The Scaling of Nucleation Rates

BARBARA N. HALE

The homogeneous nucleation rate, $J$, for $T \ll T_c$, can be cast into a "corresponding states" form by exploiting scaled expressions for the vapor pressure and for the surface tension, $\sigma$. In the vapor-to-liquid case with $\sigma = \sigma_0[T_c - T]$, the classical cluster energy of formation $\phi/kT = (16\pi^3/3)\Omega([T_c/T - 1]/(\ln S)^2 = [x_0/x]^2$, where $\Omega = \sigma_0/[k\bar{n}^{7/2}]$ and $\bar{n}$ is liquid number density. The $\Omega \approx 2$ for normal liquids. (A similar approach can be applied to homogeneous liquid to solid nucleation and to heterogeneous nucleation formalisms using appropriate modifications of $\sigma$ and $\Omega$.) The above $[x_0/x]^2$ is sufficiently tenuous that in some cases, one can use it to extract approximate critical temperatures from experimental data. In this work, we point out that expansion cloud chamber data (for nonane, toluene, and water) are in excellent agreement with $\ln J \approx \text{const} - [x_0/x]^2$ [centimeter-gram-second (cgs) units], and that the constant term is well approximated by $\ln (\Gamma_c)$, where $\Gamma_c$ is the inverse thermal wavelength cubed per second at $T = T_c$. The $\ln (\Gamma_c)$ is $\approx 60$ in cgs units (74 in SI units) for most materials. A physical basis for the latter form, which includes the behavior at small $n$, the discrete integer behavior of $n$, and a configurational entropy term, $\tau \ln (n)$, is presented.

I. INTRODUCTION

SCALED models for nucleation allow the plotting and analysis of experimental data for a spectrum of materials simultaneously. In some applications, the scaled models can provide quick estimates of critical supersaturation ratios, $S_{cr}$, or supercoolings required for onset of nucleation; the latter estimates are particularly useful when numerical substance data are unavailable. But the models offer something more far-reaching: they allow one to isolate the universal temperature dependences and to focus on the substance parameters which dominate the nucleation process.

As used here, the term "scaled nucleation model" refers to a formalism in which the nucleation rate, $J$, (and all expressions derived from $J$) is expressed in terms of $T/T_c$, $P/P_c$, and $\bar{n}/\bar{n}_c$.[1] The latter are the reduced temperature, pressure, and number density, respectively, and the subscript $c$ denotes critical point quantities. From the critical point quantities, one can form factors such as $P_c/\bar{n}_c kT_c \approx 3/8$ having numerical values nearly substance independent. Finally, scaled functional forms (generally available in the literature) for equilibrium vapor pressure, surface tension, and number density are substituted into the formalism.[1,2,7] The final result is an expression for $J$ which explicitly displays the "corresponding states" properties of nucleating substances.

The scaling of $J$ is not a new idea. Near the critical point (at $T \approx T_c$), such scaling of the nucleation rate has been considered extensively.[8-14] In particular, Binder[8] presented a scaled form for the (slightly modified) classical nucleation rate valid near $T_c$. The major difference between Binder’s form and the scaled models described here is the applicable temperature range: the expressions presented here for $J$ and $S$ are not intended for use near $T_c$ but, rather, for $T \ll T_c$—where most of the data exists.

We point out that the temperature dependence used in the present models, $[T_c/T - 1]$, is different from the $\varepsilon = \pm[1 - T/T_c]$ of critical point formalisms. Both forms are equivalent (for all practical purposes) in the standard analysis near $T_c$. However, for $T \ll T_c$, there appears to be no advantage to a series expansion in $\varepsilon$, and the $[T_c/T - 1]$ form emerges naturally from the placement of $T$ in the exponential denominator of the Boltzmann factor. It is interesting that use of $[T_c/T - 1]$, rather than $\varepsilon$, in some critical point formalisms can dramatically extend the range of applicability.[15] This result is not widely used (although recognized) by those working with critical point phenomena.

