

**NUCLEATION THEORY AND THE CLOUD-POINT \***

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On the basis of a recent proposal for the droplet distribution in the lattice-gas model, we evaluate completion times and scaled supersaturations which are consistent with existing observations in cloud-point experiments near the critical temperature. Some general concepts in nucleation theory are also reviewed.

**1. Introduction**

Nucleation theory [1–4] deals with that general class of phenomena which can be mapped onto the familiar condensation of a supercooled vapor and, in its present form, it heavily rests upon the concept of clusters (droplets, grains, etc.). Although a set of basic ideas is now rather well-established, the theory still uses many phenomenological ideas and approximations so that, in order to minimize the lack of precision, it can be better discussed in relation with simple, well-defined models. A convenient model for this purpose is the lattice-gas version of the Ising model where, for instance, precise definitions for a cluster are possible [5].

The lattice-gas model [6] consists of a regular lattice, say a simple cubic lattice, whose sites are associated to a set of occupation variables each capable of only two values,  $n_i = 1$  (particle) or 0 (hole). The system presents a (configurational) energy given by

$$H = -4J \sum'_{i,j} n_i n_j, \quad J > 0, \quad (1.1)$$

where the sum runs over all bonds, i.e. pairs of nearest-neighbor sites in the lattice. Any given system configuration  $\{n_i, i = 1, 2, \dots, N\}$  has a set of  $\rho N$  occupied sites which can be partitioned into connected subsets called clusters; that is, no member of one cluster is a nearest neighbor of a member of another and if a cluster is divided into two parts then at least one member of one part is a nearest neighbor of a member of the other part. The size  $k$  of a given cluster is defined as the number of particles which belong to it; its energy  $s$  is

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defined as the number of particle–hole bonds (including both, surface and interior ones) incident on the cluster. The average degree of compactness of clusters may be measured, at least partially, in terms of  $s_k$ , the average value of  $s$  over all clusters of size  $k$ . This information is to be combined with the knowledge of  $c_k$ , the probability for the occurrence of a cluster of size  $k$  in the system. The physical relevance of the concept of clusters comes in part from the fact that they are related in some cases to the droplets or grains observed by microscopy whose formation and subsequent growth is studied by nucleation theory. Consequently, a basic problem is to describe the system, for instance its equilibrium state at temperature  $T$  and density  $\rho$ , via explicit expressions for  $c_k$  and  $s_k$ .

Recent previous work by us [7] provides a description of the lattice-gas model in terms of clusters which, unlike classical droplet models, seems very accurate at high temperatures. It is the purpose of this paper to relate this description to the usual one in terms of the clusters free energy and to show its relevance for the analysis of some familiar concepts in nucleation theory. In particular, we apply our ideas to the homogeneous nucleation in the critical region and, following the suggestion in ref. [7b], we compute nucleation rates and completion times in reasonable agreement with recent experiments on fluids.

## 2. Droplet model and clusters free energy

A typical situation studied by nucleation theory [8] is the decay of metastable states, e.g. in a supercooled vapor. These states can be maintained for a very long time under appropriate experimental conditions but, eventually, they will decay into more stable, equilibrium liquid states. This occurs through an initial, nucleation regime where density fluctuations develop at least one droplet or cluster of critical size (by overcoming an energy barrier). Liquid clusters that form which are larger than this critical size will then grow with time, while smaller clusters will tend to shrink. These processes are determined by the transport of matter and energy to or from the interfaces and by the energy of the interfaces itself. In the nucleation regime the surface energy predominates: as the clusters are then very small their surface energy is a large fraction of their total energy. Once the new liquid phase is present in a significant amount, what becomes more important is the rate at which energy and matter are supplied to or removed from the interfaces.

The above picture suggests that the concepts of clusters and clusters free energy may play indeed a fundamental role in a quantitative description; for example to evaluate the number of liquid droplets as a function of their size in a quasi-stationary condition, the rate at which critical droplets or clusters are formed, the lifetime of a given metastable state, etc.; see, e.g., refs. [2,9,10].

