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# Nucleation phenomena: The non-equilibrium kinetics of phase change

David Reguera

Departament de Física de la Matèria Condensada, Universitat de Barcelona,  
Barcelona, Catalonia



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**Summary.** The molecules and atoms that comprise matter have the tendency to join in different aggregation states called phases. How these atoms and molecules manage to shift between these different states is one of the most fascinating processes in physics. These phase transitions are commonly controlled and triggered by a non-equilibrium physical mechanism, called nucleation, that describes the formation of the first seeds of the new phase. Nucleation is behind many phenomena of utmost scientific and technological interest, ranging from nuclear phenomena and biological assembly to galaxy formation. However, due to its rare non-equilibrium nature, it is still one of the few classical problems that remain incompletely understood. Indeed, deviations between theoretical predictions and experiments can reach several orders of magnitude. In this article, we review the essential aspects of nucleation and the challenges it poses to current research. [Contrib Sci 11(2): 173-180 (2015)]

**\*Correspondence:**

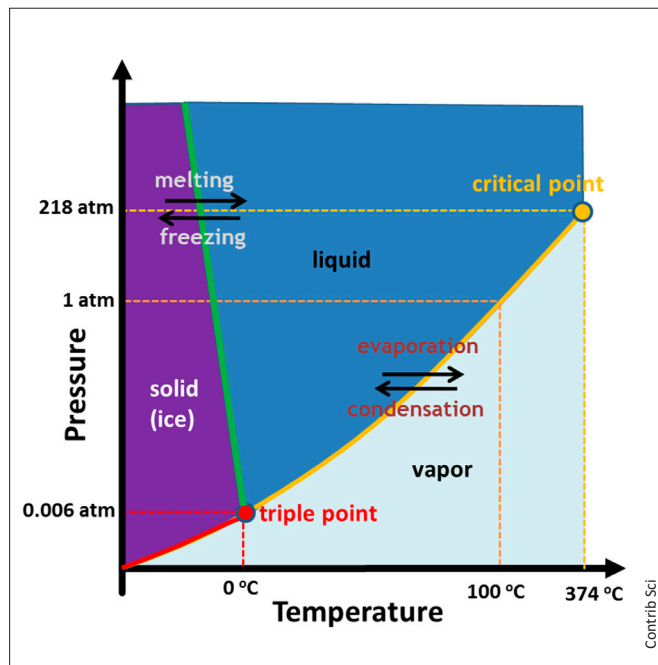
David Reguera  
Departament de Física de la Matèria Condensada  
Universitat de Barcelona, Martí i Franquès, 1  
08028 Barcelona, Catalonia  
Tel. +34-934039214; E-mail: dreguera@ub.edu

## Introduction

Matter appears in nature in different aggregation states called phases. A familiar example is water, whose molecules can be in a gaseous (vapor) state, glued together to form a liquid, or trapped in a static arrangement in a solid phase (ice). The state of a particular substance is the result of a delicate balance between thermal agitation, which tends to set molecules free, and attractive molecular interactions, which

bind molecules together. This balance sensitively depends on the thermodynamic ambient conditions, especially on the temperature, which controls the strength of the thermal agitation, and the density or pressure, which determines the average proximity between molecules. These parameters can be used to construct a phase diagram that defines the equilibrium phase, i.e., the most stable state of a particular substance under the given conditions. As an example, Fig. 1 reproduces the phase diagram of water. The solid lines indi-

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**Fig. 1.** Phase diagram of water. The most stable phase of water is shown as a function of pressure and temperature. The solid lines mark the boundaries between different phases. The triple point, i.e., the temperature and pressure at which the three phases of water can coexist, and the critical point, where the phase boundary between the liquid and the vapor vanishes, are also indicated.

cate the coexistence boundaries that define the frontiers between different equilibrium states. For instance, at ambient pressure, water prefers to be in a vapor state at temperatures above 100°C but forms ice at temperatures below 0°C. However, the division between states is not perfectly sharp. It is well known that purified water can be held as a liquid almost indefinitely at  $-10^{\circ}\text{C}$  without freezing; and a gas can be compressed several times its equilibrium pressure before the first liquid drop suddenly appears [6]. These special situations, in which a system persists for long periods of time in a phase that is not its equilibrium state, are generally called metastable states.

