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Interactive comment on “Ice nucleation terminology” *by* G. Vali et al.

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Technical Note: Ice nucleation terminology. Third draft.

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This Third Draft was developed in response to questions raised by the referees and other contributors. The changes are discussed in some detail in the separate document listing replies to each of the suggestions and comments.

Most of the changes made since the second draft center on the same questions as were deemed controversial in the original version of the terminology. This is not surprising, since those are the very points whose ambiguities in the literature have motivated the attempt to arrive at usage that resolves major misunderstandings. Most significant are the changes made in the discussions deposition nucleation (**3.5.1**), site frequency distributions (**3.4**) and nucleation rate (**3.8.2** and **3.9**).

As in the previous draft, naming of entries is followed by a brief definition printed in italics. Additional details follow in the paragraph(s) that follow in normal font. Cross-references to other entries are given in bold-face numbers.

1 General

The meanings of scientific terms evolve with time. A concise summary, at any time, of all the various interpretations attached to given terms by a broad spectrum of researchers cannot be hoped for. A common denominator can perhaps be approximated, with the understanding that future usage will diverge from that to various degrees. However, it can be hoped that the stated definitions will serve, at a minimum, to allow for more concise identification of possible deviations from them.

This terminology is an aggregate of the views of a fairly large number of scientists. While most terms are broadly understood the same way, full agreement on every term was not achievable. It remains to be seen to what extent divergences appear in forthcoming publications. Beyond that, the most important test of the proposed terminology will be how well it can be used to present new discoveries. Will new concepts require currently used terms to be discarded and new ones introduced? No doubt that will happen – sooner or later.

1.1 PHASES OF WATER

Within the range of normal atmospheric conditions water can exist in three different phases, namely vapor, liquid and ice.

The thermodynamically stable phase is defined by the existing water vapor pressure and temperature, as usually depicted in a phase diagram. A metastable state arises when conditions change from those corresponding to one stable phase to those corresponding to another. The first formation of the new stable phase from the metastable state is a nucleation event.

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1.2 ICE NUCLEATION

The first appearance of a thermodynamically stable ice phase.

The ice phase can be initiated in environments of supersaturated vapor (deposition nucleation) or supercooled liquid water (freezing nucleation). In this context, supersaturated vapor or supercooled water refers to the existence of these conditions on scales considerably larger than the ice embryo (**1.3**). Nucleation means the first development of the bulk phase, i.e. an embryo larger than the critical size (**1.3.2**), within these environments.

1.3 EMBRYO or GERM

Thermodynamically unstable aggregate of water molecules in a structure that favors further development into stable ice.

In the metastable states, clusters of the stable phase form. Molecular fluctuations lead to decay or growth. For small embryos, decay is more likely than growth. The probability of growth increases as the embryo approaches critical size.

1.3.1 Embryo size:

The size of an ice embryo expressed either as the number of water molecules making up the ice-like structure, or the linear dimension of the embryo, or the radius of curvature of its surface toward the metastable phase.

1.3.2 Critical embryo size:

The size at which the probability of growth of an embryo becomes equal to the probability of decay.

The critical size is the point of metastable equilibrium. With minimal additional increase in size, growth becomes energetically more favorable and nucleation can take place.

2 Homogeneous ice nucleation

2.1 HOMOGENEOUS ICE NUCLEATION

Ice nucleation without any foreign substance aiding the process.

2.1.1 Homogeneous deposition nucleation and homogeneous ice nucleation from water vapor

Ice nucleation from supersaturated vapor, without any foreign substance aiding the process.

Deposition nucleation is the formation of ice directly from water vapor. Because of the very high supersaturation required for homogeneous deposition nucleation of ice it is not observed in the atmosphere or in other natural systems. However, there is evidence for homogeneous ice nucleation from water vapor via processes that involve the intermediate step of homogeneous condensation of liquid, or an amorphous phase, at supersaturations below that required for deposition (Jensen and Murray, 2010).

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2.1.2 Homogeneous freezing nucleation

Ice nucleation within a body of supercooled liquid without any foreign substance aiding the process.

2.2 Homogeneous nucleation rate coefficient

The probability, or observed frequency, of ice nucleation events in unit volume of supercooled liquid or supersaturated vapor within a unit of time.