A description of the lattice-gas model states in terms of clusters was considered by us in previous papers [7] where we proposed a modification of Fisher's droplet model [11], namely one has at the coexistence line

$$c_k = c_0 k^{-\tau} \exp(-ak^{2/3}) [1 - \alpha \exp(-ak^{2/3})], \quad (2.1)$$

where  $a = a(T)$ ,  $\tau$  and  $\alpha$  are temperature (and density) independent, and  $c_0$  is determined by the sum rule

$$\rho = \sum_k k c_k. \quad (2.2)$$

The last factor in eq. (2.1) aims to represent approximately the probability of holes surrounding the "average cluster". In addition, it seems interesting to make the extra assumption that eq. (2.1) is consistent near the critical temperature  $T_c$  with the scaling behavior

$$c_k = k^{-(2+y/\delta)} f(\epsilon k^{y/\beta\delta}), \quad (2.3)$$

where  $\epsilon \equiv (T_c - T)/T_c$  and  $y$  is Binder's critical exponent [5] defining a cluster effective size  $k^y$ . By combining the above three equations one is forced to write  $\tau = 2 + y/\delta$ ,  $a(t) = a_0 \epsilon^t$  and  $t = 2\beta\delta/3y$ . Moreover, the data independently evidences [12]  $y \approx 0.45$  so that the cluster distribution is determined in this way by the usual critical exponents  $\beta$  and  $\delta$ , by the constants  $a_0$ , and  $\alpha$  and by the parameter  $c_0(T)$  which are to be determined consistently with the sum rule (2.2). That is, no temperature dependent parameters are left in eq. (2.1). At points in the one-phase region and for metastable states, on the other hand, we found a scaling form  $\sim h k^y$  with the same exponent as before ( $h \equiv \mu H/k_B T$  with the usual notation) [12] and

$$c_k(h)/c_k(h=0) = \exp(-\eta k), \quad (2.4)$$

where  $\eta = bh^{1/y}$  for small "fields", say  $|y| < 0.1$ ; contrarily, it follows the classical prediction, eq. (2.4) with  $\eta \propto h$  for  $|h| > 0.2$  [13].

Unlike classical nucleation theory, the above droplet model based on eqs. (2.1)–(2.4) with  $y = 0.45$  was shown to reproduce very convincingly the Monte Carlo equilibrium cluster distributions for the lattice-gas model over a broad range of temperatures and to contain other interesting theoretical features [7,12].

There are in practice several ways to define a relevant clusters free energy, on the other hand. A related basic quantity is the partition function for  $k$ -particles clusters. This is defined as

$$Q_k = \sum_K'' \exp(-E(K)/k_B T), \quad (2.5)$$

where the sum goes now over all translationally inequivalent  $k$ -particles clusters  $K$ ,  $E(K)$  is the energy of cluster  $K$ , and  $k_B$  is Boltzmann's constant.

From  $Q_k$  one may define an internal free energy for  $k$ -particles clusters as

$$F_k = -k_B T \ln Q_k. \quad (2.6)$$

One should notice at this point that  $F_k$  usually differs from the clusters free-energy concepts involved in most semiphenomenological approaches. In order to discuss this matter, we may consider the approximate expression

$$c_k \approx w_s^k Q_k (1 - \rho_s)^{m_k}, \quad (2.7)$$

where  $\rho_s$  and  $w_s$  are respectively the density and a renormalized fugacity at the coexistence curve, and  $m_k$  is a parameter slightly dependent on  $k$ , e.g.  $m_k = cte$  for  $k \geq 3$  [7]; this expression was used before in several different problems [7,14–17]. A very familiar concept in nucleation theory [2,9] is what can be termed as formation free energy for  $k$ -particles clusters,  $\tilde{F}_k$ , defined as

$$c_k = c_1 \exp(-\tilde{F}_k/k_B T), \quad (2.8)$$

which can then be related to the more rigorous concept  $F_k$  by using eqs. (2.6) and (2.7); it thus follows some differences between  $F_k$  and  $\tilde{F}_k$ . Similar conclusions may follow in the case of other phenomenological definitions for the clusters free energy density [7].

We can also use eq. (2.7) in order to obtain explicit expressions for  $Q_k$  or, equivalently, for  $F_k$  corresponding to the droplet model eqs. (2.1)–(2.4); the result is [7]

$$F_k/k_B T \approx ak^{2/3} + bk + \tau \ln k - \ln[1 - \alpha \exp(-ak^{2/3})] + c, \quad (2.9)$$

where  $\tau \approx 2.1$ ,  $b = \ln w_s$  and  $c = m_k \ln(1 - \rho_s) - \ln c_0$ . Note that eq. (2.9) is expected to have the same range of validity as eq. (2.7); see ref. [17] for a detailed discussion.

