpha \sim \rho_{\rm av}\tau_\alpha^{-1}, \tag{41}$$

where the subscript α has been introduced to highlight the fact that it will depend on the α calculus selected. That way, τ can be understood as the mean time required for nucleation to occur. For this purpose we follow Risken [34] to get an approximation of τ. To begin we consider stationary conditions, i.e., f and W, time independent. From the results thus obtained, a naive approximation for time-dependent conditions is readily produced by considering the semiadiabatic limit. It is easy to show that Eq. (32) can be rewritten as

$$\begin{aligned}\mathfrak{J}_s &= -f(X)e^{-\beta\Phi(X)}\frac{\partial}{\partial X}[e^{\beta\Phi(X)}P(X)] \\ &= -e^{-\beta\varphi(X)}\frac{\partial}{\partial X}[e^{\beta\Phi(X)}P(X)],\end{aligned} \tag{42}$$

with

$$\varphi(X) = W(X) - \alpha k_B T\ln[f(X)]. \tag{43}$$

If the barrier is relatively high, $\mathfrak{J}_s$ is expected to be very small. Hence, we can integrate Eq. (42) from the minimum $X = X_{\rm min}$ to the maximum $X = X_{\rm max}$ size allowed for a cluster

$$\begin{aligned}\mathfrak{J}_s\int_{X_{\rm min}}^{X_{\rm max}} e^{\beta\varphi(s)}ds &= P(X_{\rm min},t)e^{\beta\Phi(X_{\rm min})}\left(1-\frac{P(X_{\rm max})}{P(X_{\rm min})}e^{\beta\Delta\Phi}\right) \\ &\sim P(X_{\rm min})e^{\beta\Phi(X_{\rm min})}.\end{aligned} \tag{44}$$

Under these conditions, as $\mathfrak{J}_s$ is assumed to be very small we can use Eq. (33) to approximate $P(X_{\rm min}) \sim Ae^{-\beta\Phi(X_{\rm min})}$ and $P(X) \sim Ae^{-\beta\Phi(X)}$. That way, the distribution function near $X_{\rm min}$ will be approximately given by (see Ref. [34])

$$P(X) \sim P(X_{\rm min})e^{-\beta(\Phi(X)-\Phi(X_{\rm min}))}. \tag{45}$$

Then we can get the expression for the MFTP [34]

$$\begin{aligned}\tau(\alpha) &\sim \frac{P(X_{\rm min},t)e^{\beta\Phi(X_{\rm min})}\int_{X_{\rm min}}^{X_{\rm max}} e^{-\beta\Phi(s)}ds}{P(X_{\rm min},t)e^{\beta\Phi(X_{\rm min})}/\int_{X_{\rm min}}^{X_{\rm max}} e^{\beta\varphi(s)}ds} \\ &\sim \int_{X_{\rm min}}^{X_{\rm max}} e^{-\beta\Phi(s)}ds\int_{X_{\rm min}}^{X_{\rm max}} e^{\beta\varphi(s)}ds.\end{aligned} \tag{46}$$

The usual procedure [34] is to expand both exponents around $X_{\rm min} = 0$ and X_*, respectively, but in this problem such a method cannot be used since $f(X)$ goes to zero as $X \to 0$ [13,14]. Nonetheless, the main contribution to the first integral stems from the region around $X_{\rm min}$. Thus, in the case of three-dimensional (3D) nucleation the free-energy term will be governed by the surface term [13] and hence the exponent involving $\beta\Phi$ can be truncated to a good approximation as

$$\beta\widetilde{\Phi}_{\rm 3D}(X) = \beta(\Theta X^{2/3} + (1-\alpha)k_B T\ln[f(X)]), \tag{47}$$

where Θ would be a measure of the surface tension [13,14]. In contrast, for 2D nucleation, the work of cluster formation near $X_{\rm min}$ is governed by the line-tension term

$$\beta\widetilde{\Phi}_{\rm 2D}(X) = \beta(\Theta X^{1/2} + (1-\alpha)k_B T\ln[f(X)]), \tag{48}$$

with Θ being here the scaled line tension. Hence, we get

$$\int_{X_{\rm min}}^{X_{\rm max}} e^{-\beta\Phi(s)}ds \sim \int_0^\infty e^{-\beta\widetilde{\Phi}(s)}ds, \tag{49}$$

