Application of a scaled homogeneous nucleation-rate formalism to experimental data at $T << T_c$

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It is pointed out that for temperatures $T < 0.5 T_c$, where $T_c$ is the critical temperature, the classical steady-state nucleation-rate formalism of Becker and Doring predicts an approximate critical supersaturation ratio $S_c$ (for the onset of nucleation) given by $\ln S_c / \Omega^{1/2} \cong 0.53 (T_c / T - 1)^{1/2}$. $\Omega$ is a material-dependent quantity approximately equal to the excess surface entropy per molecule. For most substances $\Omega \cong 2.0$ and for associated liquids $\Omega \cong 1.5$. The experimental data (for nucleation from vapor to liquid) from diffusion chamber and nozzle beam studies are found to be consistent with the above expression. The classical theory also predicts that for a supersaturation ratio $S$ corresponding to constant $J$, $\ln S / \ln S_c - 1 \sim \ln J / \ln J_c$, where $J_c$ is a quantity evaluated at the critical point and is $\sim 72$ for most materials. Expansion cloud-chamber data for nonane, toluene, and water are also found to be consistent with these approximate scaling laws.

I. INTRODUCTION

In this paper we present an expression for the classical Becker-Doring nucleation rate $J$ in terms of a slightly modified temperature dependence, $(T_c / T - 1)$, and a relatively material-independent constant $\ln J_c$, which is evaluated at the critical point. The motivation has been to develop an expression for $J$ which can be simply compared to experimental data at temperatures far below the critical point. Of particular interest is a numerical estimate of the "critical" supersaturation $S_c$ corresponding to the onset of nucleation at a given reduced temperature $T / T_c$. The scaling of the nucleation rate has been considered extensively$^1$ and, in particular, Binder$^2$ has given a scaled form for the (slightly modified) classical nucleation rate near the critical point. The expression presented here is not applicable near $T_c$. It assumes a (classical) treatment of the prefactor, and concentrates rather on the material-dependent terms in the prefactor and on the use of the above reduced-temperature function to examine $S_c$ and factors in the free-energy barrier for $T << T_c$. The intent has been to cast the classical $J$ into a form useful for quick estimates of required supersaturations, to point out factors which can be used to transform data into relatively material-independent forms, and to suggest the $(T_c / T - 1)$ temperature dependence for data analysis far below $T_c$.

Some time ago, Wu, Wegener, and Stein$^3$ demonstrated the approximate linear relationship between $\ln S_c$ and $T^{-3/2}$ using experimental data for SF$_6$. However, the exploitation of a scaled or explicit temperature dependence of $\ln S_c$ for $T << T_c$ was apparently not further pursued until McGraw$^4$ examined a corresponding-states formalism and demonstrated that the data for $\ln S_c$ fell into identifiable groups of substances when plotted versus $T / T_c$. Motivated primarily by McGraw's results, we derived for $T << T_c$ the approximation $\ln S_c \sim 0.05 [A_0(T_c / T - 1)]^{3/2}$ and noted that the experimental data for $\ln S_c$ when plotted versus $(T_c / T - 1)^{3/2}$ fell roughly into two groups with slopes (proportional to $A_0^{3/2}$) in the ratio of 3 to 2.$^{11}$ $A = A_0(T_c / T - 1)$ is the coefficient of $n^{2/3}$ in the classical free energy of formation, $A n^{2/3} - n \ln S$, for the $n$ molecule or atom cluster. This surface-tension term is the origin of the $(T_c / T - 1)$ dependence for $\ln S$—which we note is different from the usual $\epsilon = (1 - T / T_c)$ dependence in critical-point formalisms. Rasmussen and Babu$^{12,13}$ made use of our above temperature-dependent form for $\ln S_c$ and showed that the slope of the experimental data for $\ln S_c$, when plotted versus $(T_c / T - 1)^{3/2}$, is correlated with the Eotvos constant.$^{14}$ The explicit relationship between the slope and the Eotvos constant was not given.