### 3. Nucleation rate versus completion time

Nucleation theory aims to predict, for example, whether a set of values for  $T$  and  $\rho$  in a given system correspond or not to a metastable state. This can be investigated by computing the corresponding nucleation rate, that is, the rate at which critical clusters are formed. The simplest situation, the so-called homogeneous nucleation occurs when these clusters form within the supercooled phase itself as the result of a fluctuation (and not at the surface of the container or at any other surface strange to the system). This situation can in principle be studied in the context of classical nucleation theory [18] which, albeit admittedly crude, was thought to predict accurately the limit of metastability. Actual computations [19], however, did not seem to confirm that expectation always and the discrepancies are sometimes very dramatic [20–24];

more involved computations [25,26] are also unable to explain very low nucleation rates near  $T_c$  [27].

Binder and Stauffer [2] made an observation which may in principle reconcile theory and experiment; namely, they realized that the quantity measured by experimentalists is not the nucleation rate itself but the time required for the phase separation process to go to completion. Two calculations along these lines [2,28] have shown that the reported discrepancies may be caused by the effect on cluster growth of the critical slowing down of diffusion. However, there is still some room for a noticeable disagreement between theory and experiment [23,27,29,30]. We shall show in the following section how the use of our droplet model in the estimation of the completion time may indeed produce a reasonable description of existing experimental data near  $T_c$ . We first need to introduce some related definitions and to consider some details of the experiments.

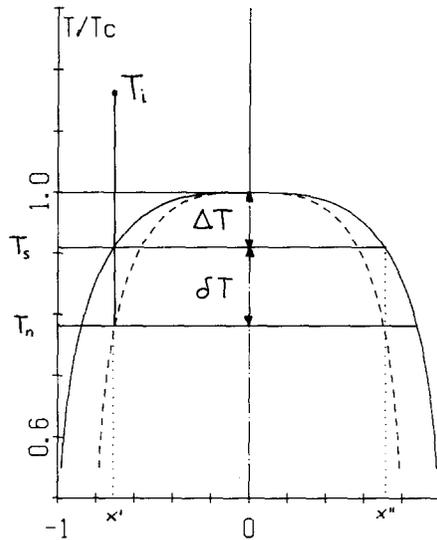


Fig. 1. Temperature–composition section of the phase diagram in a cloud-point experiment. The full line represents the coexistence curve of the system; the dashed line is the cloud-point curve obtained experimentally as described in the text, which is expected to represent somehow the metastability limit. For a given composition of the mixture,  $\Delta T$  represents the minimum quench depth below  $T_c$  to observe phase separation, while  $\delta T$  is the limit below the equilibrium separation temperature  $T_s$  to obtain supercooling. Actual experimental quenches usually proceed in several steps; the final step may begin at  $T_s$  with phases of composition  $x'$  and  $x''$  present (two-phase quenches), or above the coexistence curve at a temperature such as  $T_i$  (one-phase quenches). An ideal quench would start at “infinite” temperature ( $T_i \gg T_c$ ) and the system would then be “instantaneously” cooled to a final temperature, say  $T_n$ , the quench being instantaneous meaning that the system stays homogeneous immediately after the quench to a temperature where the equilibrium state is one of two coexisting phases.

Fig. 1 schematically represents the conditions of a typical experiment [27]. The liquid mixture is cooled from some initial equilibrium state ( $T_i$ ) into the metastable region (the region between  $T_n$  and  $T_s$  at composition  $x'$ ); the cooling proceeds until a sudden clouding of the sample is observed. This cloud-point is assumed to correspond to the metastability limit at the given composition. A cloud-point curve (represented by the dashed line in fig. 1) can then be determined by studying a number of mixtures that differ in composition. Although the supercooling (or superheating in the case of a system with a lower critical solution temperature) is accomplished in most experiments by changing the temperature of the sample at nearly constant pressure (the so-called temperature quenches), it is also possible to perform quenches at constant temperature by altering the applied pressure [31] (pressure quenches) thus moving to a different temperature-composition section of the phase diagram. For purposes of nucleation experiments, there is no fundamental distinction between these two procedures.