The ultimate reason why water can be kept in supercooled or supersaturated metastable states is the presence of an energetic barrier that hinders spontaneous transitions between different phases. The initial and crucial step required to overcome this barrier and to trigger a phase transformation is the generation of a small embryo, or *nucleus*, of the new phase within the bulk metastable substance. This fundamental mechanism of phase transformation is known as *nucleation* and it constitutes a central problem in many areas of scientific and technical interest [1,6,15,16]. Conden-

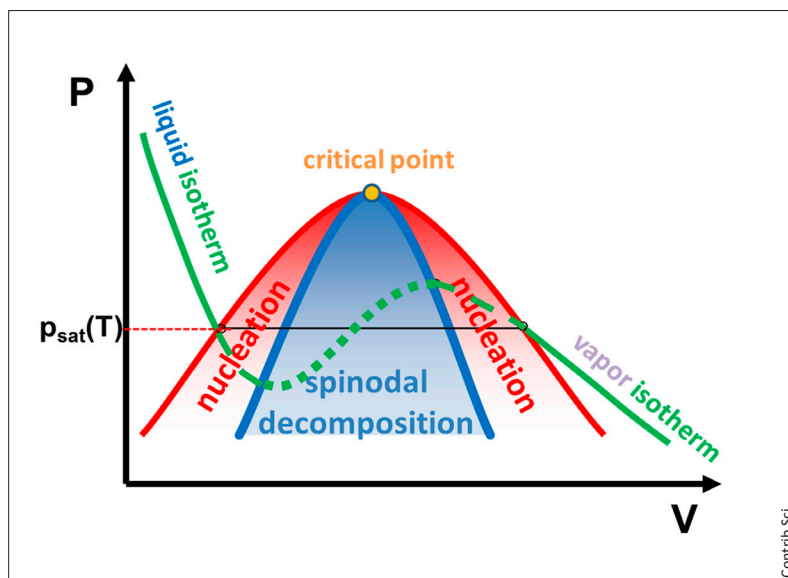
sation (liquid drop formation in a supersaturated gas), boiling (vapor formation in a superheated liquid), cavitation (bubble formation in a stretched fluid), and crystallization are perhaps the most common examples of nucleation processes. But nucleation also plays a decisive role in very different fields of science and technology.

In the atmospheric sciences, the nucleation of water droplets, ice crystals, or aerosols (liquid droplets suspended in a gas) in the atmosphere is a fundamental issue in weather forecasting and climate change [22]. Practical uses of nucleation include the induction or prevention of precipitation and hail by cloud seeding [5] and the collection of liquid water from moist air in airwells. Examples of biomedical interest encompass the cryopreservation of embryos and human tissues, the bio-mineralization of bone, teeth, and shells, the formation of kidney stones or uric acid crystals in gout, and protein aggregation/crystallization [13,17] that underlies many diseases, such as Alzheimer, sickle-cell anemia, and cataract formation. At the industrial level, control of the nucleation stage is an important requirement in the fabrication of novel and advanced materials. The stability of pharmaceutical compounds, damage to manmade materials (e.g., propellers) or tissues by cavitation, the explosive boiling of vapors, the performance of motor engines and turbines, and the extraction of oil and gas are among the many industrial problems involving different aspects of nucleation. Further examples can be cited at all scales ranging from nuclear phenomena to the formation of planets and galaxies.

But how well do we understand nucleation? Can we predict and control its outcome? As will become clear in the following, despite significant efforts, we are still very far from being able to accurately predict the occurrence of nucleation, not even in the simplest cases. In fact, the errors in predictions are not just a few percent, but often span many orders of magnitude. In this article, we discuss the particular features of nucleation that give rise to this discrepancy. For simplicity, we focus on the simplest case, that of homogeneous condensation. But the same considerations can be applied to more complex phenomena, such as protein crystallization and the self-assembly of viruses [33].