whose exact results are collected in Table I. Note that these results involve the Euler Gamma function $\Gamma(n)$. In addition,

$$\begin{aligned}\int_{X_{\rm min}}^{X_{\rm max}} e^{\beta\varphi(s)}ds &\sim \int_0^\infty e^{\beta(\varphi(X_*)-(1/2)|\varphi(X_*)|(s-X_*)^2)}ds \\ &\sim \frac{1}{2}\chi e^{\beta\varphi(X_*)},\end{aligned} \tag{50}$$

with

$$\frac{1}{\lambda} = \sqrt{\frac{\beta|\varphi''(X_*)|}{2\pi}} = \sqrt{\frac{|\alpha[\delta k_B T/\nu(X_*)^2] + W''(X_*)|}{2\pi k_B T}}, \tag{51}$$

$$\chi = \lambda\left(1+{\rm erf}\left[\frac{\sqrt{\pi}}{\lambda}X_*\right]\right). \tag{52}$$

The prefactor λ^{-1} turns into the well-known Zeldovich factor [13] z_d when one selects $\alpha = 0$, i.e., Itô calculus. In fact, χ^{-1} could be considered as a generalization of the Zeldovich factor since it plays the same role as the latter in the classical expression of MFPT [52]:

$$\tau_{\rm CNT} \sim z_d^{-1}f(X_*)^{-1}e^{\beta W(X_*)}. \tag{53}$$

The integral of Eq. (49) depends on the monomer attachment mechanism. In order to perform such an integral we use the expressions given in the literature for the most usual experimental situations (see Table I) for both homogeneous nucleation (HON) and heterogeneous nucleation (HEN): (i) $f(X) = \zeta X^{1/2}$ for 2D HEN of clusters with monolayer height, with ζ given by Eqs. (10.6), (10.7), (10.63), and (10.66) of Kashchiev [13]; (ii) $f(X) = \zeta X^{1/3}$ for 3D HON and HEN of caps in liquid or solid solutions, with ζ given by Eqs. (10.18), (10.20), and (10.24) of Kashchiev [13]; and (iii) $f(X) = \zeta X^{2/3}$ for 3D HON and HEN of caps when the monomer attachment

TABLE I. Integration of equation (49) by employing some of the most used expressions for the monomer attachment rate and the corresponding approximations of the MFPT.

Nucleation type	Mass-transport mechanism	$f(X)$	$\int_0^\infty e^{-\beta\widetilde{\Phi}(s)}ds$	τ_{MFPT}
2D HEN disks with monolayer height	direct impingement[a] interface transfer[b]	$\zeta_1 X^{1/2}$	$I_1(\alpha)=\frac{2\Gamma(\alpha+1)\zeta_1^{\alpha-1}}{\beta^{\alpha+1}\Theta^{\alpha+1}}$	$\frac{1}{2}I_1\chi e^{\beta\varphi(X_*)}$
3D HON or HEN spheres or caps from liquid or solid	volume diffusion[c]	$\zeta_2 X^{1/3}$	$I_2(\alpha)=\frac{3\Gamma((\alpha+2/2))\zeta_2^{\alpha-1}}{2\beta^{(\alpha+2)/2}\Theta^{(\alpha+2)/2}}$	$\frac{1}{2}I_2\chi e^{\beta\varphi(X_*)}$
3D HON or HEN spheres or caps from vapor, liquid, or solid	direct impingement[d] interface transfer[e]	$\zeta_3 X^{2/3}$	$I_3(\alpha)=\frac{3\Gamma((2\alpha+1)/2)\zeta_3^{\alpha-1}}{2\beta^{(2\alpha+1)/2}\Theta^{(2\alpha+1)/2}}$	$\frac{1}{2}I_3\chi e^{\beta\varphi(X_*)}$
3D HON or HEN	arbitrary	$\zeta X^{\delta/\nu}$	$I(\alpha)=\frac{3\Gamma((3/2)(\alpha\delta/\nu-\delta/\nu+1))\zeta^{\alpha-1}}{2\beta^{(3/2)(\alpha\delta/\nu-\delta/\nu+1)}\Theta^{(3/2)(\alpha\delta/\nu-\delta/\nu+1)}}$	$\frac{1}{2}I\chi e^{\beta\varphi(X_*)}$

