

Communication: Kinetics of scavenging of small, nucleating clusters: First nucleation theorem and sum rules

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Despite recent advances in monitoring nucleation from a vapor at close-to-molecular resolution, the identity of the critical cluster, forming the bottleneck for the nucleation process, remains elusive. During past twenty years, the first nucleation theorem has been often used to extract the size of the critical cluster from nucleation rate measurements. However, derivations of the first nucleation theorem invoke certain questionable assumptions that may fail, e.g., in the case of atmospheric new particle formation, including absence of sub-critical cluster losses and heterogeneous nucleation on pre-existing nanoparticles. Here we extend the kinetic derivation of the first nucleation theorem to give a general framework to include such processes, yielding sum rules connecting the size dependent particle formation and loss rates to the corresponding loss-free nucleation rate and the apparent critical size from a naïve application of the first nucleation theorem that neglects them.

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First-order phase transformations via nucleation are encountered in a variety of natural and technological processes. The vapor-phase synthesis of nanoparticles with prescribed properties for subsequent assembly into novel nanostructures is one application.¹ In the Earth’s atmosphere, the formation of new particles and their growth into cloud condensation nuclei give rise to feedback processes that modulate cloudiness, precipitation, and climate.^{2,3} The reliable modeling of such processes requires going beyond classical phenomenology towards a molecular-level description. To this end the development of so-called nucleation theorems has been particularly effective,⁴ however, in their current form, these theorems rely on restrictive assumptions that limit their use mainly to interpretation of carefully controlled laboratory measurements. Here we derive extended forms of the first nucleation theorem, and related sum rules, to include loss of molecular clusters from a prescribed nucleation and growth sequence. Loss can be due to scavenging by background aerosol and/or container walls, or removal from the nucleation volume by diffusion or phoretic forces. We also include the possibility that clusters, especially ones of sub-critical size, are lost due to their serving as heterogeneous condensation sites in a way that opens up new off-sequence channels for new particle formation. These results have direct consequences for the interpretation of atmospherically relevant field and laboratory measurements.

As demonstrated by Bowles et al.,⁵ these theorems—with emphasis on the first nucleation theorem,

$$\left(\frac{\partial W_{g^*}}{\partial \mu}\right)_{V,T} = -\Delta g^* + 1 \quad (1)$$

—are a direct consequence of the law of mass action for nucleation from an ideal vapor. W_{g^*} is the work needed to form a cluster of critical size, Δg^* is the excess number of molecules in the nucleus over that present in the same volume of parent phase and μ is the chemical potential of nucleating species present in the parent phase. Under typical laboratory and atmospheric conditions Δg^* can be approximated by the thermodynamic critical size g^* , which is given in the classical nucleation theory by the minimum of the constrained equilibrium distribution of g -mers (clusters containing g monomeric units of condensed phase), $n_g = n_1 e^{-W_g/kT}$, where n_1 is the number concentration of monomers. The connection with nucleation rate measurements is achieved by expressing the nucleation rate in Arrhenius-form, $J = K e^{-W_{g^*}/kT}$, where the prefactor K should take into account the law of mass action. These relations, involving the reversible work of cluster formation, can be described as *thermodynamic nucleation theorems*. Alternatively, *kinetic nucleation theorems* can be derived directly from the master equation approach to nucleation kinetics

using the law of mass action and detailed balance.^{6,7}

A detailed kinetic treatment of homogeneous nucleation was presented by Farkas,⁸ following Szilárd's suggestion that clusters grow or decay by absorbing or evaporating a monomer. This simplification does not usually compromise the accuracy of the theory, as in a typical case of vapor–liquid nucleation the collisions with monomers dominate the total number of collisions encountered by g -mers. Letting f_g denote the actual population of g -mers, the net forward flux between adjacent sizes, say g and $g + 1$, is given as

$$J_g = \beta_g f_1 f_g - \alpha_{g+1} f_{g+1} \quad (2)$$

where β_g is the addition rate of a monomer to a g -mer, and α_g is the evaporation rate of a monomer from a g -mer. The detailed balance condition, $\beta_g n_g f_1 = \alpha_{g+1} n_{g+1}$, where f_1 is the actual monomer concentration, which we hold as constant equal to n_1 , is used to eliminate the evaporation rate:

$$J_g = \beta_g f_1 n_g \left(\frac{f_g}{n_g} - \frac{f_{g+1}}{n_{g+1}} \right) \equiv p_g (u_g - u_{g+1}). \quad (3)$$

The new variables p_g and u_g are introduced for subsequent use. Dividing both sides of Eq. (3) by p_g and summing for $g = 1, \dots, G$, where G is a sufficiently large integer with boundary conditions $u_G = 0$ and $u_1 = 1$, and noticing that J_g is constant (J) for all g when no losses are present, we arrive at the Becker–Döring⁹ result

$$J = \left(\sum_{g=1}^{G-1} \frac{1}{p_g} \right)^{-1}. \quad (4)$$

The remarkable fact of this well-known result is that it depends only on β_g —determined from kinetic theory—and n_g .