Some time ago, Wu et al.[16] plotted $\ln S_{cr}$ vs $T^{-3/2}$ for experimental SF$_6$ vapor-to-liquid homogeneous nucleation data far below the critical point. However, the quest for a general temperature dependence of $\ln S_{cr}$ for $T \ll T_c$ was apparently not further pursued until McGraw[17] considered a corresponding states formalism and demonstrated that the data for $\ln S_{cr}$ fell into identifiable groups of substances when plotted vs the reduced temperature, $T/T_c$. Motivated by McGraw’s interesting results, we tried a scaled form for the liquid surface tension, $\sigma = \sigma_0[T_c - 1]$, and derived a universal temperature dependence for the critical supersaturation (corresponding to onset of nucleation from the vapor):

$$\ln S_{cr} \approx 0.53(\Omega[T_c/T - 1])^{1/2}$$

The $\Omega(=\sigma_0/[k\bar{n}^{7/2}])$, with $k$ representing the Boltzmann constant and $\bar{n}$ the bulk liquid number density) is a nearly universal constant with a physical interpretation of excess surface entropy/k per molecule (or atom) in the embryonic cluster. Figure 1 of Reference 1 shows experimental homogeneous vapor-to-liquid data for $\ln S_{cr}/\Omega^{1/2}$ for a number of substances[18-20] using bulk values for $\Omega$. The data for $\ln S_{cr}$ agree with Eq. [1] rather well, in spite of the scatter in data and the problems associated with extrapolations of vapor pressures. The bulk
liquid value for $\Omega$ is essentially the Eötvös constant.\textsuperscript{[25,26,27]}* Using the scaling law in Eq. [1], it was

*In 1886, Eötvös found that the quantity $\sigma(M/d)^{2/3}$, where $M$ is the molecular weight and $d$ is the density, was a linear function of temperature. In cgs units, the proportionality constant for the ideal liquid is $\approx 2.12$. For associated liquids, the constant is reduced. The Eötvös constant defined in this way is actually $\Omega$ times $k(N/\rho)^{2/3}$, where $N$ is Avogadro's number. This slight correction factor is $\approx 0.984$.

also pointed out that the data thus plotted fell roughly into two groups, with $\Omega = 2$ for ordinary liquids and $\Omega = 1.5$ for associated liquids.

A quantity used in the present models, as well as in the formulation near $T_c$, is the scaled supersaturation,\textsuperscript{[9]} $x = \ln S/A^{1/2}$, where $A$ is the coefficient of the surface term in the energy of formation, $\Delta_n^{2/3}$. With adoption of the scaled surface tension, one finds that $A = (36\pi)^{1/2} \Omega [T_c/T - 1]$. Binder and Stauffer\textsuperscript{[9]} use $A = \kappa$, where $\kappa$ is a constant proportional to the surface tension, and $x = \ln S/\kappa^{1/2} \delta$, where $\beta$ and $\delta$ are the standard critical point exponents.\textsuperscript{[9]} Near the critical point, $[T_c/T - 1] = \epsilon$ and $\beta \delta = 1.54^{[9]}$—close to the classical three-dimensional fluid value of $\beta \delta = 3/2$.

Starting with the simple form $g(n) = \Delta_n^{2/3} - \eta \ln S$ for the energy of formation (divided by $kT$) of the $n$ cluster, one can easily derive the critical cluster size, $n^c = [2A/(3 \ln S)]^{1/2}$ and $g(n^c) = (1/2) \ln S = [x_0/x]^2$, where $x_0 = 2/[3^{3/2}]$. Thus, the standard classical steady-state nucleation rate, $J$, is

$$J = J_0 \exp \left[-(x_0/x)^2\right] \quad \text{(2)}$$

where $J_0$ contains the "kinetics" of the nucleation process. Using the scaled form for $\sigma$, one finds the following "scaled energy of formation:"

$$(x_0/x)^2 = (16\pi/3)\Omega [T_c/T - 1]^3/(\ln S)^2 \quad \text{(3)}$$

As was pointed out by Binder and Stauffer,\textsuperscript{[9]} in the case that the kinetic prefactor, $J_0$, has only slight $T$ and $S$ dependence, $[x_0/x]^2 = \ln [J_0/J] = \text{constant}$ for fixed $J$. This leads directly to the approximate scaling law given in Eq. [1] for $T \ll T_c$.