The "scaled supersaturation," $x = \ln S / A^{3/2}$, from which we in part extracted the above form for $\ln S_c$, is identical in form to that of Binder and Stauffer,$^3$ $\ln S / (\beta \epsilon)^{3/2}$, where $\beta$ and $\delta$ are the standard critical-point exponents.$^{15}$ Near the critical point $(T_c / T - 1) \sim \epsilon$, and $\beta \epsilon \sim 1.54$.$^3$ (For classical three-dimensional fluids $\beta \epsilon = 3$.) In a field-theoretic model for near-critical-point nucleation, Langer and Turski$^6$ use a closely related quantity, the "scaled supercooling" $\tau = \delta T_c / (\epsilon T_c)$. The scaled supersaturation (or the scaled supercooling) influences the nucleation rate primarily via the so-called "energy of formation" of the critically sized cluster:$^7$ $(x_0 / x)^2 = (\tau_0 / \tau)^2$. The $x_0$ and $\tau_0$ are constants dependent on critical-point amplitudes.$^2-8$ In the classical theory, $x_0 = 2/(3)^{3/2}$. However, $\tau_0$ is less well defined for $T << T_c$ and not independent of $T$. The classical nucleation rate $J$ is proportional to $\exp[-(x_0 / x)^2]$ and in the case that the kinetic prefactor has only slight $S$ and $T$ dependence, the $(x / x_0)^2$ is nearly constant for fixed $J$ and leads to the approximate scaling law for $\ln S$.

Classical nucleation theory and theories applicable near the critical point differ primarily in the approximation of
the kinetic prefactor which describes the growth of the clusters subsequent to the nucleation event and before observation of macroscopic effects. In predicting critical-point phenomena the prefactor must account for diffusion-controlled growth and the vanishing of the diffusion constant as \( T \) approaches \( T_c \). For \( T \ll T_c \) diffusion-controlled growth is not in general applicable and the rate of formation of the new phase is primarily dictated by the birth (nucleation) of new phase embryos. However, in this low-temperature region the (classical) kinetic prefactor for vapor-to-liquid nucleation is proportional to the equilibrium vapor pressure squared and appears to be highly temperature and material dependent.

It is the temperature dependence of the classical kinetic prefactor which prompted Rasmussen and Babu to comment that a theoretical explanation for the observed experimental agreement with the scaling law for \( \text{ln} S_{cr} \) (Ref. 11) was lacking. We here present a method of casting the kinetic prefactor into an approximately material-independent (and \( T/T_c \)-dependent) form and show that the classical theory predicts \( \text{ln} S_{cr}/\Omega^{1/2} \sim 0.53 \) (\( T_c/T-1 \)^{1/2}) where \( \Omega \) is a material-dependent quantity approximately equal to the excess surface entropy per molecule. For most substances \( \Omega \sim 2 \), while for associated liquids \( \Omega \sim 1.5 \) and reflects the reduced entropy of the surface molecules. A modified scaling law for \( \text{ln} S \) corresponding to a constant \( J/J_c \) follows and we finally comment on the consequences of assuming a term in the energy of formation which takes into account the translation of the center of mass of the embryonic cluster. For simplicity we consider no replacement factors.

The formalism for vapor-to-liquid nucleation is presented in Sec. II and in Sec. III the results are compared with experimental \( \text{ln} S_{cr} \) for \( J \sim 1 \), \( 10^4 \), and \( 10^8 \) \( \text{cm}^{-3} \text{sec}^{-1} \). Comments and conclusions are in Sec. IV.

II. FORMALISM FOR \( J \) IN TERMS OF CRITICAL-POINT QUANTITIES

The classical Becker-Doring theory \(^1\) for the steady-state homogeneous nucleation rate \(^{19,20}\) (including the so-called Zeldovich factor \(^2\)) can be written as follows:

\[
J = J_c I(P/P_c)^\eta \exp[-(x_0/x)^2],
\]

(1)

where \( \alpha = 2 \),

\[
I = [(4/3)/(\pi^{1/2})^{1/2}] A^{1/2} (T_c/T)^{1/2} \rho_c/\rho \right)^{2/3},
\]

(2)

and

\[
J_c = (P_c/h)(\lambda_c/\rho_c)^{1/2}(P_c/kT_c\lambda_c).
\]

(3)