For an ideal vapor, incorporating the law of mass action $\mu_g = g\mu$, or $n_g \propto n_1^g$, the following result is obvious:

$$\left[\frac{\partial \ln(n_1 n_g)}{\partial \ln n_1} \right]_T = g + 1. \quad (5)$$

As defined here, β_g does not depend on n_1 [see Eq. (3)] and substitution of this last result into Eq. (4), with $p_g = \beta_g n_1 n_g$, gives the kinetic version of the first nucleation theorem,^{6,7}

$$\left(\frac{\partial \ln J}{\partial \ln n_1} \right)_T = \bar{g} + 1, \quad (6)$$

where the kinetic critical size is defined as an expectation value $\bar{g} = \sum_{g=1}^{G-1} P(g)g$ with respect to

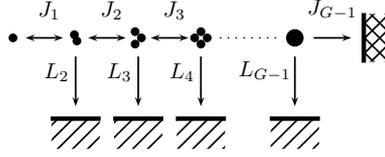


FIG. 1. A schematic description of the Szilárd process with losses.

the normalized $1/p_g$ distribution

$$P(g) = \frac{1}{p_g} \left(\sum_{g=1}^{G-1} \frac{1}{p_g} \right)^{-1}. \quad (7)$$

Although the first nucleation theorem has been tested well in cloud chamber studies of single-component and binary nucleation,¹⁰ recent atmospherically relevant field¹¹ and laboratory^{12–14} studies of sulfuric acid driven nucleation have produced inconsistent results; suggesting, for example, that new particle formation may occur via activated (with barrier) or purely kinetic (without barrier) mechanisms under nearly identical experimental conditions. Several possible reasons for this behavior have been suggested, including problems related to the experimental detection of freshly nucleated clusters¹² and the influence of other trace vapors^{13–15} on the new particle formation rate.¹⁶ Recent simulation studies have underlined the effect of wall and coagulation losses—and alternative growth paths including addition of clusters containing several H_2SO_4 molecules¹⁷—on the interpretation of the first nucleation theorem,^{18,19} an effect that has not been yet fully accounted for when applying the first nucleation theorem to laboratory or atmospheric measurements.³

To extend the kinetic nucleation theorem for cases with losses we apply the discrete model of McGraw and Marlow,²⁰ which is more appropriate at small cluster sizes than corresponding continuum presentations²¹ and allows cluster grow by condensation, evaporation, and size-dependent cluster losses. Net fluxes between g -mer and $(g+1)$ -mers are still given by Eq. (3), but each g -mer is additionally scavenged at rate L_g . The assumption of linear dependence of L_g on f_g , $L_g = q_g f_g$, where q_g is the rate coefficient that can apply to each of the loss mechanisms mentioned above, but not to removal by self-coagulation or production of smaller clusters through fragmentation, allows derivation of a closed-form solutions for the relative sensitivities of rates J_g with respect to n_1 .²²

Prior to consideration of more complex systems, it is worthwhile comparing the thermodynamic and kinetic approaches underlying derivation of Eqs. (1) and (6), respectively. Both approaches are extendable to multicomponent nucleation with the kinetic approach having advantage of working

with a directly measurable quantity, nucleation rate. The essential difference is that thermodynamic nucleation theorems focus on extrema of the free-energy surface whereas the kinetic approaches work with rate coefficients and the (possibly multiple) pathways over which nucleation can occur (cf. Ref. 23). From the kinetic viewpoint, the overall rate sensitivity for a complex system can often be expressed simply as a flux-weighted average of sensitivities over dominant paths.⁷

Using now the model described in Fig. 1, we derive two sum rules for the nucleation rates: First, from Eq. (3) we get

$$\sum_{g=1}^{G-1} \frac{J_g}{p_g} = \sum_{g=1}^{G-1} (u_g - u_{g+1}) = u_1 - u_G = 1. \quad (8)$$