In Reference 1, we show that in the classical Becker-Doring theory,\textsuperscript{[28]} the kinetic prefactor, $J_0$, for the steady-state homogeneous nucleation rate\textsuperscript{[29,30]} (including the so-called Zeldovich factor\textsuperscript{31}) can be written as follows:\textsuperscript{[11]}

$$J_0 = J[I(P_0/P_v)^{2/3}S] \quad \text{(4)}$$

where $I = 2[\bar{n}_{c}\bar{n}_c^{2/3}/(\Omega [T_c/T - 1]^{1/2} [T_c/T])^{3/2}]$, and $J_c = P_c/[h_0 \tau^c \Gamma_c]^{1/2} \cdot P_c/[kT \Gamma_c]$. The $\bar{n}_c$, $P$, $h$, $k$, $S$, and $\Gamma$ are the number density, pressure, Planck constant, Boltzmann constant, supersaturation ratio, and inverse thermal wavelength cubed ($2\pi mkT/h^2$), respectively. The $\ln J_c \approx 2 \pm 3$ (in cgs units) for most substances. If one considers a simple scaled form for the vapor pressure,\textsuperscript{*} $\ln [P_c/P_v] = W_0 [T_c/T - 1]$, it is clear

\textsuperscript{*}For most substances, $\nu = 1$ and $W_0 = L/kT_c = 7 \pm 2$, where $L$ is the latent heat of vaporization near the boiling point. For water, the vapor pressure data is well fitted by $\ln [P_c/P_v] = 7.49[T_c/T - 1]^{1.074}$ from 273 to 300 K.

that $J_0$ has a strong $T$ dependence, not easily argued away. The question is, then, why does the scaling law in Eq. [1] work so well?

It has been known for some time that the standard
classical nucleation rate (using literature surface tension formulae) has some serious problems. In a "worst case" scenario, the classical nucleation rate can deviate by as much as seven orders of magnitude (for a single set of data) over a temperature range of 50 K. Part of this problem is attributable to the extrapolation (beyond experimental verification) of equilibrium vapor pressure and surface tension formulae. It is well known, for example, that a 15 pct deviation in surface tension produces an error of \( \approx 10^{17} \) in the nucleation rate, \( J \). Revisions and improvements on the classical model have been proposed— including the addition of translational and rotational free energy of the center of mass of the cluster by Lothe and Pound, "replacement" factors, and computer calculations of free energies for small clusters. Efforts to develop a successful model have been thwarted by the lack of extensive experimental data over a wide range of \( T \) and \( S \). With the expansion chamber data of Anderson and co-workers and of Schmitt and co-workers, however, one can begin to place some stringent tests on the temperature dependence of the theory.

The success of Eq. [1] offers a message: the simple scaled surface tension gives a \( T \) dependence to the energy of formation, which, to first approximation, is universally applicable. This should not be viewed as ruling out other "scaled" forms for \( \sigma \) (such as that of Guggenheim and McGraw) which might provide improvement in some cases. In the next sections of the present work, we present a simple formalism for the energy of formation, \( g(n) \), which not only leads to Eq. [1] but predicts the experimental expansion cloud chamber nucleation rate, \( J_{\text{exp}} \), for nearly 850 data points for toluene (and nonane) to less than an order of magnitude. For water, the agreement is within two orders of magnitude.

II. AN ENERGY OF FORMATION INCLUDING INTEGER AND SMALL \( n \) EFFECTS

In Reference 48, we point out the need to consider the effects of small \( n \) and the integer property of \( n \). First, the energy of formation must be zero at \( n = 1 \). This is not a new idea but one which has been rarely used. The correction introduces a term in the energy of formation which increases the nucleation rate by roughly a factor of \( 10^4 \) (say for water) to \( 10^7 \) (for nonane).