## The problem of condensation

To better illustrate the physical nature of the nucleation process let us focus on a simple and well-known example: the condensation of a vapor. In most practical instances, condensation, as well as the majority of phase transitions,



**Fig. 2.** Mechanisms of phase transition. A representative phase diagram in terms of the pressure ( $P$ ) and volume ( $V$ ) of a simple fluid. The green line shows an isotherm, showing the values of  $P$  as a function of the volume of the system for a given constant temperature ( $T$ ).  $P_{\text{sat}}(T)$  is the value of the saturation pressure at this particular temperature, at which the liquid and vapor phases coexist. The red line is the coexistence curve of the liquid (left branch) and the vapor (right branch) at all temperatures, ending at the critical point. The blue line is the spinodal, below which the fluid is mechanically unstable (indicated by the dotted lines) and is transformed into a new phase by a spontaneous mechanism known as spinodal decomposition. Nucleation is the mechanism of phase transition between the coexistence curve and the spinodal, where the system is in a metastable state (represented by the dashed lines in the isotherm).

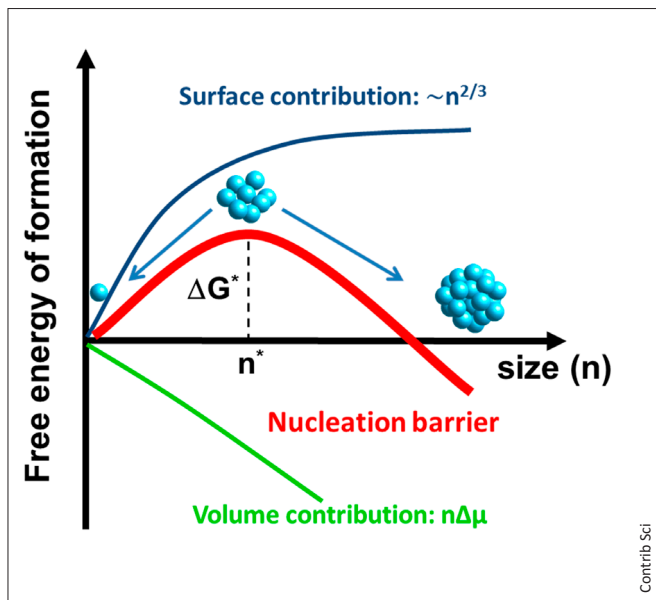
preferentially occurs in the presence of surfaces on impurities, by a mechanism known as *heterogeneous nucleation*. However, in the following we describe the simplest situation, that of *homogeneous* condensation occurring in the bulk of a pure substance.

Figure 2 shows a representative phase diagram of a simple model fluid in terms of pressure and volume. The green line indicates the pressure of the system as a function of the volume that it occupies at a fixed temperature. At large volumes, the system is in the vapor state. As the volume is reduced, the pressure increases up to a point at which the liquid phase begins to be more favorable. At this so-called saturation pressure, the vapor can coexist with the liquid, whose properties are defined by the left branch of the green curve. If the volume is further reduced, the vapor becomes supersaturated and remains in a metastable state (indicated by the dashed green line) until the phase transformation takes place. If we trace the values of the saturation pressure at different temperatures, we obtain the curve representing the coexistence of the liquid and the vapor, indicated by the red solid line in Fig. 2. The blue line represents the spinodal, which is the locus of points at which the mechanical stability requirement of a positive isothermal compressibility (i.e., that the volume of a system

becomes smaller as more pressure is applied to it) is first violated. These two lines delimit the two basic mechanisms of a phase transition. Below the spinodal line, the vapor phase is thermodynamically unstable, and the phase transformation proceeds spontaneously by a barrierless mechanism known as *spinodal decomposition*. In the region between the spinodal and the coexistence lines, the system is metastable and the phase transformation occurs by the nucleation of the first embryos of the new phase and their subsequent growth.