The \( \rho, P, h, k, S, \) and \( \lambda \) are the number density, pressure, Planck's constant, Boltzmann's constant, supersaturation ratio, and inverse thermal wavelength cubed, \( (2\pi mkT/h^2)^{3/2} \), respectively. The subscript \( c \) denotes critical-point quantities. The form for the exponent, \( (x_0/x)^2 \), follows from the classical free energy of formation for the \( n \) atom or molecule cluster, \( g(n) = A_n n^{2/3} - nB_n \), where \( B = \text{ln} S \). Classically, \( A \) is equal to the surface tension (divided by \( kT \)) times the area per surface molecule. From \( dg(n^*)/dn = 0 \), one readily obtains the number of molecules in the critical cluster, \( n^* = (2A/3B)^3 \), and \( g(n^*) = 0.5n^*B = (x_0/x)^2 \). The \( x_0 = 2/(3)^{1/2} \).

If one assumes the form \( \sigma = \sigma_0(T_c - T) \) for the surface tension (where \( \sigma_0 \) is a material-dependent constant), \( \Omega = (36\pi)^{1/3}(T_c/T-1) \). The \( \Omega = \sigma_0/k/\rho^{2/3} \) can be interpreted as an effective excess surface entropy per molecule (in units of \( k \)) in the embryonic cluster. The bulk liquid value for \( \Omega \) (the Eotvos constant) is approximately 2 for most liquids. For associated liquids \( \Omega \) is smaller (\( -1.5 \)) and reflects the reduced excess entropy for surface molecules. The corresponding values of \( A_0 \) are about 10 for ordinary substances and 7 for associated liquids. This approximate material independence of \( A_0 \) was noted when calculating thermodynamic properties of microscopic clusters using Monte Carlo methods and effective pair potentials. In some preliminary work it was found that \( A_0 \approx 10 \) for Lennard-Jones argon clusters and \( A_0 \approx 7.5 \) for Rahman-Stiller-Stillinger central-force (rigid-molecule) water clusters. These values of \( A_0 \) correspond to \( \Omega \approx 2.1 \) and 1.6 for (Lennard-Jones) argon and (rigid-molecule central-force) water, respectively.

Using Eqs. (1) and (2), the scaled supersaturation \( \text{ln} S/A^{1/2} \) becomes

\[
\text{ln} S/A^{1/2} = x_0 (\text{ln} J_c)^{-1/2} \delta_0,
\]

(4)

where

\[
\delta_0 = [1 - \alpha(\text{ln}(P_c/P_0) - \text{ln} S)/\text{ln}(J_c/J) + \text{ln}(\text{ln}(J_c/J))^{-1/2} + 1.072W_0(T_c/T-1)^{1/2}/[2 \text{ln}(J_c/J)]
\]

(5a)

\[
\sim 1 + 0.772W_0(T_c/T-1)^{9/4} \text{ln}(J_c/J) \text{ln}(J_c/J)
\]

(5b)

for \( 0.3 < T/T_c < 0.5 \). For \( \text{ln} J_c = 0, \delta_0 \sim 1.13 \pm 0.04(T_c/T-1)^{9/4} \). In obtaining this approximation, \( \rho_c/\rho \right)^{1/2} \) and

\[
\text{ln}(P_c/P_0) \sim W_0(T_c/T-1)^{9/4}
\]

(6)

are used. \( W_0 \) and \( \eta \) are approximately \( 7 \pm 2 \) and 1, respectively, for most substances, and \( W_0 \) can be roughly represented by \( L/kT_c \), where \( L \) is the latent heat of vaporization near the boiling point. While there is some cancellation of the \( \text{ln}(P_c/P_0) \) term by \( \text{ln} S \) and \( \text{ln} I \) in Eq. (5a), \( \text{ln} I \) contributes less than 1.5% to \( \delta_0 \) and the major contribution to the approximation in Eq. (5b) comes from \( \text{ln}(P_c/P_0) \). For substances (such as toluene) which have relatively small values of \( W_0 \) and large values of \( \Omega \) (nonassociated liquids) there is a considerable cancellation of \( \text{ln}(P_c/P_0) \) by \( \text{ln} S \) and the temperature dependence of \( \delta_0 \) is weak. Finally, one can show that \( \text{ln} J_c \approx 72 \) to within 3% for most substances. For example, the values are 72.8, 74.7, 71.8, 70.8, and 73.7 for the substances ethanol, water, toluene, nonane, and argon, respectively. Since the square root of \( \text{ln} J \) enters into the expression for \( \text{ln} S_{cr} \), a 3% error in \( \text{ln} J_c \) produces a 1.5% error in \( \text{ln} S_{cr} \). Using \( \text{ln} J_c = 72 \) the following approximate scaling laws result:

\[
\text{ln} S_{cr}/\Omega^{1/2} \sim 0.53(T_c/T-1)^{1/2} \text{ for } J \sim 1 \text{ cm}^{-3} \text{ sec}^{-1}
\]

