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The Accuracy of the Approximations in Classical Nucleation Theory

E. Richard Cohen[1]

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The mathematical approximations involved in the theory of homogeneous nucleation are shown to produce negligible error in the predicted rates of nucleation.

KEY WORDS: nucleation; condensation; supersaturation; numerical approximation.

In the previous paper(1) J. L. Katz has discussed the corrections to classical nucleation theory which arise from the distinction between a thermodynamic drop of liquid and a "cluster" of molecules. In this paper we shall investigate the mathematical approximations which are inherent in proceeding from the classical theory to the practical working expressions. Although the discussion here will restrict itself to the classical theory, it is expected that the conclusions of the paper will be valid also for any modifications of that theory. In particular, we shall show that there is no significant error in the calculated nucleation rates due to the mathematical approximations which are usually made, and that any errors introduced by the *mathematical* approximations are generally unimportant even for a "critical" nucleus containing as few as ten molecules.

The "classical" theory of nucleation leads to the following expression for the rate of nucleation,

$$J = \beta \Big/ \sum_{i=1}^{\infty} \frac{1}{s_i n_i} \tag{1}$$

where n_i is the density of embryos containing i molecules and s_i is the surface area of such an embryo.

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[1] Science Center/North American Rockwell Corporation, Thousand Oaks, California 91360.

With the assumption that $s_i = s^0 i^{2/3}$, and using the classical expression for the free energy of an embryo, one obtains$^{(1)}$

$$J = \beta s^0 N \Big/ \sum_{i=1}^{\infty} i^{-2/3} \exp[-i \ln S + \gamma i^{2/3}] \equiv \beta s^0 N / I \tag{2}$$

where $\gamma = \sigma\pi^{1/3}(6v_0)^{2/3}/kT$, and S is the supersaturation, P/P_e.

The sum can be evaluated by noting that the maximum term occurs for i approximately equal to $\bar{x} = (2\gamma/3 \ln S)^3 = \bar{u}^3$ which in most instances is much larger than 1. The sum I can therefore be approximated by an integral:

$$I' = \int_0^{\infty} x^{-2/3} \exp[-x \ln S + \gamma x^{2/3}]\, dx = 3 \int_0^{\infty} \exp(\gamma u^2 - u^3 \ln S)\, du \tag{3}$$

The first approximation, the replacement of the sum I by the integral I', can be investigated numerically quite readily. The error in this replacement will be significant only if $\bar{x}$ is small. In such a case one may expand the exponent in Eq. (3) in a power series and obtain a relatively rapidly convergent expression:

$$\begin{aligned} I' &= \int_0^{\infty} x^{-2/3} e^{-x \ln S} \sum (n!)^{-1} (\gamma x^{2/3})^n\, dx \\ &= \sum \frac{\gamma^n \Gamma[(2n+1)/3]}{n!(\ln S)^{(2n+1)/3}} \end{aligned} \tag{4}$$

Equation (4) can be compared with the direct evaluation of the sum in Eq. (2). The results of some numerical calculations are shown in Fig. 1. For all supersaturations the error in replacing the sum by an integral is of little importance for any nucleation rate of practical interest, for which I is in the range 10^{15} to 10^{30}. The small values of I covered by Fig. 1 would correspond to nucleation rates which are physically meaningless. The ratio I'/I differs significantly from unity only for rates of nucleation larger than 10^{24} nuclei cm^{-3} sec^{-1}. At such enormously high rates the central assumption of nucleation theory—the existence of an equilibrium thermodynamic distribution of cluster sizes—must certainly break down. We therefore conclude that, for any realistic situation, the approximation of replacing I by I' causes negligible error in the calculation.

In order to evaluate I' for larger values of $\bar{u} = \bar{x}^{1/3}$, we can write, with $t = u - \bar{u}$

$$I' = 3e^{p/2} \int_{-\bar{u}}^{\infty} \exp[-\tfrac{3}{2}\bar{u}t^2 \ln S - t^3 \ln S]\, dt, \qquad p = \bar{x} \ln S \tag{5}$$

The integrand is approximately Gaussian with a standard deviation of $(3\bar{u} \ln S)^{-1/2}$ in the variable t. This transforms into a relative standard deviation $\sigma_x/\bar{x} = (\tfrac{1}{3}\bar{x} \ln S)^{-1/2}$. The accuracy with which the Gaussian approximates the integrand is therefore determined by the parameter $p = \bar{x} \ln S$. If $\bar{x}/\sigma_x = (2\gamma)^{3/2}/9 \ln S > 3$ there is little error in extending the lower limit of the Gaussian integral to $-\infty$. To do so, however, one must be able to neglect the cubic term in the exponential. This may be done, since for $t = -\bar{u}$ the exponent is $-\tfrac{1}{2}\bar{x} \ln S$. Neglecting the term $t^3 \ln S$ gives an