The degree of metastability of a vapor is usually measured in terms of the supersaturation, defined as the ratio between the actual pressure of the vapor and the saturation pressure. As mentioned in the Introduction, a metastable phase can persist over long periods of time. This feature reflects the fact that the development of the new phase must surmount an energy barrier. This barrier becomes infinity at the coexistence curve and vanishes at the spinodal and is thus strongly dependent on temperature and supersaturation. The origin of this barrier and the means by which it is overcome are explained below.

In a supersaturated vapor, thermal agitation of the molecules induces density fluctuations. These fluctuations generate small aggregates of molecules (clusters) with proper-



**Fig. 3.** Nucleation barrier. Schematic representation of the free energy of liquid cluster formation as a function of the number of molecules contained by the cluster (red line). This free energy landscape is derived from two contributions: a volume term (green line), proportional to the number of molecules and to the difference in chemical potentials between the old and the new phases, and a surface term (blue line) associated with the cost of forming a new interface between the incipient liquid and the vapor phase. The sum of these two terms gives rise to a barrier. The maximum is located at the *critical cluster size*  $n^*$  and its height is known as the *nucleation barrier*  $\Delta G^*$ . Liquid clusters smaller than the critical size will slide down the barrier until they disappear, whereas clusters larger than the critical size will tend to grow spontaneously.

ties similar to those of the stable phase, in our case, tiny liquid droplets. The formation of these small droplets is favored by an energy decrease associated with a more stable liquid phase under the given conditions. This energy gain is proportional to the number of molecules or the volume of the cluster. However, the construction of the new phase from the bulk metastable phase requires the creation of an interface between the two phases, which implies an energetic cost proportional to the droplet surface. The competition between these two effects gives rise to the nucleation barrier, as illustrated in Fig. 3.

Surface effects are dominant for small clusters and hence tiny droplets tend to disintegrate. However, there is a characteristic size at which volume effects override surface contributions and clusters tend to grow spontaneously. This size, signaling the top of the free energy of cluster formation, is known as the *critical size* and the energy required in its formation constitutes the nucleation barrier. The rate at which critical-sized embryos are formed is the nucleation rate and its prediction is one of the major goals of nucleation theories.

## Classical nucleation theory

Although the first studies of phase equilibrium and metastability of undercooled substances date back to the investigations of Fahrenheit in the 18th century [7], the study of the kinetics of nucleation was initiated by the pioneering work of Volmer and Weber [23] in 1926 and of Farkas in 1927 [8]. The field was subsequently developed by the contributions of Becker and Döring [3], Frenkel [11], and Zeldovich [34], among others. These investigations collectively gave rise to classical nucleation theory (CNT) [1,6,15,16].

According to CNT, the initial stages of droplet formation are modeled as a sort of chemical reaction in which a cluster of a particular number of molecules grows or shrinks by the addition or loss of one molecule at a time. Thus, a balance equation can be formulated describing the evolution over time of the cluster population of a given size in the system. The relationship involves two different size-dependent parameters: the rate at which molecules attach to a cluster and the rate at which they evaporate from it. The rate of attachment can be rather accurately quantified using kinetic theory of gases [19], as the rate of thermal collisions. However, the detachment rate depends very sensitively on the arrangement and interactions between molecules and is thus hard to model.

CNT circumvents this problem by resorting to detailed balance considerations. At equilibrium conditions, to maintain a balance in the population of cluster sizes, the rates of attachment and detachment should be connected to the differences in the free energies of clusters of different sizes. Accordingly, the unknown detachment rate can be expressed as a function of both the attachment rate and the free energy of formation of a cluster of any given size.