(7)

and

\[
\text{ln} S \sim \text{ln} S_{cr}[1 + \text{ln}(J_c/(2\text{ln} J_c))]
\]

(8)
for larger \( J \) of physical interest. The major deviations from these approximate scaling laws occur at low temperatures where \((T_c/T - 1)\) is large \((>1.5)\). One can show also that the critical cluster size (for onset of nucleation) takes the form

\[
n^* \sim (3/4\pi)^{1/2}(\ln J_c/\Omega)^{3/2}(T_c/T - 1)^{-3/2}
\]

\[
\sim 106(2/\Omega)^{3/2}(T_c/T - 1)^{-3/2}.
\]

(9)

In expansion chamber experiments it is often more convenient to use the supercooling. Equation (6) (with the approximation \( \eta = 1 \)) and Eq. (7) yield

\[
\delta T^* W_0/\Omega^{3/2} \sim 0.53(T_c/T - 1)^{3/2},
\]

(10)

where

\[
\delta T'=(T_c/T_{\text{final}} - T_c/T_{\text{initial}}).
\]

(11)

It is interesting to consider the modification to Eq. (7) when one includes the free energy associated with the translation of the center of mass of the cluster.\(^{17}\) For simplicity, replacement factors\(^{18}\) are not considered. In this case the right-hand side of Eq. (1) is multiplied by \((\lambda kT/P)(n^*)^{3/2}\exp(-\frac{1}{\Delta})\) and one considers the \( n^* \) to be modified by the small \((\sim 3\%)\) correction factor,

\[
[1+3/(2n^*\ln S)]^{-3} \sim [1+(\frac{1}{3})(x/x_0)^2]^{-3}.
\]

The resulting \( J = J_c \) is given by Eq. (1) with \( \alpha = 1 \), \( I \) replaced by

\[
I'=[(4/\pi)^{1/2}]^{1/2}3^3/4(x_0/x)^{9/2}(T/T_c)
\]

\[
\times(\rho_e/\rho)^{2/3}A(-7/4),
\]

(12)

\( J_c \) replaced by

\[
J_c'=P_c(\lambda_c/\rho_c)/h,
\]

(13)

and \( \delta_0 \) replaced by \( \delta_0(\alpha = 1, I = I', J_c = J'_c) \). Inclusion of the center-of-mass translational free energy reduces by one the power of \( P/P_c \) in the prefactor of \( J_c \). This softens the temperature dependence of the prefactor and predicts a \( \ln S_{ct} \) which is more nearly linear in

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FIG. 1. Natural logarithm of the threshold \((J = 1\ \text{cm}^{-3}\ \text{sec}^{-1})\) supersaturation ratio \( S_{ct} \), divided by \( \Omega^{3/2} \) from diffusion chamber and nozzle beam experimental data. The data points are for toluene (Ref. 33) (△), nonane (Ref. 32) (×), water (Ref. 28) (□), \( n \)-butylbenzene (Ref. 33) (○), sulfur hexafluoride (Ref. 9) (+), carbon tetrachloride (Ref. 34) (◇), chloroform (Ref. 34) (◇), ethanol (Ref. 31) (○), octane (Ref. 33) (＊), argon (Ref. 30) [taken from McGraw (Ref. 10), Fig. 1] (▼), and acetic acid (Ref. 29) (▲). The dashed line is 0.53 \((T_c/T - 1)^{3/2}\) from Eq. (7). The values used for \( \Omega \) are (Ref. 12) 2.35 for nonane, octane, and \( n \)-butylbenzene; 1.5 for water and ethanol; and 2.0 for SF\(_6\). For the remaining substances the ideal gas value 2.12 is used (Ref. 14).
\( T_c / (T - 1)^{3/2} \). In addition, \( \ln J_c \) is almost universally 86 and the prefactor for \( J_1 \) becomes less material dependent. For example, for water, ethanol, toluene, nonane, and xenon the values of \( \ln J_c \) are 86.2, 86.1, 86.7, and 86.5, respectively. The value for argon (84.4) is notably smaller. The resulting scaling law (without replacement factors) is

\[
\ln S_c'/A^{3/2} = x_0(\ln J_c)^{-1/2} \delta_0 
\]

