Kinetic nucleation theory: A new expression for the rate of homogeneous nucleation from an ideal supersaturated vapor

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The "kinetic theory" of homogeneous nucleation developed by Katz and Wiedersich is extended to derive a new expression for the rate of nucleation from an ideal supersaturated vapor. Compared to the classical expression for the nucleation rate, the new expression has a slightly different dependence on supersaturation, and a substantially different dependence on temperature. A comparison of the new expression with experimental data on nucleation rates of several organic liquids indicates that in some but not all cases the new expression gives much closer agreement with the data than does the classical expression. Discrepancies between the theory and the data are ascribed mainly to the physical assumptions of the theory presented, which are the same as in the classical theory—particularly, that the physical properties of microscopic clusters are the same as those of the bulk liquid.

INTRODUCTION

The rate of homogeneous nucleation from a supersaturated vapor has been the subject of theoretical investigations dating to the 1920s. The classical theory was developed by Volmer and Weber,\textsuperscript{1} Becker and Döring,\textsuperscript{2} Zeldovich,\textsuperscript{3} and others. A number of investigators, most notably Lothe and Pound,\textsuperscript{4} and Reiss, Katz, and Cohen,\textsuperscript{5} have proposed modifications to the classical theory, in which the basic approach of the theory was retained while various alternative models were proposed for the term involving the Gibbs free energy of cluster formation.

Classical theory assumes that cluster growth and decay are dominated by monomer addition (condensation) and its inverse process (evaporation). For an ideal vapor the condensation rate is known from gas kinetic theory. The evaporation rate is then obtained by reference to the metastable equilibrium which would exist for a vapor at the same temperature and supersaturation ($S > 1$) as the vapor in question, constrained to a steady state by Maxwell demons—monomers are continually replenished by the artificial disassociation of clusters which grow beyond a certain size.

In 1977 Katz and Wiedersich\textsuperscript{6} pointed out that a nucleation theory could be developed without invoking such a constrained equilibrium: the evaporation rate could be obtained instead with reference to the stable equilibrium of a saturated vapor ($S = 1$) at the same temperature as the vapor in question. Following Katz and Donohue\textsuperscript{7} we shall term this alternative procedure a "kinetic approach" to nucleation theory. While inherently interesting, the approach does not appear to have affected nucleation rate calculations in the literature, at least not for the case of ideal vapors, apparently because in this case, as noted by Katz and Donohue, the result is "identical to classical nucleation theory."

In this paper we extend the kinetic theory of nucleation, and obtain a result which differs significantly from classical theory. A comparison of the new expression with recent experimental data on nucleation of several organic liquids is also presented.

KINETIC NUCLEATION THEORY

We begin by recapitulating the main elements of the kinetic theory.\textsuperscript{6,7} While this theory was developed in more general terms, we restrict our consideration to the case of an ideal vapor. With only one exception—regarding the equilibrium state to which the evaporation rate should be referred—we retain all the assumptions of the classical theory. We assume that mass accommodation coefficients equal unity, that clusters are spherical and charge neutral, that London-van der Waals forces can be neglected, and that the physical properties of a cluster are the same as those of the bulk liquid.

Cluster growth and decay can be represented by the "reaction"
\[
A_1 + A_{g-1} \leftrightarrow A_g,
\]
(1)
where $A_g$ represents a cluster containing $g$ molecules (a g-mer). The net rate of g-mer formation $J_g$ (cm$^{-3}$ s$^{-1}$) can be written
\[
J_g = \beta s_{g-1} n_{g-1} - E_g n_g,
\]
(2)
where $n_g$ represents the concentration (cm$^{-3}$) of g-mers, $s_g$ is the surface area of a g-mer, $\beta$ represents the monomer flux to the surface (cm$^{-2}$ s$^{-1}$), and $E_g$ is the g-mer evaporation coefficient (s$^{-1}$). Under the stated assumptions $\beta$ can be taken from ideal gas kinetic theory,
\[
\beta = \left( \frac{kT}{2\pi m_1} \right)^{1/2} n_1,
\]
(3)
where $k$ is Boltzmann's constant and $m_1$ is the mass of a monomer.