CNT therefore rephrases a complicated kinetic problem in simpler equilibrium thermodynamic terms. The free energy of formation of a tiny liquid droplet is then evaluated using crude approximations. The first one is to consider the vapor phase as nearly ideal, i.e., neglecting the interactions between its molecules. Next, the incipient liquid drop is modeled as a tiny spherical drop with a sharp interface and the same thermodynamic properties as the macroscopic liquid. With these assumptions the critical cluster size and the height of the nucleation barrier can be evaluated using just three simple variables: the surface tension, the saturation pressure, and the density of the liquid, assumed to be incompressible.

Knowing the height of the barrier, the nucleation rate (i.e., the rate at which critically sized clusters form per unit

volume and unit time) can be evaluated as the rate of jumping over the nucleation barrier. When this barrier is high, as is the case in most practical instances, the rate turns out to be proportional to the exponential of the barrier height, which is expressed in units of the characteristic thermal energy  $k_b T$ , where  $k_b$  is Boltzmann's constant. Therefore, CNT provides a very simple expression to predict the rate at which any phase transition occurs, using simple expressions and thermodynamic parameters that are available for most substances.

## How good is CNT?

CNT has dominated our understanding of nucleation during the last several decades. The secret of its success is its striking simplicity and the initially reasonable agreement between experimental results and the theory's predictions for the metastability limits of the majority of substances.

With the recent development of new and very accurate experimental techniques able to measure actual nucleation rates, the molecular details of nucleation are slowly being revealed. Nowadays, the real-time experimental observation of the appearance and growth of nuclei and small crystals at the nanoscale [12,32] is becoming feasible. At the same time, in the context of condensation, experiments using different techniques, such as thermal diffusion chambers, expansion chambers, and nozzles, have provided accurate measurements of the homogeneous nucleation rates of different substances, including water and alcohols [18]. In these experiments, the vapor is quickly supersaturated either by a temperature gradient or by a fast expansion, and the rate of appearance of the new phase is monitored by optical techniques. The results have revealed the shortcomings of CNT, in particular its common tendency to incorrectly predict the temperature dependence of nucleation rates. CNT generally overpredicts the rates at high temperatures and underpredicts the values at low temperatures. But the most serious problem is that these discrepancies are not a small factor or percentage, but can reach many orders of magnitude (Fig. 4).

Perhaps the most dramatic example is the case of argon condensation. Argon is a noble gas with a nearly ideal behavior and its equilibrium properties can be reasonably described by simple intermolecular potentials. It was therefore expected to provide the perfect test of the validity of CNT. However, as shown in Fig. 4, the results of recent experiments have exposed our lack of understanding of nucleation [14]. The discrepancies between CNT predictions and the measured rates can reach more than 20 orders of magni-

tude! This is metaphorically equivalent to the difference between predicting flooding and not having a drop of rain throughout the entire age of the universe. This is a record hard to beat in any scientific discipline manifesting the peculiar non-equilibrium characteristics of nucleation.

## Why does CNT fail?

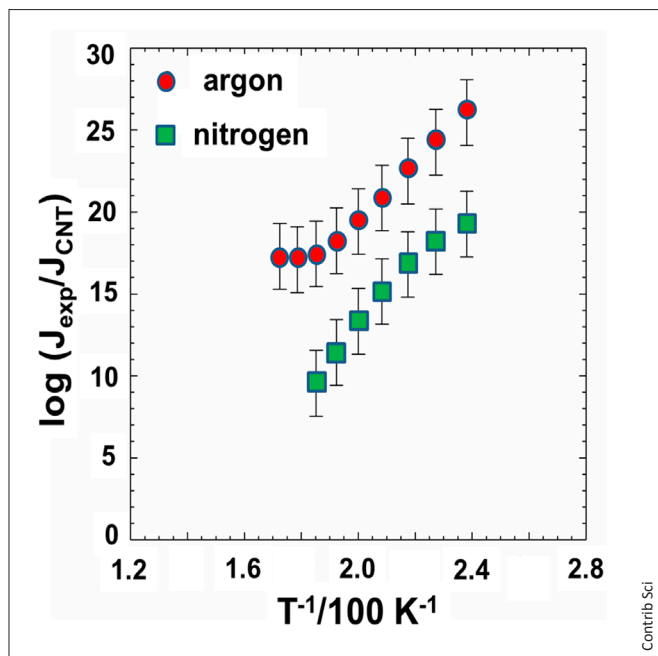
Classical nucleation theory uses macroscopic and equilibrium arguments to describe a non-equilibrium process that occurs in most cases at nanometer scales. Approaching the problem from this perspective has been the cause of long-standing controversies and of the misunderstanding of several key concepts. In addition, as evidenced by modern experimental and simulation techniques, the simplified scheme used in CNT is insufficient to accurately characterize the process of nucleation.