[a] ζ_1 prefactor multiplying $N^{1/2}$ in Eqs. (10.6) and (10.7) of Ref. [13].
[b] ζ_1 prefactor multiplying $N^{1/2}$ in Eqs. (10.63) and (10.66) of Ref. [13].
[c] ζ_2 prefactor multiplying $N^{1/3}$ in Eqs. (10.18), (10.20), and (10.24) of Ref. [13].
[d] ζ_3 prefactor multiplying $N^{2/3}$ in Eqs. (10.3)–(10.5) and (10.9) of Ref. [13].
[e] ζ_3 prefactor multiplying $N^{2/3}$ in Eqs. (10.60)–(10.65) of Ref. [13].

frequency is controlled by direct impingement or by interface transfer, with ζ given by Eqs. (10.3), (10.4), (10.5), (10.9), (10.60), (10.61), (10.64), and (10.65) of Kashchiev [13]. Hereafter the integral of Eq. (49) will be called $I(\alpha)$. From Eq. (46) we can finally give the approximation of the MFPT

$$\tau(\alpha)\sim\tfrac{1}{2}\chi I(\alpha)f(X_*)^{-\alpha}e^{\beta W(X_*)}, \tag{54}$$

which makes a comparison with that predicted by CNT (54) possible:

$$\frac{\tau(\alpha)}{\tau_{\mathrm{CNT}}}=\frac{z_d^{-1}[1+\alpha\mathcal{O}((X_*)^{-2})]^{-1/2}f(X_*)^{-\alpha}I(\alpha)}{z_d^{-1}f(X_*)^{-1}}$$
$$=I(\alpha)f(X_*)^{1-\alpha}[1+\alpha\mathcal{O}((X_*)^{-2})]^{-1/2}, \tag{55}$$

which under backward Itô calculus turns into

$$\frac{\tau(\alpha=1)}{\tau_{\mathrm{CNT}}}\sim I(1). \tag{56}$$

The approximations are not exactly the same, even though $\alpha=1$ produces the same FPE, because we follow a different route to derive τ.

One immediately observes the similitude of Eq. (54) with Kramers' law. In fact, the former is in accord with the latter with a prefactor deduced analytically. Furthermore, Eq. (54) allows us to reach an approximation of the nucleation rate via Eq. (41). Now this result can be extended as a first-order approximation for time-varying conditions, as shown by Getfert and Reimann [51] for slow time-dependent Kramers-Moyal coefficients. Thus, under the assumption of the semiadiabatic limit and following the notation introduced by Getfert and Reimann [51], the instantaneous MFPT can be estimated as

$$\tau(\alpha;t)\sim\tfrac{1}{2}\chi(t)I(\alpha,\kappa(t))f(X_*,\kappa(t))^{-\alpha}e^{\beta W(X_*,\kappa(t))}. \tag{57}$$

While these results can be very useful in characterizing the time required to start the phase transition, we must bear in mind that they are approximations. To get more accurate estimates of this characteristic time an exact numerical integration of the above equations can be performed. Indeed, the best estimation will be determined via stochastic integration of Eq. (15). The main advantage of a numerical approach is that it is valid for both time-independent and time-dependent coefficients.

V. CONCLUSION

In this work an alternative route to derive the classical theory of nucleation has been introduced. Over the past century, CNT has been exposed to intense examination, which has reported many of its flaws and strengths. One of the most remarkable strengths of this framework is the majestic simplicity underlying its formulation. However, several different equations for the size distribution resulted from such an extensive investigation. Based on the ideas that constitute the classical theory, a unified equation can be reached, starting from a unified Itô-Stratonovich stochastic equation.

From a heuristic derivation, the initially unknown coefficients of the proposed stochastic equation were obtained. This stochastic cluster-growth law was interpreted under a general stochastic calculus, despite what is usually done. As a result, our postulated model recovers the cluster-growth law postulated by Becker and Döring [7] and Tunitskii [8] if slowly varying energy barriers and Itô integration convention are considered. Indeed, such an assumption will be always true within the range of applicability of CNT since the initial state is near equilibrium. Besides that achievement, we employed the tools of the theory of stochastic processes to go from the stochastic equation to a unified FPE. It is called unified given the fact that it contains both the classical Zeldovich-Frenkel equation when we select backward Itô convention and the equation derived by Lutsko and Durán-Olivencia [32] for the usual Stratonovich calculus.