Classical nucleation theory (CNT) relates the nucleation rate coefficient to the properties of the liquid and the net rate at which molecules are added to the ice embryos. Empirically, the nucleation rate is determined from the frequency of events as a function of supersaturation or temperature: $J_v = \frac{1}{V} \cdot \frac{1}{N} \cdot \frac{\mathrm{d}N}{\mathrm{d}t}$, using N to denote the number of nucleation events and V to denote the total volume observed. Here the subscript v is added to the usually employed symbol J in order to focus on the fact that the homogeneous nucleation rate coefficient refers to unit volume of vapor or liquid and to distinguish it from similar expressions for heterogeneous nucleation. It is recommended to use the symbols $J_v(S)$ and $J_v(T)$. The quantity J_v has dimension of $(\mathrm{L}^{-3}\mathrm{t}^{-1})$ (cgs units of $(\mathrm{cm}^{-3}\mathrm{sec}^{-1})$).

Freezing rate (**3.7**) has not entered the literature for homogeneous nucleation but it can be applied to represent experimental results. For homogeneous nucleation, the freezing rate is directly proportional to the nucleation rate coefficient and the volume of the sample units: $R = J_v \cdot V = \frac{1}{N} \cdot \frac{\mathrm{d}N}{\mathrm{d}t}$.

In practice, it is not always possible to ensure that all sample units are free of INPs so that the apparent freezing rate observed may lead to an incorrect value for J_v, or the freezing rate has to be seen as the sum of various contributions (e.g. Koop et al. 1997).

3 Heterogeneous ice nucleation

3.1 HETEROGENEOUS ICE NUCLEATION

Ice nucleation aided by the presence of a foreign substance so that nucleation takes place at lesser supersaturation or supercooling than is required for homogeneous ice nucleation.

3.2 INP, INM, INE, etc.

Ice nucleating particle (INP), molecule (INM), entity (INE), material, matter, substance, object, item, unit, or else, that is assumed to be the agent responsible for observed heterogeneous nucleation.

Because of the variety of materials and forms that can be responsible for heterogeneous ice nucleation, it is impractical to have a single designation that covers all possibilities and is sufficiently informative. It is preferred that authors refer to what is the nucleating agent in each particular case in the manner most appropriate for the system studied. The form of the designation, IN plus a third letter, may be helpful enough for effective communication. The term "nucleator" is also used as a general reference to the object whose presence is responsible for observed ice nucleation.

Reference to an INP (or equivalent) does not, in general, specify the composition of the particle, but refers to the unit that carries the nucleating substrate. A number of different terms have been used in the literature for this. For decades, the terms “ice nucleus” or “ice nuclei” were used almost exclusively with reference to atmospheric aerosol that could initiate ice, that is individual particles, each of which resulted in the formation of one ice crystal. While it was recognized that only a specific location on the particle surface is actually where ice begins to form, the entire particle was referred to as the ice nucleus. This led to confusion. The concept of a “site” appeared in the literature to narrow the identification of an ice nucleus. With the entry of ice nucleation studies to systems other than clouds and also involving biological substances (bacteria, fungi, etc.) usage became more confusing because focus expanded to nucleation by entities other than aerosol particles. In all, the term “ice nucleus” has become both overused and vague. For atmospheric applications, or in more general when dealing with many separate entities, it is more appropriate to use ice nucleating particle, INP, or the other forms listed in the definition, to refer to individual units – INPs, or other forms – to refer to a collection of them. Since ice nucleation is more complicated than condensation nucleation, due to the different modes it can follow, using “ice nuclei” in the general sense similar to “condensation nuclei” is overly ambiguous and can be misleading.

3.3 SITE

Preferred location for ice nucleation on an INP, or equivalent.