The cloud-point can be located by specifying the scaled supersaturation defined as  $A \equiv \delta T / \Delta T$ ; one may also define the relative supercooling as  $X = \Delta T / \epsilon T_c = 1 / (1 + A)$ .

#### 4. An explicit calculation

Metastability is essentially a dynamical phenomenon which should in principle follow from kinetic equations for the evolution of the cluster distribution  $c_k$  such as the one proposed by Becker and Döring [32,1,18]. These can be written as a continuity equation,

$$\partial c_k(t) / \partial t + \partial J_k(t) / \partial k = 0, \quad (4.1)$$

where  $J_k$  is a current given by

$$J_k(t) = -a_k c_k^{\text{eq}} \frac{\partial}{\partial k} [c_k(t) / c_k^{\text{eq}}]; \quad (4.2)$$

here  $c_k^{\text{eq}}$  is the equilibrium value for  $c_k(t)$ , which is related to the clusters formation free energy  $\tilde{F}_k$  by eq. (2.8), and  $a_k$  is the rate at which  $k$ -particles clusters absorb monomers to form  $(k+1)$ -particles clusters.  $J_k = 0$  at equilibrium, while  $J_k = J = \text{constant}$  in the simplest nonequilibrium steady-state situation. These equations are solved by Becker and Döring [32,18] assuming the boundary conditions:

$$\lim_{k \rightarrow 0} c_k^{\text{st}} = c_k^{\text{eq}}, \quad \lim_{k \rightarrow \infty} c_k^{\text{st}} = 0, \quad (4.3)$$

which correspond to a steady state with a source of clusters at  $k=0$ ; consequently it is also assumed that once a cluster grows to a specified large

size (say,  $k > k_c$ ), it is removed from the system. The nucleation rate is then given by

$$J = \left[ \int_0^\infty dk (a_k c_k^{\text{eq}})^{-1} \right]^{-1}, \quad (4.4)$$

and it follows that

$$J = c_0 a_1 \left[ \int_0^\infty dk \frac{k^{\tau-x} \exp(-bh^{1/y}k + a_0 \epsilon^t k^{2/3})}{1 - \alpha \exp(-a_0 \epsilon^t k^{2/3})} \right]^{-1}, \quad (4.5)$$

where we have introduced the equilibrium cluster distribution properties (2.1)–(2.3) and the usual hypothesis [15,16]  $a_k = a_1 k^x$ ;  $\epsilon = 1 - T/T_c$  as before. The integral in eq. (4.5) can then be evaluated by the saddle-point method to obtain [33]:

$$J = \frac{c_0 a_1}{\sqrt{\pi}} \left( \frac{3}{2} \right)^{3(\tau-x)+1} (bh^{1/y})^{3(\tau-x+2/3)} (a_0 \epsilon^t)^{-3(\tau-x+1/2)} e^{-m} (1 - \alpha e^{-3m}), \quad (4.6a)$$

where

$$m = \frac{4}{27} a_0^3 b^{-2} \epsilon^{3t} h^{-2/y}. \quad (4.6b)$$

The exponent  $m$  has the classical scaling behavior [28] when  $y = 1$  (the classical value), as expected, so that  $y < 1$  introduces a correction to that. The prefactor in eq. (4.6) also differs from previous computations [2,28], mainly due to our explicit introduction of the exponent  $x$  associated to the rate  $a_k$ . Our nucleation rate expression also differs from previous ones in the correction  $(1 - \alpha e^{-3m})$  which is expected to contribute (by decreasing  $J$ ) at large relative supercoolings.

Now, we may relate the constants in eq. (4.6) to the characteristic constants associated to the critical behaviour, i.e.

$$(\rho_c - \rho)/\rho_c = B \epsilon^\beta, \quad h = 0, \quad (4.7a)$$

$$(\rho_c - \rho)/\rho_c = D^{-1/\delta} h^{1/\delta}, \quad \epsilon = 0, \quad (4.7b)$$

and

$$\rho = \sum_{k=1}^{\infty} k c_k; \quad (4.7c)$$

having in mind that  $t = 2\beta\delta/3y$ ,  $\tau = 2 + y/\delta$ , and that

$$\rho_c = c_0 (1 - \alpha) \sum_{k=1}^{\infty} k^{-\tau+1} = c_0 (1 - \alpha) \zeta(\tau - 1), \quad (4.7d)$$

where  $\zeta(x)$  represents Riemann's zeta function, which follows from eqs. (4.7c),