(14a)

\[ -0.44(T_c / (T - 1)^{1/2}. \]

(14b)

For \( J > 1 \), \( \ln S' \) is related to \( \ln S_c' \) via Eq. (8) with \( J_c = J_c' \).

III. COMPARISON WITH EXPERIMENTAL DATA

The approximations in Eqs. (7) and (8) serve as good predictors for \( \ln S \) over a range of nucleation rates. Figure 1 shows experimental homogeneous vapor-to-liquid data for \( \ln S_c'/\Omega^{3/2} \) for a number of substances, using bulk values for \( \Omega \). The data for \( \ln S_c' \) conform to the approximate scaling law in Eq. (7) rather well in spite of the scatter in data and the approximation of \( \Omega \) by the bulk value. In fact, the \( \ln S_c' \) data appear to be more linear in \( (T_c / (T - 1)^{3/2} \) than the corrections to Eq. (7) [via \( \delta_0 \), Eq. (5b)] would indicate. The linearity of the data of Katz et al. for toluene is particularly striking, and it is noteworthy that almost all of the Katz data fit this linear dependence extremely well. In Fig. 2 is plotted the \( J \sim 10^4 \) cm\(^{-3}\)/sec expansion cloud-chamber data of Miller, Anderson, and Kassner for water and of Schmitt, Adams, and Zalabsky for toluene and nonane. The expansion chamber data appear to be consistent with the \( (T_c / (T - 1)^{3/2} \) temperature dependence for \( \ln S / \Omega^{1/2} \) as predicted by Eqs. (7) and (8).

It is interesting to compare the experimental nonane data for \( J \sim 1 \) (Katz et al.), \( J \sim 10^4 \) (Schmitt et al.), and \( J \sim 10^8 \) (Wagner and Strey) in a way which emphasizes the role of prefactor and exponent for \( J \). The exponent

\[
(x_0/x)^2 = (16\pi/3)(T_c / (T - 1)^3 / (\ln S)^2 \Omega^3 ,
\]

and if one uses \( \Omega = \sigma / (kT_St)^{3/2}(T_c / (T - 1)) \) the standard classical model obtains. For most nonassociated liquids the \( \Omega \) so calculated is stable with respect to \( T \) in the

FIG. 2. \( \ln S / \Omega^{1/2} \) for \( J \sim 10^4 \) cm\(^{-3}\)/sec\(^{-1}\) from the expansion chamber data for water (Refs. 35 and 36) (□), nonane (Ref. 38) (×), and toluene (Ref. 37) (△). The dashed line is the prediction from Eq. (8).
range of $T/T_e$ of interest) to about 1%. The stability of these values will depend somewhat on the choice of extrapolation for $\sigma$ and $\rho$ at low temperatures. In Fig. 3 is plotted the log of the prefactor versus $(x_0/x)^2$ for these data in the classical model. The three sets of data fall not too far from the straight line — which is the prediction of the classical model. The dashed lines above (below) the solid line indicate errors in $J$ of $10^{-3}$ ($10^{+3}$). While the Wagner and Strey data and the Katz et al. data appear to be closer in magnitude to the classical model prediction, the expansion chamber data of Schmitt et al. show a more nearly linear relationship. The low-temperature data correspond in general to smaller values of $(x_0/x)^2$. Thus in Fig. 3 the high-temperature (expansion chamber) data lie furthest from the solid line and the classical model prediction.