Direct experimental evidence for deposition nucleation (e.g. Mason 1957; Anderson and Hallett 1976) points to the role of specific locations on the surfaces which promote nucleation with greater effectiveness than other locations. Similar evidence is available with freezing nucleation in terms of repeated freezing of samples at nearly the same temperatures but that evidence is less direct than for deposition where the locations can be visually identified. Sites are thought to arise due to non-uniform surface properties of INPs that result in different binding energies to water molecules and incipient ice structures. Sites are considered important for both deposition and freezing nucleation. Observed nucleation on, or within, a sample is taken as being due to the most effective site found in it. Sites of various effectiveness are assumed to occur on the surfaces of most materials. In principle, sites have identifiable properties, as distinct from assumed spontaneous formation of embryos at some unpredictable location on a surface.

3.4 SITE FREQUENCY DISTRIBUTION

The number of sites causing nucleation per unit surface area of the INP, or equivalent as functions of temperature or supersaturation. Quantitative measure of the abundance of sites of different ice nucleating effectiveness.

A number of different methods have been used in the literature to quantitate the frequency of occurrence of different temperatures or supersaturations at which ice nucleation has been observed and/or modeled. Most of these descriptions are direct representations of measurements. Time is left as an implicit factor specific to each experiment, i.e. the singular approximation (**3.8**) is applied.

The distribution of sites, or integrated site density (Connolly et al. 2009; Niemand et al. 2012) expresses the number of sites per unit surface area of INPs that cause nucleation by some value of temperature or supersaturation. Hoose and Möhler (2012) used INAS (Ice Nucleation Active Site) density to refer to this quantity. The quantity is designated as $n_s(T)$, or $n_s(S)$, with dimensions L^{-2} (cgs units of (cm^{-2})).

Interpreting the results of freezing experiments with subdivided sample units (e.g. particles randomly distributed into liquid volumes), the number concentration of sites are derived as the differential or cumulative nucleus spectra (Vali 1971): $k(T) = \frac{1}{V\cdot(N_0-N_F(T))}\cdot\frac{\mathrm{d}N_F(T)}{\mathrm{d}T}$ and $K(T) = -\frac{1}{V}\cdot ln(1-\frac{N_F(T)}{N_0})$. Site density with reference to surface area and the cumulative nucleus spectrum, for freezing, are related as $K(T) = n_s(T)\cdot A$.

The foregoing descriptions assume that that the nucleation rate is equal to zero at temperatures higher (supersaturations lower) than the characteristic temperature (supersaturation) of the site and equal to infinity beyond that. Thus, these definitions rely on the singular description (**3.8.1**) with T_c for each site replaced by the observed freezing temperature T.

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Marcolli et al (2007) used contact angle as a surrogate to express site effectiveness. That idea was further developed by Welti et al. (2012) in the α-pdf model. Niedermeier et al. (2011, 2014) constructed the Soccer Ball Model to describe the distribution of sites of different effectiveness. Hartmann et al. (2013) modeled the distribution of sites among sample units. In these cases, the site density is represented using distributions of parameters in the CNT formulations of the nucleation rate coefficient and thus there is a link to the stochastic description (**3.9**), but the characterization of sites of different effectiveness is an important element of these treatments.

Site frequency distributions should always include some indication of the time scale of the experiment which is being interpreted. This allows various experiments to be compared more effectively.

3.5 MODES OF HETEROGENEOUS ICE NUCLEATION

Distinctions in the mode of nucleation are made on the basis of the process envisaged to lead to nucleation.

Definitions of nucleation modes were given by Vali (1985) with a focus on atmospheric processes. Several of the definitions given below broaden and alter those definitions .

3.5.1 Deposition nucleation

Ice nucleation from supersaturated vapor on an INP or equivalent without prior formation of liquid.

It is difficult to ascertain whether or not ice nucleates from (supersaturated) vapor without any liquid forming. Similarly to the homogeneous case, deposition nucleation may have a transitory stage in which liquid is present but does not develop to a macroscopic, observable, quantity. It has also been theorized that condensation in voids and cavities followed by freezing can account for many observations that appear to be deposition (Marcolli, 2014), but this process is better viewed as freezing followed by depositional growth. Observations of what is believed to be deposition nucleation need to critically examine the ability to discern details of the process.

3.5.2 Freezing nucleation

Ice nucleation within a body of supercooled liquid ascribed to the presence of an INP, or equivalent.