(2.1) and (2.3) when  $\epsilon = h = 0$ , one has after some algebra [33]

$$a_0 = \left[ \frac{By \zeta(\tau - 1)(1 - \alpha)}{\delta \Gamma(1 - 3y/2\delta)(1 - \alpha 2^{3y/2\delta})} \right]^{2\delta/3y} \quad (4.8a)$$

and

$$b_0 = \left[ \frac{y \zeta(\tau - 1)}{\delta D^{1/\delta} \Gamma(1 - y/\delta)} \right]^{\delta/y}, \quad (4.8b)$$

where  $\Gamma(x)$  represents the gamma function. Here  $\tau$ ,  $y$  and  $\alpha$  are to be interpreted as parameters of the droplet model in section 2, and the thermodynamic amplitudes  $B$  and  $D$  and the critical exponent  $\delta$  are expected to be given by the experiments; that is, no free parameters are left in eqs. (4.6).

The completion time  $t_c$ , defined as the time required for the phase separation to go halfway to completion, may now be related to the nucleation rate  $J$ ; for instance [28]

$$t_c^{-1} \approx c_L \hat{D}^{3/5} \left[ 1 - \left( \frac{A}{1+A} \right)^\beta \right]^{1/5} J^{2/5}, \quad (4.9)$$

where  $\hat{D} = D_0 \epsilon^r$  represents the diffusion coefficient and  $c_L \approx 1.7\beta^{-1/5}$ . Binder and Stauffer [2] proposed

$$t_R^{-1} \approx c_{BS} \hat{D}^{3/5} (1+A)^{-3/5} J^{2/5}, \quad (4.10)$$

where  $c_{BS} \approx 1.23 \beta^{3/5}$ , which gives essentially the same order of magnitude estimate for the less rigorous ‘‘typical time of observation’’  $t_R$ . By introducing eq. (4.6) in eq. (4.9) a relation between  $t_c$  and  $A$  follows (involving  $\epsilon$  and  $h$ ) where the parameters are given, for instance, by experimental data obtained in critical point measurements which are independent of cloud-point observations.

## 5. Numerical results and comparison with experiment

The above relation between  $t_c$ ,  $A$ ,  $\epsilon$  and  $h$  can be reduced to a more useful one by introducing the equation of state, that is,  $h = A(\hat{c}\epsilon)^{\beta\delta}$  [34]. We then have an explicit relation between  $\epsilon$  and  $A$ , namely

$$\epsilon = \gamma g(A) A^{-6\theta(\tau-x+2/3)/5y} \exp(2\theta\lambda A^{-2/y}/5) \quad (5.1a)$$

with the notation

$$g(A) = \left\{ \left[ 1 - \left( \frac{A}{1+A} \right)^\beta \right]^{1/5} [1 - \alpha e^{-3\lambda A^{-2/y}}]^{1/5} \right\}^{-\theta} \quad (5.1b)$$

and

$$\theta = 5[3\nu + 3\beta\delta(\tau - x + 1)/y]^{-1}. \quad (5.1c)$$

One may notice here that eq. (5.1) seems to imply  $A \rightarrow \infty$  as  $\epsilon \rightarrow 0$  according to  $A \sim \epsilon^{-\eta}$  where  $\eta \approx 0.69$ . This is smaller than the value we obtain following the assumptions in previous work, namely we obtain  $\eta = 0.90$  [2] and  $0.78$  [28]. Unfortunately, we do not know of any experimental data close enough to  $T_c$  to determine the exponent  $\eta$  (see fig. 2); nor is it clear to us whether one should expect such a sharp divergence near  $T_c$ .