It is pointed out in Reference 48 that an approximate form for the free energy of formation can be obtained from a statistical mechanical formalism for the \( n \)-cluster number concentration based on the law of mass action. This approach indicates that the "surface" free energy term for a small cluster can be estimated by summing over free energy differences (between the \( n' \) and \( n' - 1 \) clusters) from \( n' = 2 \) to \( n' = n \). If one follows this procedure, the sum over terms, \[ \sum \delta_n = \delta [An^{-2/3}] = \left(2/3\right)An^{-1/3}, \] from \( n' = 2 \) to \( n' = n \) leads to the following for the \( n \)-cluster.

\[ \sum \delta_n = An^{2/3} - A - \left[A/3\right] \left[1 - n^{-1/3}\right] \]

The first term in Eq. [5] results from integrating

\[ (2/3)An^{-1/3} \] from \( n' = 0 \) to \( n' = n \) and is an approximation. The second term corrects for the integration from 0 to 1, which is not included. Further, since \( n \) is an integer and the \( \delta_n \) are constant in the interval \( (n' - 1, n') \), the integration overestimates the sum. All the terms, \( \delta_n \), lie below the curve \( (2/3)An^{-1/3} \) in the region \( (n' - 1) \leq x \leq n' \). The area to be subtracted for each \( n' \) is \( \left[(1/2) \left(2/3\right)A(n' - 1)^{-1/3} - n'^{-1/3}\right] \). The sum from \( n' = 2 \) to \( n' = n \) of the areas to be subtracted is \( (A/3) \left[1 - n'^{-1/3}\right] \), the last term in Eq. [5].

The expression in Eq. [5] should replace the \( An^{2/3} \) term in the classical energy of formation. However, the added terms destroy the approximate agreement with experiment. (We note that the classical model, while not perfect, does give approximate agreement with experiment.) Some time ago, Fisher included a term \( \tau \ln(n) \) in the energy of formation and estimated \( \tau \approx 2.19 \) from critical exponents. Kiang et al. also considered this term, and recently, Dillman and Meier included this term with surprising success.

We recently calculated the free energy differences between (small) \( n \) and \( n - 1 \) water clusters in a Monte Carlo simulation. As expected, the free energy differences fell along a straight line when plotted vs \( n^{-1/3} \). But for \( n < 6 \), the free energy differences dropped dramatically and appeared to fall on another line with larger slope. Upon replotting the free energy differences with a term \( \tau \ln(n) \) added (this term is negligible for large \( n \)), all free energy differences fit a simple \( n^{-1/3} \) dependence. This exercise suggested that the \( \tau \ln(n) \) dependence (a \( n^{-1/3} \) factor in the configurational integral) should be considered more carefully.

In what follows, we assume that the \( \tau \ln(n) \) term is included in the energy of formation and examine the consequences. If one assumes, as do Dillman and Meier, that the density and pressure of the vapor are given by simple sums over the \( n \)-cluster concentrations, the \( \tau \) can be approximated (at the critical point) from the ratio of two Riemann zeta functions, \( \Sigma n^{-s} = z(x) \), where the sum runs from 1 to \( \infty \). This surprising result requires some additional assumptions but appears to be quite consistent with Fisher's estimate of \( \tau \approx 2.19 \) for a simple model. Finally, one finds \( z(\tau) = z(\tau - 1) = Z_\tau \), where \( Z_\tau = P_\tau /kT_\tau N_\tau \), the critical compressibility. For water, \( \tau = 2.166 \), and for nonane, \( \tau = 2.19 \). With this additional \( \tau \ln(n) \) term, the energy of formation, \( g(n) \), becomes

\[ g(n) = An^{2/3} \left[1 + (1/3n)\right] - (4/3)A + \tau \ln(n) - (n - 1) \ln S \]

where the term \( \ln S \) is added to \( g(n) \) so that \( g(1) = 0 \). Note that the kinetic prefactor, \( J_0 \), already contains \( N_i/N \), the monomer concentration in the supersaturated state, and that the function \( \exp[-g(n)] = N_n/N_i \).