Multiplying both sides by $J = \left(\sum_{g=1}^{G-1} 1/p_g \right)^{-1}$ from Eq. (4) yields the first sum rule:

$$\sum_{g=1}^{G-1} P(g) J_g = \bar{J}_g = J, \quad (9)$$

that is, at steady state the $P(g)$ -averaged transition rate equals the homogeneous nucleation rate without losses. As the fluxes in Fig. 1 are conserved, at each size g ,

$$J_g = J_{g-1} - L_g. \quad (10)$$

Equations (9) and (10) imply that the net forward rates at small sizes are larger than the corresponding loss-free rates, and smaller at large sizes.²⁴ The addition of cluster loss tends to promote the assumption of steady state used in the derivation of Eqs. (9) and (10). This is because cluster losses actually drive the system towards steady state faster than would otherwise happen without the loss.²⁵ Additionally, it has been shown that background aerosol, which increases scavenging loss, widens the stability range of steady-state conditions in dynamical systems involving coupled nucleation and growth.²⁶

Taking the derivatives of both sides of Eq. (9), completing the logarithms of differentials, and applying Eqs. (5)–(7) to evaluate the derivatives of p_g , J , and $P(g)$ we get after some algebra the second sum rule:

$$\sum_{g=1}^{G-1} \left[\left(\frac{\partial \ln J_g}{\partial \ln n_1} \right)_{T, \{q_g\}} - g \right] P(g) J_g = J. \quad (11)$$

This sum rule involving both rates and rate sensitivities can be seen as a generalization of the kinetic first nucleation theorem, as Eq. (11) reduces to Eq. (6) for the loss-free case with $J = J_g$.

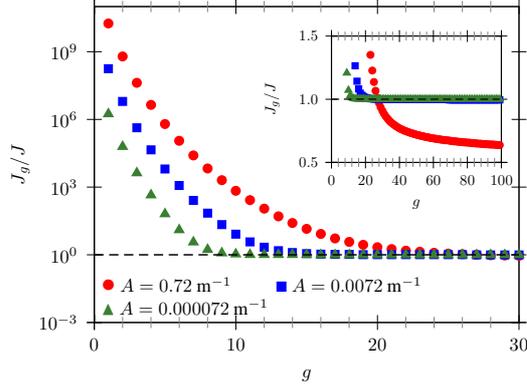


FIG. 2. Normalized formation rates of a g -mer as a function of g and A at $S = 10$. Dashed line denotes $J_g = J$. Inset shows in linear scale how in the case of large losses $J_g \leq J$ for large g .

It should be noted that Eqs. (9) and (11) do not depend on the nature of losses as long as self-coagulation and fragmentation of clusters can be neglected.

To illustrate the new sum rules we perform calculations for a model condensable vapor—a proxy to ethanesulfonic acid that facilitates comparison with previous work^{20,21,27–29}. Table SIII lists properties of the model compound.²² Losses of clusters are taken to be due to Brownian coagulation with background aerosol with specific surface area density A varying from particle-free conditions ($A = 0 \text{ m}^{-1}$) to a high value of A typical of a severe duststorm; an intermediate value $A = 0.072 \text{ m}^{-1}$, which gives a loss rate comparable to the diffusion loss from the nucleation zone in a thermal diffusion cloud chamber,²⁷ was used in earlier work.²⁰ Fuchs surface areas³⁰ are implied throughout. Results are shown in Figs. 2 and 3. Figure 2 shows that the net growth rates can be considerably larger with loss than without for clusters of sub-critical size. This behavior can be rationalized by the fact that the loss channel is more important for clusters that are, in effect, trapped by the thermodynamic barrier and thus have more time to experience loss. Super-critical clusters are able to grow much faster and thus do not get lost that efficiently at any given size. Similar behavior is seen in continuous models for nucleation with loss.^{28,29} As can be seen by comparing Figs. 2 and 3(a), qualitatively similar behavior is observed whether the loss rate is increased by increasing A at fixed S (Fig. 2) or the saturation ratio is decreased at fixed A [Fig. 3(a)]. This similarity is related to the importance of a non-dimensional loss parameter, $L = A/(A_1 f_1)$, where A_1 is the surface area of monomer, introduced independently in slightly different contexts in Refs. 20 and 30. In what follows, only the effect of a varying saturation ratio at fixed background aerosol surface area is considered.