Since CNT involves many crude approximations, there are many potential sources of error. Most of them are related to the so-called *capillary approximation*, which considers nucleating clusters as homogeneous spherical drops with a sharp interface and the same properties as the bulk liquid, including the surface tension of its planar interface. But the real interface is not sharp; rather, there is a relatively smooth change in properties from the liquid phase to the vapor. In addition, the properties of small droplets, for instance their density, may differ from those of the bulk macroscopic fluid.

Another important factor is the potential influence of non-isothermal effects and temperature fluctuations. During the condensation process, whenever a molecule is incorporated into a liquid cluster the amount of latent heat that is released may be significant enough to heat it up. Since the nucleation rate is exponentially sensitive to temperature, temperature variations in the cluster will alter nucleation rates considerably. To properly thermalize the experimental system, a second inert gas, called a carrier gas, is usually employed. Its main role is to get rid of this extra heat. However, the potential influence of the pressure of this carrier gas is also questionable, since in some experiments it seemed to influence the nucleation rate. Other non-equilibrium effects, related, for instance, to the presence of temperature, density, or velocity gradients, may also lead to important effects.

There have also been several theoretical concerns regarding self-consistency, the proper accounting of translational and rotational degrees of freedom, and the inability of CNT to account for the existence of the spinodal, (i.e., in which the barrier towards the formation of the new phase com-





**Fig. 4.** Failure of CNT. Plot of the ratio of the nucleation rates of argon and nitrogen as measured in a cryogenic pulse chamber and the predictions by CNT, as a function of the inverse of temperature. The deviations in both cases range from 10 to 25 orders of magnitude; a clear temperature trend is also evident.

pletely vanishes) [20]. An accurate check of these factors within an experimental system is not easily performed. There are several features of nucleation that complicate the testing of hypotheses and the formulation of accurate predictions. The first is its non-equilibrium nature, given that nucleation is essentially a kinetic process that occurs at out-of-equilibrium conditions. The second is the activated nature of the process, which implies that the rate depends exponentially on the barrier; this makes nucleation extraordinarily sensitive to small variations of the parameters involved and thus very difficult to control and measure experimentally. Third, the appearance of the critical cluster that initiates a phase transition is a random process. Finally, the most important entity in nucleation, the tiny embryos of the new phase, are completely unstable, of nanometric dimensions, and typically contain very few molecules. Thus, an accurate measurement of their properties is very difficult to achieve. Experiments are hard to perform and thus have largely been done in substances of practical interest, such as water, alcohols, and sulfuric acid. Although their results have provided invaluable information about real nucleation rates, the extremely small time and length scales involved in nucleation have limited our capabilities to characterize the microscopic details of this process.

At the theoretical level, there have been many important developments aimed at correcting and overcoming the limitations of CNT. Since the free energy barrier is the dominant factor in the nucleation rate, most theoretical work has focused on calculating accurately the equilibrium energy of critical nucleus formation. Theories aimed at improving the capillarity approximation and thus providing a more realistic description of the properties of nucleating clusters have achieved promising results. In particular, density functional theory [21], which describes the free energy of a cluster in terms of a smooth density profile, has solved some of the inconsistencies of CNT. However, this approach often requires the use of accurate functionals and intermolecular potentials, which are not available, not even for common substances such as water. Many phenomenological theories have tried to correct the nucleation barrier by incorporating extra terms. Together with newly formulated kinetic theories they have met with different degrees of success. Unfortunately, many developments that seem to correct some of the limitations or inconsistencies of CNT turn out to worsen the predictions (increase the deviations) with respect to the experimental results.