Further specifications of modes are:

> **Immersion-freezing** refers to ice nucleation initiated by an INP, or equivalent, located within the body of liquid.
>
> **Contact-freezing** is initiated by an INP, or equivalent, at the air-water interface as the INP comes into contact with the liquid, or forms at an air-liquid-particle triple interface.
>
> This process is defined as separate from immersion freezing because of empirical evidence that some INPs are more effective in this mode than when immersed in the liquid (Shaw, Durant and Mi, 2005). There is as yet no definite clarification for how to distinguish this mode from immersion freezing. Some laboratory evidence points to a difference depending on whether the particle is inside the liquid or outside it; these are described as inside-out versus outside-in nucleation. In the atmosphere, preactivated particles may cause freezing when coming into contact with supercooled liquid droplets.

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Condensation-freezing is defined as taking place when freezing is initiated concurrently with the initial formation of liquid on a cloud condensation nucleus (CCN) at temperatures below the melting point of ice. This was envisaged as a possible sequence in clouds but evidence for its existence is minimal. Whether condensation-freezing on a microscopic scale, if it occurs, is truly different from deposition nucleation, or distinct from immersion-freezing, is not fully established. Hence, reference to this mode of nucleation requires added circumspection.

Other modes of freezing nucleation reported in the literature are electro-freezing, evaporation-freezing, mechanical shock freezing and collision-freezing. Evidence available at this time does not permit general definitions to be established for these processes.

3.6 FRACTION FROZEN

The ratio of the cumulative number of sample units frozen at T *to the original number* N_0*:* $f = \frac{N_F}{N_0}$ *with* N_F *given as either a function of time or of temperature.*

Frozen fraction represents the results of experiments with sample units drawn from the same original volume. It can be used when the sample units are gradually cooled or when held at a fixed temperature. Similar quantities can be readily defined for nucleation modes other than freezing.

3.7 FREEZING RATE

Freezing rate expresses the results obtained from an experiment in which the freezing of a number of sample units is observed.

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Freezing rate is expressed as a function of the number of sample units frozen at time t: $R = \frac{1}{N_0 - N_F(t)} \cdot \frac{\mathrm{d}N_F(t)}{\mathrm{d}t}$. The freezing rate for given T has units of inverse time, e.g. (sec^{-1}). The freezing rate function is a direct description of empirical observations with distributed samples and can be used both for experiments in which the samples are steadily cooled or others in which the temperature is held constant. Freezing rate is related to the time derivative of the frozen fraction (**3.6**): $R = \frac{1}{1-f(t)} \cdot \frac{\mathrm{d}f(t)}{\mathrm{d}t}$. Freezing rate for any particular sample is dependent on the volumes of the sample units and on the INP contents (site density or nucleus spectrum) of the liquid. It is also influenced by dissolved substances. For polydisperse sample volumes the freezing rate needs to be specified by volume range.

For homogeneous nucleation, the freezing rate is usually called nucleation rate. In the stochastic description of heterogeneous nucleation the terms freezing rate and nucleation rate are interchangeable, but using "freezing rate" makes it clearer that one refers to observed frequencies of events and not the more abstract rate coefficient or site nucleation rate.

Some duplication exists in the use of the term freezing rate between discussing nucleation of sample units, or talking about growth of ice. The distinction has to be clarified explicitly if not evident from the context.

3.8 SITE-SPECIFIC DESCRIPTIONS/MODELS

3.8.1 Singular description (time independent)

Description/model of observed nucleation events for a population of sample units containing INPs (or equivalents) and assuming that the preferred sites have a spectrum of different nucleating abilities. Also referred to as the deterministic description of ice nucleation. No time-dependence is taken into account.

This description is based on evidence that points to sites having well-defined, albeit not perfectly stable, potentials for promoting nucleation. Each site is then characterized by the temperature, or supersaturation, at which it is observed to nucleate ice for a given mode. For freezing, a characteristic temperature T_c is used to specify the effectiveness of the site or INP. The time history of the sample is not taken into account. In that sense, the singular description is often referred to as deterministic. The singular description is expressed quantitatively by site density, or by nucleus spectra (**3.4**).

3.8.2 Site nucleation rate

Site nucleation rate expresses the probability per unit time that nucleation takes place on a given site of an INP (or other) involved.