In Fig. 4 is a comparison of the temperature dependence of the log of the prefactor and $(x_0/x)^2$ for the three sets of nonane data. For the diffusion chamber data it is assumed that $J = 1$ cm$^{-3}$ sec$^{-1}$. The prefactor has a smooth linear dependence on $(T_e/T - 1)$. However, the temperature dependence of $(x_0/x)^2$ differs for the three sets of data and none of the data appear to have quite the “classical model” form. This could be in part the result of the sensitivity of $(x_0/x)^2$ to the assumed temperature dependence of $\ln P_0$ and $\sigma$. Both Schmitt et al. and Wagner and Strey found major discrepancies in comparing their data with the classical model at low temperatures. For example, Schmitt et al. (using an equilibrium vapor pressure different from the vapor pressure used by Katz and Wagner and Strey) found that their data disagreed with the classical model by factors of $10^5$ in $J$ at low temperatures. On the other hand, Wagner and Strey (using an expression for the surface tension different from that used by Schmitt et al. and Katz) found that their data disagreed with the classical model by factors of as much as $10^6$ at low temperatures. As can be seen in Fig. 3, the vapor pressure and surface tension formulas used by Katz bring all the data into approximate mutual agreement with the classical model. We note that this does not imply that these particular formulas are without problems. This dilemma emphasizes the need to sort out competing temperature dependences of terms in $(x_0/x)^2$, and to assume a valid equilibrium vapor pressure at low

![FIG. 3. $\ln[J_e/J(P/P_0)^2]$ vs the classical energy of formation, $(x_0/x)^2$, for the nonane diffusion chamber data of Katz et al. (Ref. 32) ($\times$); the nonane expansion chamber data of Schmitt et al. (Ref. 38) where $J = 10^4$ ($\cdot$); and the nonane expansion chamber data of Wagner and Strey (Ref. 39) ($\triangle$), where $J = 10^6$. The $x = A^{1/2}/\ln S$ is the scaled supersaturation. The solid line is the prediction of the classical theory for $J$, and the lower (upper) dashed line indicates the range of data corresponding to $J \times 10^4$ ($J \times 10^{-3}$). $\Omega$ is calculated from $\sigma / [kT_p^{1/2} (T_e/T - 1)]$, as prescribed by the classical model.](image)
FIG. 4. Classical model prefactor of $J$ (open symbols) and $(x_0/x)^2$ (closed symbols) vs $(T_c/T - 1)$ for (a) the nonane $J = 10^4$ data of Schmitt et al. (Ref. 38) (■) and the $J = 10^4$ data of Wagner and Strey (Ref. 39) (▲) and (b) the nonane $J = 1$ data of Katz et al. (Ref. 32) (◊). The equilibrium vapor pressure and surface tension formulas as given by Katz (Ref. 32) are used for all the data. The dashed lines guide the eye through the prefactor data points.
temperature. Finally, it seems appropriate to note that the expansion chamber data of Kassner, Miller, and Anderson 35,36 and of Schmitt et al. 37,38 offer stringent tests for the temperature dependence of the theory, and it is unfortunate that these data have been so long overlooked. It is noted, however, that the nonane and toluene expansion chamber data appear to give values of \( \ln S \) which are slightly smaller than the classical model would predict at high temperatures. An approximate value of \( \Omega = 2.35 \) can be extracted from the Schmitt data 38 by plotting the \( \ln(J/S^2) \) versus \((16\pi/3)(T_c/T - 1)^{3/2}/(\ln S)^2 \). It is interesting that this is the value of the Eotvos constant for nonane cited by Rasmussen 12 and that if one uses \( \Omega = 2.35 \) the data of Schmitt et al. agree with the classical model to less than a factor of 10 at all temperatures.

Some comments on the scaling law in Eq. (14) are relevant. The softened temperature dependence of the kinetic prefactor for \( J \) [which predicts a more linear dependence of \( \ln S \) on \((T_c/T - 1)^{3/2}\)] and the more nearly material independence of \( \ln J \) merit some consideration. However, it is well known that \( J/\lambda \) (without replacement factors) is \( \sim 10^{-7} \) and unless the corresponding \( \Omega \) could be increased by 15% the scaling law in Eq. (14) does not agree with experiment.