The evaporation coefficient is evaluated following the usual procedure of chemical kinetics. At equilibrium $J_g = 0$, thus
\[
E_g = \beta s_{g-1} \left( \frac{n_{g-1}}{n_g} \right),
\]
(4)
where the superscript "$e$" denotes equilibrium conditions. It is over the choice of equilibrium state for evaluating Eq. (4)
that the classical and kinetic theories diverge. Following the
kinetic theory, we refer to the stable equilibrium (phase and
thermal) of a saturated vapor.

Substituting Eq. (4) into Eq. (2), and rearranging,
\[
\frac{J_e}{\beta \sigma_{-1} n_{-1}^{*}} = \frac{n_{-1}}{n_{-1}^{*}} - \frac{\beta^*}{\beta} \frac{n_e}{n_e^{*}}, \tag{5}
\]
where
\[
\frac{\beta}{\beta^*} = \frac{n_1}{n_1^*} = S. \tag{6}
\]

At steady state, \(J\) becomes independent of \(g\). Both sides of
Eq. (5) are now divided by \(S^{-1}\) and summed from \(g = 2\)
to an arbitrarily large value \(g = G\). Successive terms on the
right-hand side cancel. Solving for \(J\), the result is (shifting
indexes in the summation)
\[
J = \left[ \sum_{g=1}^{G-1} (\beta \sigma g^e S^{-1}) \right]^{-1} \left[ 1 - \frac{n_0}{S n_0^e} \right]. \tag{7}
\]

For \(S > 1\), and sufficiently large \(G\), the last ratio can be
neglected in comparison with unity.

Following the same mathematical procedure as in classical
theory, the summation is now converted to an integral:
\[
J = \left[ \int_{0}^{\infty} \frac{dg}{\beta \sigma g^e S^G} \right]^{-1} \frac{1}{\int_{0}^{\infty} e^{-H(g)} dg}, \tag{8}
\]
where we have introduced
\[
H(g) = \ln(\beta \sigma g^e S^G). \tag{9}
\]

Expanding \(H\) in a Taylor series about a size \(g^*\), where its first
derivative equals zero, and truncating after the quadratic
term,
\[
H(g) \approx H(g^*) + \frac{1}{2} (g - g^*) \left( \frac{d^2 H}{dg^2} \right)_{g=g^*}. \tag{10}
\]

Substituting this result in Eq. (8), the integral is seen to be of
the form of the error function, with the final result
\[
J = \left[ \frac{H^*(g^*)}{2\pi} \right]^{1/2} \exp[H(g^*)]. \tag{11}
\]

To specify \(H\) we require an expression for \(n_e^*\) in Eq. (9). We
assume that the equilibrium cluster population obeys a
Boltzmann distribution,
\[
n_e^* = N \exp \left[ - \frac{\Delta G(g)}{kT} \right], \tag{12}
\]
where \(N\) is a normalization constant and \(\Delta G(g)\) is the Gibbs
free energy of \(g\)-mer formation in the equilibrium state.

In classical theory the free energy is derived from ther-
odynamic arguments pertaining to the constrained equi-
librium, giving
\[
\frac{\Delta G}{kT} = \Theta g^{2/3} - g \ln S, \tag{13}
\]
where \(\Theta\) is a dimensionless surface energy:
\[
\Theta = \frac{\sigma_1}{kT}, \tag{14}
\]
\(\sigma\) being surface tension (dyn cm\(^{-1}\)). In rewriting Eq. (13)
to apply to the stable equilibrium \((S = 1)\) of the kinetic the-
ory, it might seem logical to write, as do Katz and Donohue,\(^7\)
\[
\frac{\Delta G}{kT} = \Theta g^{2/3}. \tag{15}
\]
In that case Eq. (9) becomes
\[
H(g) = \ln \beta + \ln(s_1 g^{2/3}) + \ln N - \Theta g^{2/3} + g \ln S, \tag{16}
\]

and from its definition \(g^*\) is then the solution to
\[
\frac{\Theta g^{2/3} - 1}{g^*} = \frac{3}{2} \ln S. \tag{17}
\]