Site nucleation rate, J_{site}, is a function of temperature (for freezing) and other factors reflecting the nature of the nucleating site. The term is adopted from the description of homogeneous nucleation where nucleation rate refers to an observed volume or ensemble of drops. Applied to a site, the term has a narrower focus but the same meaning, i.e. probability of nucleation within unit time interval.

In cases where data fit the stochastic model (**3.9.1**), i.e. all INP surface area (or mass) appears to be entirely equivalent in its ability to nucleate ice, the nucleation rate coefficient $J_s(T)$ replaces the site nucleation frequency J_{site} as the relevant quantity.

Site nucleation rate has dimension of inverse time (cgs units of (sec^{-1})).

3.8.3 Time-dependent site-specific descriptions/models

*Descriptions that encompass definitions of site density distributions (**3.4**) and account for the time-dependence of freezing nucleation.*

Each site is assumed to be defined by its characteristic temperature and by the site nucleation rate (**3.8.2**) associated with it (Vali and Stansbury 1966, VS66; Vali 2014). The abundance of sites of different characteristic temperatures is specified by some form of the site frequency distribution (**3.4**) such as the nucleus spectra. The site nucleation rate is defined in **3.8.2**.

The singular description (**3.8.1**) is an approximate solution in which the site nucleation rate is assumed to be a step function from 0 to ∞ at T_c.

The site nucleation rate function may depend on the value of T_c and is thus designated as $J_{\mathsf{site},T_c}(T)$. The characteristic temperature T_c for each site (**3.4**) is defined by the temperature at which the nucleation rate J_site has a specific value C: $J_{\mathsf{site},T_c}(T_c) = C$. Empirical evidence points to J_site being a steep function of temperature (similarly to homogeneous nucleation). Empirical determination of J_site has only been approached indirectly (e.g. Vali 2008, Wright and Petters 2013) since multiple examples of sites with the same T_c are not identifiable a priori. Theoretical guidance is sparse due to the lack of detail about the nature of ice nucleating sites.

3.9 STOCHASTIC DESCRIPTION/MODEL

Description/model of the frequency of nucleation events in a population of sites, or of sample units, which all have equal probability for nucleation to take place in them within a period of time.

3.9.1 Stochastic description

This description assumes that there are large numbers of sites of equal effectiveness on the surfaces of INPs and interprets observations in terms of a nucleation rate coefficient, i.e. the freezing rate per unit surface area or per unit mass. Thus, this description employs $J_s(T)$ with units of (cm^{-2}sec^{-1}), and $J_m(T)$ with units of (g^{-1}sec^{-1}). Empirical values of $J_s(T)$ are obtained from $R(T)$ via $J_s(T) = \frac{R(T)}{A}$. If the number of sites of the same effectiveness per unit surface area is $n_S(T)$ then $J_s(T) = n_s(T) \cdot J_{\text{site}}(T)$, where $J_{\text{site}}(T)$ is the site nucleation rate (probability of nucleation) for given parameters. From these values of $J_s(T)$, the site density n_s can be derived if $J(T)$ is taken from theory (e.g. CNT) or is independently determined.

As mentioned in **3.8.2**, the heterogeneous nucleation rate coefficient can be applied to cases where all INP surface area appears to nucleate ice with equivalent efficiency. In other cases the relevant quantity is the site nucleation rate J_{site}.

3.9.2 Stochastic description for multi-component systems

The foregoing description (**3.9.1**) is valid for the case when all sites are considered identical. This case is termed the single component model in Broadley et al. (2012) and Herbert et al. (2014). The case when sites of different effectiveness are considered is a multi-component stochastic model (MCSM). The essence of this approach is to allow for different site characteristics by varying critical parameters (usually the contact angle) in the CNT formulation of the nucleation rate coefficient and assuming some frequency distribution for that parameter. Variants of this approach have been presented by Marcolli et al (2007), Niedermeier et al. (2011 and 2014), Welti et al. (2012) and Savre and Ekman (2015) among others. In these formulations, sites are characterized by their frequency, say $n_{s,i}$, and a corresponding function $J_{s,i}$, using the second subscript, i, to indicate assignment to a specific value of the contact angle (or other parameter). In effect this is very similar to the time-dependent site-specific description (**3.8.3**) with a theory-based nucleation rate coefficient instead of the J_{site} and an assumed, or fitted, frequency distribution instead of an empirical one (**3.4**).