## The challenge of understanding and accurately predicting nucleation

Simulations are increasingly becoming an impressive tool to characterize the rate of appearance and the structure of nucleation events at the molecular scale [2]. The development and application of novel simulation algorithms has shed light on the nucleation rates of different substances, in addition to providing direct access to the molecular and thermodynamic details of the respective processes. Simulations mimic the motion of molecules using a variety of different methods [10]. They include molecular dynamic simulations, which essentially solve Newton's equations of motion for all molecules in the system, and Monte Carlo simulations, which explore different molecular configurations by proposing random displacements. Given the rare and stochastic nature of nucleation, more sophisticated techniques, such as umbrella sampling [2] and transition path sampling [4], have been developed to cover longer time scales.

We recently developed an accurate simulation method to analyze the real non-equilibrium kinetics of nucleation. Our method was first applied to molecular dynamics simulations, because they best reproduce the dynamics of the process avoiding artifacts. However, molecular dynamics simulations


are restricted to conditions characterized by very high supersaturations, which are often far from experimentally achievable. This limitation is due to the stochastic nature of the process, that requires good statistics, and the short time scales that can be achieved in simulations (typically on the order of microseconds). At these very high supersaturations, very small critical cluster sizes and nucleation barriers are expected; thus, the discrepancies should be larger and the limitations of CNT even more evident.

To obtain accurate results, we developed a series of techniques based on the concept of mean first-passage time (MFPT). Our approach enabled the accurate evaluation of nucleation rates and critical cluster sizes [29] as well as a kinetic reconstruction of the full free energy landscape of cluster formation [26]. In addition, we analyzed and quantified the importance of finite size effects and different thermostating procedures [27,28,31], which we then used to design efficient simulation in terms of computational cost.

Equipped with these techniques, we performed molecular dynamics simulations to explore the quantitative influence of several controversial aspects regarding the accuracy of CNT [30]. One question we sought to answer is the influence on nucleation rates of temperature fluctuations and the heating up of the nucleating embryos due to the unavoidable release of latent heat [28]. Although the proper definition of temperature and its fluctuations remains controversial for small systems, the important conclusion of our studies on vapor condensation, at least for non-associating vapors, is that the impact of temperature fluctuations follows the classical predictions of non-isothermal nucleation [9] and does not dramatically alter the nucleation rates. We were also able to unravel, both theoretically and using simulations, the controversial “pressure effect” associated with the thermalizing carrier gas and to accurately describe its influence on the rates of nucleation [25]. Finally, we also looked carefully at how nucleation takes place at extreme supersaturations, at the crossover between nucleation and spinodal decomposition [24].

The results of our studies suggest that, despite its crude approximations and simplifications, CNT turns out to be not very far off in its predictions. Amazingly, in most cases CNT is able to fairly accurately predict the number of molecules in the critical cluster, even for critical clusters containing as few as five or ten molecules, in which case all macroscopic thermodynamic assumptions are doomed to fail. In addition, while our simulations confirm that CNT incorrectly predicts the height of the nucleation barrier, it is off only by a constant, which depends solely on the temperature. However,

given the exponential dependence of nucleation rates on barrier height, even a single constant can yield a prediction that is off by several orders of magnitude.

If the discrepancy lies solely with a temperature-dependent constant, what is the physical origin of this constant and how can CNT be corrected accordingly? This is still an unsolved question, but there are several encouraging clues regarding its answer. The incorporation of fluctuations, which are important for small clusters, and curvature corrections of the surface tension seem to be the most promising routes. Further investigations are underway. They seek to shed light on this fundamental process and to solve this classical problem and thereby open the door to understanding and thus controlling nucleation in more complicated situations. 

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**Competing interests.** None declared.

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