For most realistic cases \(\Theta g^{2/3} > 1\). With this approxi-
mation we obtain
\[
g^* = \left( \frac{2 \Theta}{3 \ln S} \right)^1, \tag{18}
\]
which is identical to the "critical size" of classical theory.
Combining Eqs. (9), (11), (12), (15), and (18), we finally obtain
\[
J = \frac{N \beta S}{3 (\Theta / \pi)^{1/2}} \exp \left[ - \frac{4}{27} \left( \frac{\Theta}{\ln S} \right)^2 \right]. \tag{19}
\]

As Katz and Donohue\(^7\) commented, the result of classical
theory appears to have been recovered.

**NEW EXPRESSION FOR THE NUCLEATION RATE**

Upon closer inspection, however, the kinetic theory is
found to yield a result which differs from classical theory.
We focus on Eq. (12), the equilibrium cluster distribution.

To begin with, the normalization constant \(N\) is not the
same in the two theories. If in either theory we take \(N = n_1\),
then
\[
N_{eq} = n_1, \tag{20}
\]

while
\[
N_{kin} = n_s, \tag{21}
\]
where \(n_s\) represents the equilibrium monomer concentration
for a saturated vapor. Classical theory does in fact adopt Eq.
(20). Thus in the kinetic theory \(N\) is smaller than in the
classical theory, by a factor \(n_s / n_s = S\).

Equation (20) together with Eq. (13) for \(\Delta G\) deter-
mines the cluster distribution for the constrained equi-
librium of classical theory. Aside from the physical unreality
of this distribution, it will be noticed that it is internally in-
consistent, as Eq. (12) is obviously not satisfied for monomers.
It is straightforward within the context of classical theory to
rewrite the expression for the cluster distribution to make it
self-consistent,\(^8\) but the problem has mostly been neglected,
as only the value of \(n_e^*\) around \(g = g^*\) is finally needed.

In the kinetic theory there is no need to accept this state
of affairs. Equation (12), with \(N\) given by Eq. (21), is satis-
fied for monomers if \(\Delta G(1) = 0\). Indeed this must hold,
because \(\Delta G(1)\) represents the difference in chemical potential
between a molecule in the vapor and a molecule in the con-
densed phase, for a system at an equilibrium saturation state.
But the condition of phase equilibrium is precisely that these
chemical potentials are equal, thus \(\Delta G(1) = 0\). Therefore,
\(\Delta G(g)\) can be evaluated simply as the difference in Gibbs
free energy between a \(g\)-mer and a monomer, both consid-
erated to be in the condensed phase. If we adopt the same physical assumptions as in the classical theory, this gives

$$\frac{\Delta G}{kT} = \Theta (g^{2/3} - 1), \quad (22)$$

so that the final result for the equilibrium size distribution of kinetic theory is

$$(n_e^2)_{\text{kin}} = n_e \exp \left[ - \Theta (g^{2/3} - 1) \right]. \quad (23)$$

Comparing Eq. (22) to Eq. (15), the difference seems minor. The derivatives of $\Delta G$ with respect to $g$ are unaffected, hence neither $g^* \Theta$ nor $H^*(g^*)$ in Eq. (11) change. However, $H(g^*)$ in Eq. (11) is now increased by the quantity $\Theta$. That is, $J$ is multiplied by $e^\Theta$.