III. THE NUCLEATION RATE AND EXPANSION CLOUD CHAMBER DATA

The energy of formation now has extra terms containing \( n \), and one must revise the classical expression for
the critical cluster, \( n^* \). For the \( g(n) \) of Eq. [6], \( n^* \) satisfies the following condition:\[^{[48]}\]

\[
\begin{align*}
n^* &= \left[ \frac{2A}{(3 \ln S)} \right]^3 \cdot \left[ 1 - \frac{\tau}{(n^*)^3} \ln S \right] + \left( \frac{A}{9} \right) \left[ \ln \left( n^* + \frac{1}{3} \right) \ln S \right]^{-3} \quad [7a] \\
&= \left[ \frac{2A}{(3 \ln S)} \right]^3 \cdot f(n^*) \quad [7b]
\end{align*}
\]

Equation [7] can be solved iteratively via \( n^*_n = \left[ \frac{2A}{(3 \ln S)} \right]^3 f(n^*_{n-1}) \) until \( n^*_n = n^*_n \). With the above expression for \( n^* \), one can show that the nucleation rate is given by

\[
\ln J = \ln J_0 + 4A/3 + 3\tau/2 - \tau \ln (n^*) - 1/2 \ln S - \left[ x_0 / x \right]^2 f(n^*) \quad [8]
\]

Several unexpected cancellations appear to be present in Eq. [8]. For example, when one uses Eq. [8] to analyze expansion cloud chamber data for toluene\[^{[44]}\] and nonane,\[^{[45]}\] one finds that

\[
\ln J = 60 - \left[ x_0 / x \right]^2 \text{ (in cgs units)} \quad [9a]
\]

\[
\ln (\Gamma_c/s) = \left[ x_0 / x \right]^2 \quad [9b]
\]

See Figures 1 through 3, where both Eqs. [8] and [9] are compared with the experimental values of \( J \) in the expansion cloud chamber data. (For this analysis, the nonane vapor pressure given by Hung et al.\[^{[33]}\] was used; the toluene data was analyzed as given by Schmitt et al.\[^{[44]}\]) Not only do both expressions give amazing agreement with the data, both expressions appear to be equivalent. In Eq. (9b), the \( \ln \Gamma_c \) is used to indicate the similarity to a critical point quantity which is nearly 60 (in cgs ur:ts) for most substances.

We can explain this agreement of the two expressions in part. For example, the bothersome \( T \) dependence in \( \ln J_0 \) (from \( -2 \ln [P_c/P_0] \)) is almost exactly canceled by the \( 4A/3 \) term. (Recall that the \( 4A/3 \) term resulted from requiring \( g(1) = 0. \) The \( -\tau \ln (n^*) \) term is about \(-9\) and, to first order, replaces the "effect" of the now missing \(-2 \ln [P_c/P_0] \) term. Most interesting is that \( An^* - 1/3 = (3/2) \ln S \), and this cancels part of the \( 2 \ln S \) term. Since \( f(n^*) \approx 1 \), the last term in Eq. [8] is approximately \(-[x_0 / x]^2 - (A/6) n^* - 1/3 - (3/2) \tau \). Thus, an approximate form for Eq. [8] is

\[
\ln J = \ln J_0 + \ln (I) - \tau \ln (n^*) + 1/2 \ln S - \left[ x_0 / x \right]^2 \quad [10a]
\]

\[
= 72 + 1 - 9 + 1/2 \ln S - \left[ x_0 / x \right]^2 \quad [10b]
\]

\[
= 64 + 1/2 \ln S - \left[ x_0 / x \right]^2 \text{ (cgs units)} \quad [10c]
\]

If one uses Eq. [10c] to calculate \( J \), one finds nucleation rates which do not agree as closely with the data as Eqs. [8] or [9]. Clearly, there is cancellation which is not explained by the above simple arguments. If Eq. [9] is correct for homogeneous nucleation, developers of nucleation models have somehow made a very simple problem difficult, and another view of the nucleation process is in order.