3.9.3 Comparison of stochastic and site-specific descriptions

While the CNT-derived nucleation rate coefficient in the stochastic description (**3.9.1**) and the site nucleation rate in the site-specific description (**3.8.3**) arise from the same need to describe the probability of nucleation, different underlying assumptions are incorporated in the two cases. To apply the stochastic description to a given data set, the function J_s is taken to extend over the range of observed freezing temperatures in the sample. For the site-specific description the function J_{site} is assumed to rise very rapidly over a narrow range of temperatures and the spread in observed freezing temperatures is ascribed to differences in the effectiveness of sites. The two descriptions lead to divergent predictions about the time-dependence of nucleation (Vali, 2014; Herbert et al., 2014). That time-dependence can not be determined from a single continuously cooled experiment with a sample but need more elaborate tests.

The multi-component (and similar) descriptions (MCSM; **3.9.2**) present a view similar to the time-dependent site-specific description (VS66; **3.8.3**). The degree of similarity is determined by the range of temperatures over which the nucleation rate coefficients $J_{s,i}(T)$ for species i assume empirically relevant values in the MCSMs in comparison with the range of < 1C for the site nucleation rate $J_{\text{site}}(T)$ in VS66.

3.10 AQUEOUS SOLUTIONS

Dissolved substances in water change the equilibrium phase boundaries and influence ice nucleation.

In many atmospheric and other systems dissolved materials are present in water and alter the conditions for ice nucleation. The magnitudes of the induced changes are determined by the concentration and type of the solute(s) as expressed by water activity and additional factors both for homogeneous nucleation (**2.1**) and for immersion-freezing nucleation (**3.5.2**) by different types of INPs (**3.2**) (Koop et al. 2000; Knopf and Alpert 2013; Wex et al. 2014).

3.11 PRE-ACTIVATION AND MEMORY EFFECTS

Mode or efficacy of observed nucleation influenced or altered by the pervious temperature/humidity history of the INP, or equivalent.

Experiments have shown that prior exposure to low temperature or high humidity, or a combination of both leads to enhanced activity in comparison with what the INP, or equivalent, would exhibit otherwise. Such effects may introduce ambiguity in diagnoses of the mode of activity (**3.5**) in laboratory experiments or in atmospheric or other natural systems. Certain INP characteristics (composition, configuration, surface properties) may favor such effects. Explanations of the effects focus on the potential for cracks, pores and other features on surfaces to hold ice even under conditions where bulk ice would be unstable.

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Interactive Discussion

Discussion Paper

Table 1. Nomenclature (with CGS units indicated).

A	total surface area of INPs in a sample unit [cm^2]
f	fraction of samples frozen (**4.6**)
$J(T)$	nucleation rate (probability of freezing) per unit time as a function of temperature [s^{-1}]
$J_s(T)$	nucleation rate per unit time and per unit surface area of INPs [cm^{-2} s^{-1}]
$J_m(T)$	nucleation rate per unit time and per unit mass of INPs [g^{-1} s^{-1}]
$J_v(T)$	homogeneous nucleation rate per unit time and per unit sample volume (**3.2**) [cm^{-3} s^{-1}]
$J_{site}(T)$	nucleation rate on a specific site (**4.11**) [s^{-1}]
$k(T)$	differential nucleus spectrum; number of sites active within a 1C interval at T per unit sample volume [cm^{-3} C^{-1}]
$K(T)$	cumulative specgtrum, or integrated volume density of active sites : number of sites active above T per unit sample volume [cm^{-3}]
$n_s(T)$	surface density of sites (number per unit surface area of INPs) active above T [cm^{-2}]
N	number of samples units of same type and state at any instant during an experiment
N_F	number of samples frozen
N_0	total number of samples in an experiment
R	freezing rate per unit time [s^{-1}]
S	supersaturation
T	temperature [C]
T_c	characteristic temperature for a nucleating site [C]
V	volume of sample unit [cm^3]
CNT	classical nucleation theory