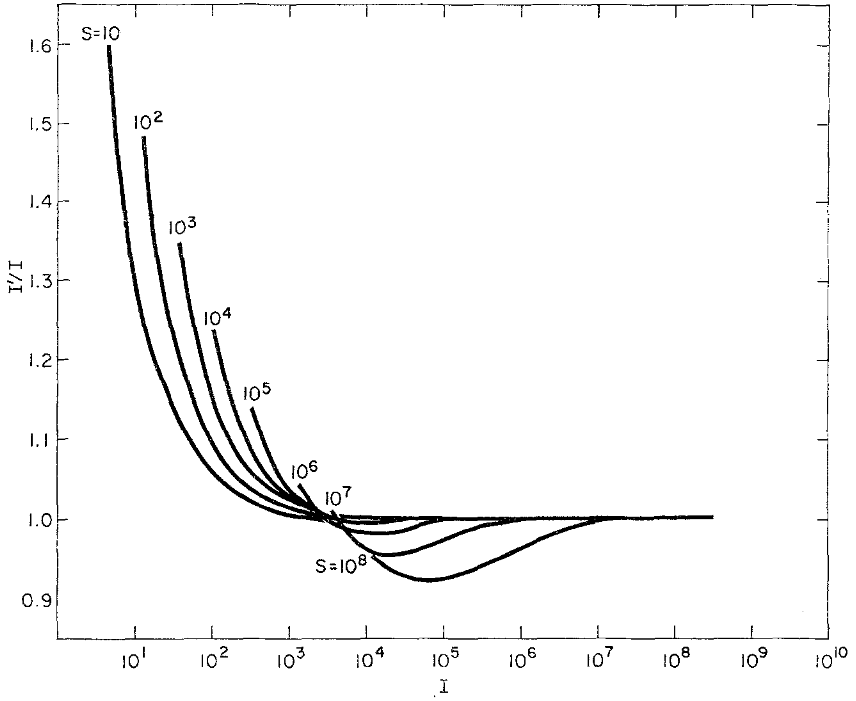

Fig. 1. The ratio of the approximating integral I' [Eq. (3)] to the discrete summation I, for various values of supersaturation S. For each value of S' the curve is plotted only for $x \geqslant 1$. All of the values of I in this figure correspond to unrealistically rapid nucleation rates; for realistic rates and supersaturations the error in replacing the sum by an integral is completely negligible.

exponent $-\frac{3}{2}\bar{x}\ln S$. For $p = \bar{x}\ln S \gg 1$ the relative difference in the two exponentials $e^{-3p/2}$ and $e^{-p/2}$ is extremely large, but since each is still small in comparison with unity little error is introduced in any case.

If we therefore neglect the cubic term in the exponent and allow the lower limit of the integral to go to $-\infty$ we find

$$I' \approx I_0 = \bar{u}(6\pi e^{p}/p)^{1/2}. \tag{6}$$

Equation (6) represents the usual approximation.

In order to evaluate the error in replacing I' by I_0, the integral can be rewritten, by adding and subtracting I_0, in the *exact* form

$$\begin{aligned} I' &= I_0 + 3e^{p/2}\left[\int_{-\bar{u}}^{\infty} e^{-\gamma t^2}[e^{-t^3\ln S} - 1]\,dt - \int_{\infty}^{-\bar{u}} e^{-\gamma t^2}\,dt\right] \\ &= I_0 + 3e^{p/2}\left\{2\int_0^{\bar{u}} [\cosh(t^3\ln S) - 1]\,e^{-\gamma t^2}\,dt - \int_{\bar{u}}^{\infty} e^{-\gamma t^2}[1 - e^{-t^3\ln S}]\,dt\right\} \end{aligned} \tag{7}$$

The integrand in the first integral has a maximum at t^*, where

$$t^* = \bar{u}\tanh(\tfrac{1}{2}t^{*3}\ln S), \qquad 0 < t^* < \bar{u}, \tag{8}$$

at which point the integrand has the value

$$\frac{2t^{*2}\exp(-\gamma t^{*2})}{\bar{u}^2 - t^{*2}}$$

The integral is therefore bounded by

$$0 < 2\int_0^{\bar{u}} e^{-\gamma t^2}[\cosh(t^3 \ln S) - 1]\,dt < \Delta_1 = 4\bar{u}t^{*2}(\bar{u}^2 - t^{*2})^{-1}\exp(-\gamma^{*2}) \tag{9}$$