III. COMMENTS AND CONCLUSIONS

We have presented a form for the homogeneous vapor-to-liquid nucleation rate (Eq. [8]) which agrees with all of the experimental expansion cloud chamber data of

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TOLUENE DATA of SCHMITT et al.

![Fig. 2.—Comparison of the experimental homogeneous nucleation rate data for toluene of Schmitt et al.\(^{[44]}\) with (a) Eq. [9], \( \ln J = \ln \Gamma_c - \left[ x_0 / x \right]^2 \) and (b) Eq. [8], \( \ln J = \ln J_0 - \tau \ln (n^*) + [3/2] \tau + \ln S - 1/2 \left[ x_0 / x \right]^2 f(n^*) \). \( \Omega = 2.12, \tau = 2.20, \) and \( \ln \Gamma_c = 63.1 \text{ /s/cm}^2 \). \( J \) is in \( \text{s/cm}^2 \).](image-url)
Schmitt and co-workers for toluene\textsuperscript{[44]} and nonane\textsuperscript{[45]} to considerably less than an order of magnitude. Furthermore, the expression appears equivalent to the much simpler expression in Eq. [9], \( J = 60 - [x_0/x]^2 \), and indicates that the \( T \) dependence in the standard classical nucleation rate kinetic pre-factor, \( J_0 \), is canceled by additional terms in the energy of formation. For water, the agreement is less satisfying. Still, the agreement is within two orders of magnitude over a 50 K temperature range—a result not often attributable to nucleation models.

It is important to re-emphasize that small errors in an extrapolated vapor pressure formula produce large anomalies in experimental nucleation rate data. Also, a point not yet much appreciated is that a surface tension formula which does not have the correct scaling property can produce similarly confusing results. Either of these difficulties can destroy agreement (such as we have found) with a model for \( J \), independent of the merits of the model. Therefore, we cautiously stress that the success of Eqs. [8] and [9] in predicting the \( J \) for toluene, nonane, and water is dependent upon having used the correct “extrapolation” of the vapor pressure formulae and the scaled surface tension.

Keeping the above comments in mind, it is possible that for data from other measuring devices, such as the diffusion chamber or the fast expansion chamber, where ambient pressures are different, Eqs. [8] and [9] could be less successful. We have analyzed Katz’s diffusion chamber data for nonane using the \( T, S \), and experimental \( J \) reported in Reference 32 and find that the agreement is significantly better than for the standard classical model. But rather than falling on a line, as do the data in Figures 1 and 2, the diffusion chamber data separate into lines of “constant” \( T \), differing from the predicted value by factors of 10\textsuperscript{2}. Without repeating Katz’s calculations for \( S, T, \) and \( J_{\text{max}} \) using Eq. [8] for \( J \), it is not possible to make a reliable comparison with the diffusion chamber data for nonane. Using the same vapor pressure formula, we estimated a recalculated \( S \) for Wagner and Strey’s nonane\textsuperscript{[56]} data and found agreement with Eqs. [8] and [9] to about three orders of magnitude. Wagner and Strey’s data for \( T, S, \) and \( J \), reported in Reference 56, give excellent agreement with Eqs. [8] and [9].

In summary, it is hoped that the success of the simple model in Eq. [9] and its unsophisticated counterpart given by Eq. [8], together with the modified energy of formation in Eq. [6], will be of interest. It appears that we should consider carefully the \(-A\) and \( r \ln (n) \) terms in the energy of formation. We note that the \((1/3)An^{-1/3}\) term in \( g(n) \) could be interpreted as small \( n \) dependence of cluster free energy or of “effective” surface tension. It can be incorporated into the \( An^{-2/3} \) term to give \( An^{-2/3}(1 + 1/(3n)) \)—an expression similar to Tolman’s curvature correction for the surface tension.\textsuperscript{[37]} The sign is different, however, as is the “\( r \)” dependence. Finally, if Eq. [9] is correct, there is still much work to be done, and it is hoped that others will pursue the reason for nature’s insistence on simplicity in homogeneous nucleation phenomena.

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REFERENCES


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