The constants  $\gamma$  and  $\lambda$  in eq. (5.1) are related to the previous ones by

$$\gamma = (t_c c_L D_0^{3/5} \Lambda^{2/5})^{-\theta} \quad (5.2a)$$

and

$$\lambda = \frac{4}{27} a_0^3 b^{-2} \hat{c}^{-2\beta\delta/y}, \quad (5.2b)$$

where

$$\Lambda \equiv \frac{c_0 a_1}{\sqrt{\pi}} \left( \frac{3}{2} \right)^{3(\tau-x)+1} \frac{(b \hat{c}^{\beta\delta/y})^{\tau-x+2/3}}{a_0^{-3(\tau-x+1/2)}}. \quad (5.2c)$$

In order to extract numerical consequences we thus need some values for the involved experimental parameters. This fact prevents one from performing a stringent test of the result (5.1): the most of what is available in the literature are order-of-magnitude estimates and the above equations are rather sensitive to the values of those parameters. Nevertheless, an outstanding agreement between theory and experiment follows with the information at hand. This can be showed, for instance, by interpreting  $\lambda$  and  $\gamma$  in eq. (5.1) as two adjustable parameters, trying to fit the available experimental data with that equation, and checking a posteriori whether the resulting values for  $\lambda$  and  $\gamma$  are consistent with eq. (5.2) and the known values for the experimental constants. The first evidence in favor of eq. (5.1) is the fact that a single pair of values for  $\lambda$  and  $\gamma$ , independently of the temperature and the substance investigated, describes very satisfactorily all the available data; this is shown in fig. 2. Even more, the values needed to reach that agreement ( $\lambda = 7.5 \times 10^{-3}$ ,  $\gamma = 8 \times 10^{-6}$ ) can be explained at the light of the reported values of the constants in eqs. (5.2), namely assuming the current experimental values for the critical exponents ( $\beta = 0.355$ ,  $\nu = 0.64$  and  $\delta = 4.5$ ) and for the critical amplitudes ( $B = 2$ ,  $D = 0.61$ ) [35], the parameters  $y = 0.45$ ,  $\tau = 2 + y/\delta = 2.1$  and  $\alpha = 0.95$ , which are consistent with the droplet model parameters found independently [7], the kinetic coefficient exponent  $x = 1/3$  [16], the diffusion coefficient amplitude  $D_0 \sim 10^{-3}$  cm<sup>2</sup>/s for CO<sub>2</sub> [36], the completion time which is  $t_c \sim 1-100$  s for different substances [28], the critical density for CO<sub>2</sub>  $\rho_c = 6.38 \times 10^{21}$  cm<sup>-3</sup> [35], and  $\hat{c} \approx 5.3$  in CO<sub>2</sub> [34]. We thus conclude that further investigation along the present lines might indeed lead to the interpretation of a large class of experiments and clarify some underlying questions in nucleation theory; more accurate experiments as the ones described in fig. 1 will be needed for

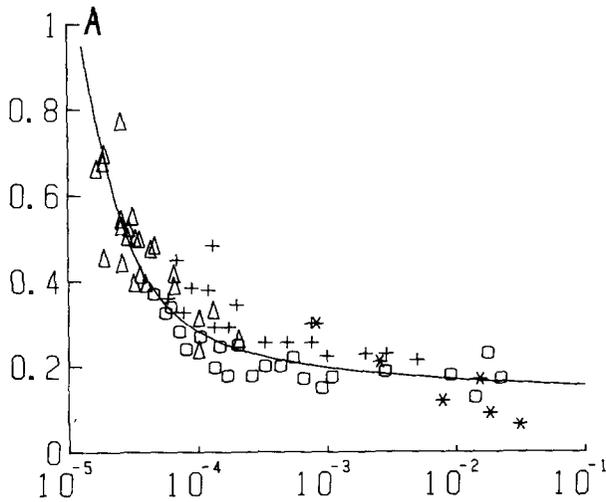


Fig. 2. Scaled supersaturation  $A$  versus reduced temperature  $\epsilon = 1 - T/T_c$ . The solid line corresponds to the prediction eq. (5.1) with  $\lambda = 7.5 \times 10^{-3}$  and  $\gamma = 8 \times 10^{-6}$ , both in agreement with eqs. (5.2). The symbols represent experimental data as follows: ( $\Delta$ ) isobutyric acid + water mixtures [27], (+) perfluoromethylcyclohexane + methylcyclohexane mixtures [20,27], ( $\circ$ ) methanol + cyclohexane mixtures [21], and (\*)  $\text{CO}_2$  [23,27].

that purpose. Finally, we also notice that the availability of more accurate experimental data should finally allow to test the predictions from more elaborated and detailed theory [15,17,37] for the nucleation rates and for the time evolution of the cluster distribution.

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