Another interesting result generated by this stochastic formalism was found while studying the short-time propagators. They constitute the tools required to know the probability for a cluster to grow or shrink. Surprisingly, when we set the initial cluster to be critical (whose growth law is supposed to be purely random), we found that all the interpretations of the noise give a tendency to grow. It could be argued that this fact would be enough to make us select Itô's interpretation. Nevertheless, the only interpretation that has reported the ability to produce a covariant theory has been the Stratonovich calculus [32]. Furthermore, the study of the general covariance of the theory reported another interesting result, namely, the Zeldovich-Frenkel equation cannot be fixed to be covariant.

This result indeed sheds some light on the question of whether or not it is worth trying to fix CNT by considering much more sophisticated models for the cluster.

Finally, estimates of the nucleation time and rate were computed. The approximation we reached for these quantities was specifically applied to the most typical experimental situations. An inevitable similarity to the CNT expressions appeared. A comparison with such an expression was performed by computing their ratios.

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APPENDIX: SHORT-TIME PROPAGATOR

In order to get the expression of the short-time propagators in a general α convention, we follow the procedure introduced by Wissel [53], which was also used by Risken [34]. The formal solution of a general FPE can be written as (see, e.g., Ref. [34])

$$p(x,t|x',t') = \vec{T}\exp\left[\int_{t'}^{t}\mathcal{L}_{\rm FP}[x(s),s]ds\right]\delta(x-x'), \quad \text{(A1)}$$

where $\mathcal{L}_{\rm FP}$ denotes the Fokker-Planck operator (A3) and $\vec{T}$ is the time-ordering operator. For small time intervals $\tau = t - t'$, Eq. (A1) can be approximated by

$$p(x,t+\tau|x',t) = [1+\mathcal{L}_{\rm FP}(x'+\alpha\Delta x,t)\tau + \mathcal{O}(\tau^2)]\delta(x-x'), \quad \text{(A2)}$$

where we have used the stochastic integral [45] introduced in Eq. (2). Now we can perform the differentiation in the Fokker-Planck operator

$$\mathcal{L}_{\rm FP}(u(x),t) = -\frac{\partial}{\partial x}D^{(1)}(u(x),t) + \frac{\partial^2}{\partial x^2}D^{(2)}(u(x),t), \quad \text{(A3)}$$

with $u(x) = \alpha x + (1-\alpha)x'$. Accordingly, we obtain

$$\begin{aligned}\mathcal{L}_{\rm FP}(u(x),t) =& -\alpha\frac{\partial D^{(1)}}{\partial x}(u(x),t) + \alpha^2\frac{\partial^2 D^{(2)}}{\partial x^2}(u(x),t)\\ &-\left[D^{(1)}(u(x),t) - 2\alpha\frac{\partial D^{(2)}}{\partial x}(u(x),t)\right]\frac{\partial}{\partial x}\\ &+ D^{(2)}(u(x),t)\frac{\partial^2}{\partial x^2}. \quad \text{(A4)}\end{aligned}$$

By substituting Eq. (A4) into (A2) and using the Taylor expansion of the exponential function we get

$$p(x,t+\tau|x',t) = e^{\mathcal{L}_{\rm FP}(u(x),t)\tau}\delta(x-x'). \quad \text{(A5)}$$

With the aim of obtaining an exponential function, the Fourier representation of the Dirac δ function will be used. Thus, we finally obtain the short-time propagator

$$\begin{aligned}&p(x,t+\tau|x',t)\\ &= \exp\left(-\alpha\tau\frac{\partial D^{(1)}(u(x),t)}{\partial x}\alpha^2\tau\frac{\partial^2 D^{(2)}(u(x),t)}{\partial x^2}\right.\\ &\quad\left.-\frac{\{x-x'-[D^{(1)}(u(x),t) - 2\alpha(\partial D^{(2)}/\partial x)(u(x),t)]\tau\}^2}{4\tau D^{(2)}(u(x),t)}\right)\\ &\quad\times[\sqrt{4\pi\tau D^{(2)}(u(x),t)}]^{-1}. \quad \text{(A6)}\end{aligned}$$

As can be checked, this short-time propagator recovers those presented by Dekker [54] and Risken [34] [e.g., Eqs. (4.55) and (4.55a) of Ref. [34]] for $\alpha = 0$ and $\alpha = 1$, respectively. This derivation can be seen as an alternative route to that carried out by Lau and Lubensky [45].

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