We can also write for the second integral,

$$\int_{\bar{u}}^{\infty} e^{-\gamma t^2}(1 - e^{-t^3 \ln S})\,dt < \Delta_2 = \frac{e^{-\gamma\bar{u}^2}}{2\gamma\bar{u}} \tag{10}$$

If $t^* \gg \bar{u}$, we can solve Eq. (8) approximately to obtain

$$\tfrac{1}{2}t^{*2}\bar{u}\ln S = \tfrac{1}{3}\gamma t^{*2} = 1 \tag{11}$$

Then $\frac{1}{2}t^{*3}\ln S = \sqrt{2/p}$ is small, justifying the expansion of the hyperbolic tangent leading to (9). A series expansion for the root of (8) can be written:

$$t^* = \bar{u}\sqrt{2/p}\left[1 + \frac{1}{3p} + \frac{17}{30p^2} + \cdots\right]$$

If $p \gg 1$, $\Delta_2 = (\bar{u}/3p)\exp(-3p/2)$ will be much smaller than Δ_1 and we find

$$0 \leqslant (I' - I_0)/I_0 \leqslant \frac{24e^{-3}}{(6\pi p)^{1/2}}[1 + 0(1/p)] \tag{12}$$

Although Eq. (12) provides bounds on the value of I', these bounds are not extremely close. The bound $0.2752(\bar{x}\ln S)^{-1/2}$ gives $(I' - I_0)/I_0 < 0.055$ for $\bar{x}\ln S = 25$, and $(I' - I_0)/I_0 < .0275$ for $\bar{x}\ln S = 100$. The actual values are 0.0121 and 0.002835 and the correct behavior is more nearly proportional to $1/p$ than to $1/\sqrt{p}$.

A more precise evaluation of Eq. (5) can be found by expanding the factor $\exp(-t^3 \ln S)$ in a power series:

$$I' = 3e^{p/2}\int_{-\bar{u}}^{\infty} e^{-\gamma t^2}\left[\sum_{n=0}^{\infty}\frac{(\ln S)^{2n}}{2n!}t^{6n} - \sum_{n=0}^{\infty}\frac{(\ln S)^{2n+1}}{(2n+1)!}t^{6n+3}\right]dt$$

If one now simply interchanges the order of summation and integration, the resultant sums are divergent. We can however obtain an asymptotic expression by carrying the sums to a finite limit and bounding the remainder term. We find

$$I' = 3\sqrt{\frac{\pi}{\gamma}e^p}\left[1 + \sum_{n=1}^{N-1}\frac{(\ln S)^{2n}}{(2\gamma)^{3n}}\frac{(6n-1)!!}{(2n)!} + O\left(\left[\frac{(2N/e)^3}{\bar{x}\ln S}\right]^N\right)\right] + \gamma^{-1/2}o(e^{-p}) \tag{13}$$

In this expression the term containing $o(e^{-p})$ represents the term Δ_2 calculated in Eq. (9), whereas the other "order" term expresses the effect of the truncation of the series expansion. Since for $N \to \infty$ this term is not small but grows without bound, we choose a value of N which is smaller than that value which will make the expression in the parentheses a minimum. Equation (13) is then a valid asymptotic expansion for I'. We find

$$I' = I_0 \left[1 + \frac{5}{18(\bar{x} \ln S)} + \frac{385}{648(\bar{x} \ln S)^2} + \frac{85085}{34992(\bar{x} \ln S)^3} + \cdots \right] \tag{14}$$

Although Eq. (14) is an adequate expression only for $\bar{x} \ln S \gg 1$, this is actually the only region of parameter space which is of practical interest in homogeneous nucleation, for which $\bar{x} \ln S$ is always of the order of 100. For methanol at 300°K, supersaturation varying from 1.54 to 1.77 changes the nucleation rate from 1 $\text{cm}^{-3}\ \text{sec}^{-1}$ to $10^{12}\ \text{cm}^{-3}\ \text{sec}^{-1}$, while $\bar{x} \ln S$ changes only from 125 to 71. As another example, for mercury at the same temperature, S varies from 4.1×10^6 to 88.6×10^6 to produce the same 10^{12} change in nucleation rate, but $\bar{x} \ln S$ is 140 for 1 $\text{cm}^{-3}\ \text{sec}^{-1}$ and 97 for $10^{12}\ \text{cm}^{-3}\ \text{sec}^{-1}$. The value of the summation in Eq. (1), therefore, lies in all cases of practical interest above 10^{10}, in which case the approximation I_0 is accurate to better than 1%.