IV. COMMENTS AND CONCLUSIONS

The expression for the classical Becker-Doring nucleation rate presented here emphasizes the \( (T_c/T - 1) \) dependence, the relatively material-independent quantity \( \ln J \), and the overall weak temperature dependence of the prefactor for \( J \) when predicting \( \ln S \) at \( T \ll T_c \). The scaling law in Eq. (7) appears to describe the experimental \( \ln S \) for onset of nucleation rather well, and points out the usefulness of \( \Omega \) in characterizing critical supersaturation values. An interpretation of \( \Omega \) is the effective excess entropy per surface molecule in the embryonic clusters. The fact that the bulk value for this quantity is nearly 2 for most substances and reduced to about 1.5 for associated liquids provides a convenient rule of thumb for estimating critical supersaturations for a wide variety of materials. The linearity of the data for \( \ln S \) [when plotted versus \((T_c/T - 1)^{3/2}\)] underscores the role of the \( \frac{1}{2} \) exponent for the \( A^{1/3} \) surface energy contribution in the classical energy of formation far below \( T_c \). Katz's 33 toluene data and the cloud-chamber data 35-38,43 for larger nucleation rates \( J \sim 10^5 \) yield exponents for \((T_c/T - 1)\) surprisingly close to 1.5. A comparison of the diffusion chamber and expansion chamber nonane data (with \( J \) ranging from 1 to \( 10^5 \)) indicates that the classical model does a credible job of predicting \( J \). There does appear to be, however, some anomalous temperature dependence in the \((x_0/x)^2\) data. Related to this anomaly are uncertainties in the low temperature dependence of the equilibrium vapor pressure, which can generate apparent discrepancies as large as \( 10^8 \) between data and the classical model. A careful consideration of the competing temperature factors in \((x_0/x)^2\) appears to be in order. Finally, we note the temperature functions considered here in predicting a general form for \( \ln S \) and suggest that \((T_c/T - 1) \) might be useful in analyzing phenomena far below the critical temperature. A modified supercooling, \((T_c/T - T_c/T)\), and the equilibrium vapor pressure in the form \( \ln(P_c/P_0) = W_0(T_c/T - 1) \) appear to be interesting examples.

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B. N. Hale in Proceedings of the 56th Colloid and Surface Science Symposium, Virginia Polytechnic Institute, Blacksburg, Virginia (1982) (unpublished). A derivation of \( \ln S/\lambda^{3/2} \) \( \sim 0.05 \) was presented and the relation compared with experimental data for \( \ln S \) vs \((T_c/T - 1)^{3/2}\). The figure presented was essentially identical to Fig. 1 of Rasmussen and Babu (Ref. 12). Mention of the Symposium paper can be found in Ref. 19 of Rasmussen et al. (Ref. 13).
In 1886 Eotvos 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 \( \sim 2.12 \). For associated liquids, the constant is reduced. F. H. MacDougall, Physical Chemistry (Macmillan, New York, 1936), p. 96. The Eotvos constant defined in this way is actually \( \Omega \) times \( k(N_s)^{2/3} \), where \( N_s \) is Avogadro's number. This slight correction factor is \( \sim 0.984 \).
22The $\Delta G^*/k$ notation appears to have been first used by D. Turnbull and J. C. Fisher, J. Chem. Phys. 17, 71 (1948).
23A linear fit to the surface tension data for liquids is quite successful over a wide range of temperatures, including a region not too far from the critical temperature (but outside the region of interest for critical phenomena). Some liquids (such as water) show anomalies in the slope near the freezing point. These anomalies are apparently related to the properties of associated liquids.
24Eotvos constants for a variety of materials are given in Ref. 12. In comparing the results of the scaling laws in this paper with the data, the ideal value of 2.12 is used for the majority of substances. Exceptions are 1.5 for water and ethanol and 2.35 for nonane, octane, and n-butylbenzene. For SF6, the value 2.0 from Ref. 12 is used. The latter values agree approximately with $\sigma/(kT_c/kT - 1)$ for these substances for $0.35 < T/T_c < 0.50$. For example, this classical formula gives $2.44 \pm 0.01$ for nonane, $2.35 \pm 0.02$ for octane and n-butylbenzene, $2.17 \pm 0.03$ for toluene and carbon tetrachloride, $2.10 \pm 0.01$ for chloroform, $1.45 \pm 0.05$ for water, and $1.40 \pm 0.02$ for ethanol.
41Selected Values of Properties of Hydrocarbons and Related Compounds, American Petroleum Institute Research Project 44, Thermodynamics Research Center, Texas A & M University, College Station, Texas, 1965 (unpublished).