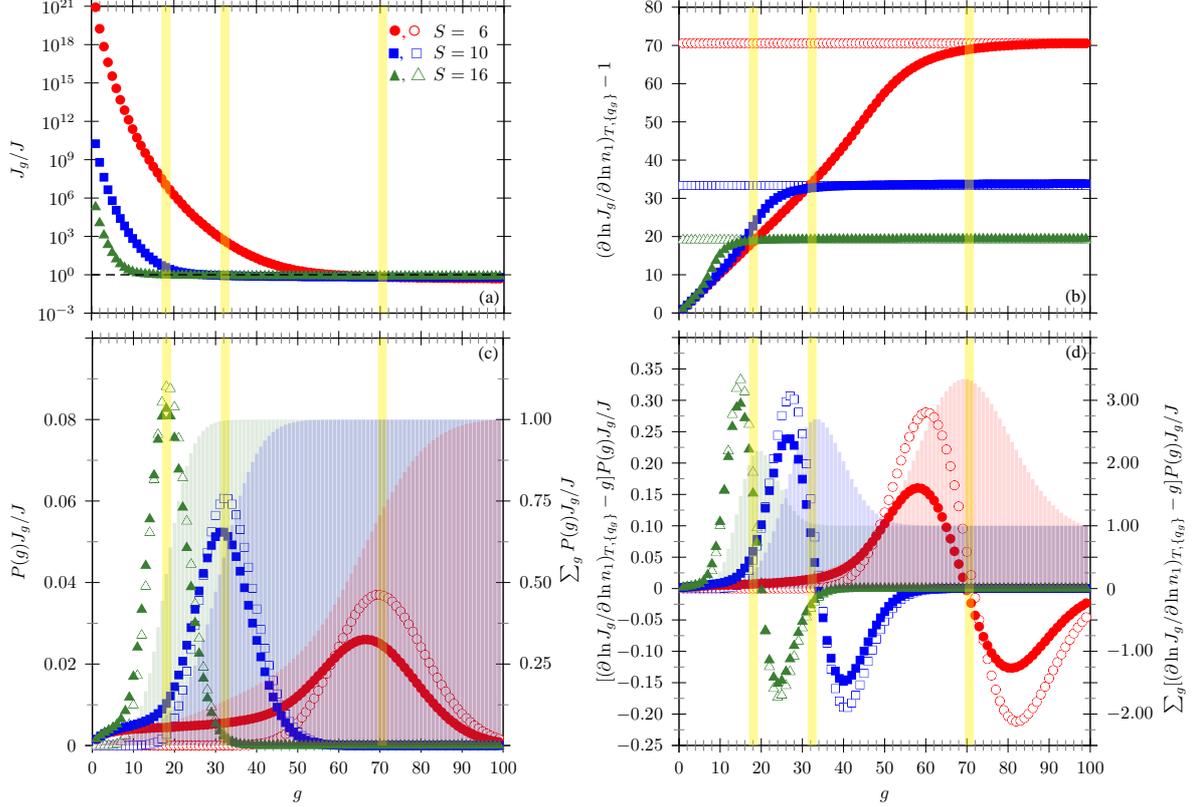


FIG. 3. (a) Normalized formation rates of a g -mer as a function of g at different saturation ratios with a fixed $A = 0.0072 \text{ m}^{-1}$. (b) Apparent results \tilde{g} of naively applied first nucleation theorem as a function of cluster size g , note the linear regime for small g . Open and filled symbols refer to loss-free and lossy cases, respectively. (c, d) Distributions $P(g)J_g/J$ and $\left[(\partial \ln J_g / \partial \ln n_1)_{T, \{q_g\}} - g \right] P(g)J_g/J$ (markers and values at left axes) and their cumulative sums (for lossy cases only; histograms and values at right axes). In all panels, yellow vertical lines indicate the locations of the loss-free critical sizes \bar{g} from Eq. (6).

Figure 3(b) shows size dependent sensitivities of $\ln J_g$ with respect to $\ln n_1$ at constant T [term in parenthesis in Eq. (11)] as a function of g (filled symbols). The result, if naively interpreted, would indicate an apparent critical size (\tilde{g}) that can differ appreciably from the kinetic critical size determined in the loss-free case (\bar{g}), which, in turn, is very close to the actual number of molecules in the critical nucleus, g^* , of homogeneous nucleation theory. For the smallest clusters, the apparent critical size depends linearly from the size at which the rate is determined, i.e. $\tilde{g} \approx g$.²² For clusters larger than \bar{g} , slight overestimates are obtained. Thus, it is possible to obtain estimates \tilde{g} biased into either direction, if the effect of loss is neglected. The quantitative deviation depends in a complicated manner on p_g and q_g [Eq. (S6)].