Combining the effects of our evaluations of $N$ and $\Delta G$, we find the following relation between the nucleation rates obtained by the kinetic and classical theories:

$$J_{\text{kin}} = \frac{e^\Theta}{S} J_{cl}. \quad (24)$$

Equivalently,

$$J_{\text{kin}} = v_i \left( \frac{2\sigma}{\pi m_s} \right)^{1/2} n_e^2 S \exp \left[ \Theta - \frac{4\Theta^3}{27(\ln S)^2} \right], \quad (25)$$

where $v_i$ is monomer volume and $\beta$ has been replaced using Eq. (3).

As we agree with Katz and Wiedersich that the kinetic approach is correct, we conclude that, to within the limitations of the physical model, Eq. (25) is valid for the rate of homogeneous nucleation from an ideal supersaturated vapor.

THE FACTOR $e^\Theta/S$

The factor $e^\Theta/S$ in Eq. (24) represents an often large—and strongly temperature dependent—correction to the classical theory. Commonly encountered values of $\Theta$ range from $\sim 3$ (methanol at 350 K) to $\sim 50$ (mercury at 290 K). For many substances in the range where they have stable vapors $\Theta$ lies in the range $\sim 10$–25. For example, for $n$-nonane $\Theta(300$ K) = 11.6, while $\Theta(200$ K) = 23.0.

The surface tension of most liquids can be written in the form

$$\sigma = C_1 - C_2 T, \quad (26)$$

where $C_1$ and $C_2$ are positive constants. Thus Eq. (24) can be rewritten as

$$\frac{J_{\text{kin}}}{J_{cl}} = \frac{1}{S} \exp \left( a \frac{T}{T} - b \right), \quad (27)$$

where

$$a = C_1 s_1 / k \quad (28)$$

and

$$b = C_2 s_1 / k. \quad (29)$$

The liquid density—and hence the effective value of $s_1$—is itself temperature dependent, but much less so than is $\sigma$. Thus Eq. (27) gives the form of the difference in temperature dependence as well as magnitude of the kinetic nucleation rate compared to the classical expression.

COMPARISON WITH EXPERIMENTAL DATA

A substantial body of experimental data exists regarding the “critical supersaturation” required to initiate homogeneous nucleation for various substances. However, these data do not provide a very sensitive quantitative test of theoretical expressions, because a small uncertainty in the measured critical supersaturation corresponds to a large uncertainty in nucleation rate. Recently experiments have been reported in which nucleation rates themselves were measured as a function of temperature and supersaturation for several organic compounds. We consider the data of three groups of experimenters. Adams, Schmitt, and Zalabks used a single-piston fast expansion chamber to measure nucleation rates of ethanol, toluene, and $n$-nonane. A double-piston expansion chamber was used by Wagner and Strey to measure nucleation rates of $n$-nonane, and by Strey, Wagner, and Schmeling to do the same for six $n$-alcohols. Hung, Krasnopolzer, and Katz used an upward thermal diffusion cloud chamber to determine $n$-nonane nucleation rates.

In comparing these data with either the classical or the kinetic expression for the nucleation rate, it is important to note that not only are nucleation experiments notoriously difficult, but also that significant uncertainties exist with regard to physical properties (particularly surface tension and vapor pressure) of the substances tested. For example, Hung et al. reevaluated the earlier $n$-nonane data of Wagner and Strey and Adams et al. using values for physical properties which were based on a critical assessment of the literature. Hung et al. found that at a given temperature and supersaturation the predicted nucleation rate (using classical

![FIG. 1. Comparison of predicted and measured nucleation rates for $n$-nonane. Data are from Adams et al. (Ref. 11), Wagner and Strey (Ref. 12), and Hung et al. (Ref. 14). The theoretical nucleation rate is obtained either using the classical expression or from the kinetic expression, Eq. (25). This figure corresponds to Fig. 7 in Hung et al. (Ref. 14), in which their recommended property values are used in calculating the theoretical nucleation rates for all three sets of experiments. Each point on the graph represents the geometric mean of the corresponding value for the several data points of each experimental isotherm.](http://ojps.aip.org/jcpo/jcpcr.jsp)
theory) was changed by up to four orders of magnitude compared to the value calculated by the earlier investigators, simply on the basis of assuming different property values. Thus the comparisons discussed below could change as better property data become available.