An interesting feature that is apparent from Figs. 2 and 3 is that the first nucleation theorem seems to approximately hold if applied to the rate $J_{\bar{g}}$ determined at the loss-free kinetic critical size \bar{g} . However, it is premature to say whether this behavior is of general nature, or a consequence of the model system; the effect of losses on the gradient $u_g - u_{g+1}$ is mainly important at sizes smaller than \bar{g} [see, e.g., Fig. S1(b)]. It would also be possible to define a kinetic critical size for the lossy case, \hat{g} , by averaging g with respect to the generalized distribution $P(g)J_g/J$: in such case the second sum rule could be written as²²

$$\hat{g} + 1 = \sum_{g=1}^{G-1} \frac{J_g P(g)}{J} \left(\frac{\partial \ln J_g}{\partial \ln n_1} \right)_{T, \{q_g\}}. \quad (12)$$

As can be interpreted from Fig. 3(c), at least for our model cases \hat{g} is well approximated by \bar{g} . However, there is no unambiguous physical interpretation of \hat{g} , as there is no single rate limiting step corresponding the bottleneck for the observed nucleation rate, though the thermodynamic critical size g^* appears in the theoretical estimates for the transient time scale of nucleation also in such case.^{25,31}

Figures 3(c) and (d) demonstrate the first and second sum rules, respectively. In Panel (c), the distribution $P(g)J_g/J$, generalizing Eq. (7), is given together with its cumulative sum. These cumulative sums are given for the cases with loss only: under loss-free conditions it is clear that the cumulative distributions approach unity as the distribution $P(g)$ is normalized, in the case of Panel (c), and the second sum rule, demonstrated in Panel (d), reduces to Eq. (6). These figures show the effect of applying the first nucleation theorem to the formation rates of clusters of different size, and illustrate the validity of Eqs. (9) and (11) for a realization of the flux network model illustrated in Fig. 1.

In a recent simulation study with qualitatively similar findings, Ehrhart and Curtius¹⁸ used the SAWNUC sulfuric acid–water nucleation³² model to study sensitivity of nucleation rate to changes in vapor phase sulfuric acid concentration as a function of cluster size and scavenging rate. Similar behavior was also seen in simulations of the binary sulfuric acid–ammonia system using another modeling approach (ACDC).¹⁹ However, for an even more nonideal system of sulfuric acid and dimethylamine, a more complicated behavior was observed,¹⁹ which is likely due to kinetic effects and/or breakdown of the Szilárd mechanism.

Yet another loss process that can be approximately cast into linear form is the heterogeneous nucleation on the small sub-critical clusters in the presence of, e.g., an organic vapor.³³ This is essentially a new channel for growth that opens up, thereby effectively removing clusters from the

growth sequence illustrated in Fig. 1. Conversely, collisions of sub-critical clusters with existing ambient nanoparticles, for which we can also consider single large organic molecules,³⁴ can also result in crossing of the heterogeneous nucleation barrier. Earlier applications of the (kinetic) first nucleation theorem on such cases have produced meaningless estimates for \bar{g} .^{17,35} However, when considering some fraction of each loss rate L_g actually resulting in a channel contributing to the observed new particle formation, an extension of the first kinetic nucleation theorem can be derived [Eq. (S21)]. In this case the resulting apparent critical size \tilde{g} is smaller than the corresponding \bar{g} , being either characteristic size for the heterogeneous nucleus, if only one path is available, or a flux-weighted average over possible homo- and heterogeneous pathways.³⁶ This mechanism, together with the observation of the linear estimate for the apparent critical size at small sizes, also casts some doubts on the interpretation of measurements from particle size magnifiers when used to detect critical clusters at low nucleation rate (e.g. Ref. 12). In reality the working fluid may be condensing on clusters of sub-critical size leading to too small an estimate of \bar{g} .

As demonstrated by our results—as well as recent simulation studies^{18,19}—a naïve application of the first nucleation theorem when sub-critical cluster losses are expected can lead to seriously biased estimates on the critical cluster size, and consequently on the mechanism behind the new particle formation, even if the other known deficiencies¹⁹ of the analysis have been appropriately considered. The fundamental concepts behind nucleation theorems, like mass action and detailed balance, still apply but the theorems themselves need correction to yield physically meaningful results. Here we have provided sum rules that can be used to identify and/or correct these biases. Besides applications to analysis of field and laboratory measurements of new particle formation, derived sum rules can also find applications in control of chemical vapor deposition and vapor-phase synthesis of nanomaterials in inhomogeneous medium,²⁹ and also in a broader context to other types of nucleation processes that can be described using the Szilárd model.

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