Hung et al. compiled the data from all three groups on nucleation of n-nonane (C_{9}H_{20}), encompassing a wide range of temperature and supersaturation. The results are shown in Fig. 1, which plots the ratio of the theoretical nucleation rate \( J_{th} \) (using either theory) to the measured nucleation rate \( J_{exp} \). At lower temperatures the kinetic nucleation rate is much closer to the classical rate than to the measured values, but at higher temperatures the situation reverses. The ratio of the theoretical nucleation rate to the measured rate is temperature dependent using either theory, but the factor \( e^{\beta} \) is much larger at the low-temperature end than at high temperatures, thus the kinetic theory tends to mitigate this effect.

Figure 2 shows the results of Schmitt et al. on nucleation of toluene (C_{6}H_{5}). In this case the kinetic theory does dramatically better than the classical theory over the full temperature range of the experiments, regarding both magnitude and temperature dependence.

The results of Strey et al. for the n-alcohol vapors are shown in Figs. 3–5. The consistent trend of these results is that the ratio of theoretical to measured nucleation rates...
shows an exponential temperature dependence, which is less
strong for the kinetic theory than for the classical theory.
For the two highest of these alcohols, pentanol and hexanol
(Fig. 3), the kinetic nucleation rate is closer to the data than
is the classical rate. For the lowest alcohols, methanol and
ethanol (Fig. 5), the data of Strey et al. indicate that both
theories tend to overpredict the nucleation rate, but the clas-
sical rate is closer. The results for ethanol of Schmitt et al.9
are also shown in Fig. 5. These lie below the results for Strey
et al. for unknown reasons. The results for the middle alco-
hols, propanol and butanol (Fig. 4), lie in between the re-
results for the higher and lower alcohols.

Strey et al.15 argue that their results are suspect in all
those cases where the ratio of the classical nucleation rate to
the measured rate exceeds unity. This is because these cases
respond to the highest vapor pressures, in which the heat of
association of oligomers may have significantly perturbed
the temperature in their adiabatic expansion chamber. On
this basis they suggest that the comparison of theory to their
data is not trustworthy for methanol and ethanol, nor for
propanol and butanol at the highest temperatures. If this
argument is correct, we are left to consider only their results
for pentanol and hexanol, and for propanol and butanol at
the lowest temperatures. In all of these cases the kinetic the-
ory predictions lie within about two orders of magnitude
of the measurements, which is probably within the combined
uncertainties of experiment and property values.

SUMMARY AND CONCLUSIONS

The kinetic nucleation theory of Katz and Wiedersich
has been extended to derive a new expression for the rate of
homogeneous nucleation from an ideal supersaturated va-
por. This theory differs from the classical theory of nuclea-
tion primarily in that evaporation rates are evaluated by re-
ferring to the stable equilibrium of a saturated vapor, rather
than to the constrained and metastable equilibrium of a su-
persaturated vapor. The new expression for the nucleation
rate exceeds the classical expression by a factor $e^{\Theta}/S$, where
$\Theta$ is a dimensionless, temperature-dependent surface ten-

dion.

In comparing the new expression to recent data on nu-
cleation rates of hydrocarbons and alcohols, the agreement
was found to be remarkably good for toluene, but inconclu-
sive for the other substances. We believe that the most likely
source for discrepancies between the new expression and ex-
perimental data lies in the physical assumptions of the the-
ory, which at this point are the same as in the classical theory.
In particular, the strong influence of the factor $e^{\Theta}$ highlights
the significance of the capillarity approximation. Values of
$g^*$ for the conditions of the data shown herein varied within
the range 10–100. The assumption that clusters this small
have a surface energy equal to the macroscopic surface ten-
sion of a flat liquid surface is certainly open to question. As
better data become available on the properties of clusters,
however, these can be incorporated into a nucleation theory
which should, we believe, be based on the kinetic rather than
the classical approach.

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