Figures 2a and 2b show the deviation of the sum I from its asymptotic value I_0 for the range of parameters of practical interest. Figure 2a covers the range of values of S appropriate to water and organic liquids. Figure 2b extends the data to values appropriate to metals such as mercury with large surface tensions. The oscillations in the ratio I/I_0 which are present in Fig. 2b but are absent in Fig. 2a reflect the

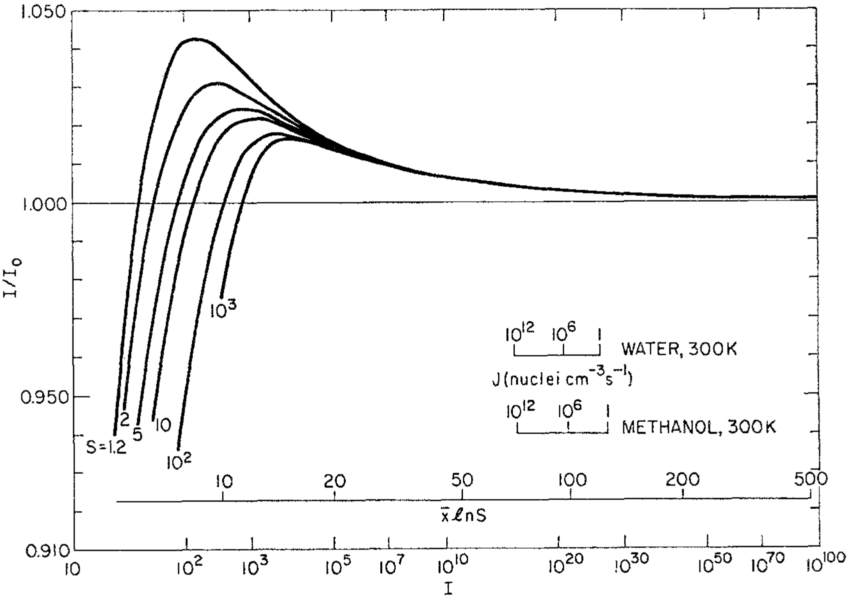

Fig. 2a. The deviation of I from its approximating value I_0, for the range of parameters appropriate to water and organic compounds. In order to indicate the region of practical interest a scale of nucleation rates for water and methanol at 300°K is also indicated.

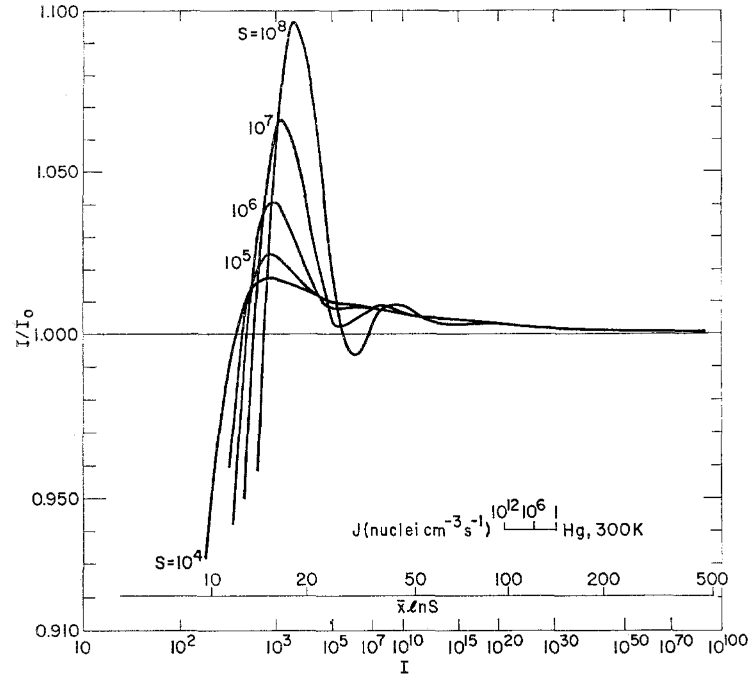

Fig. 2b. The deviation of I from its approximating value I_0, for the range of parameters appropriate to mercury and other high-surface-tension liquids. In order to indicate the region of practical interest a scale of nucleation rates for mercury at 300°K is also indicated.

discrete nature of the sum I. When $\ln S$ is larger than $(2^{2/3} - 1)\gamma - \frac{2}{3}\ln 2 = 0.5874\gamma - 0.4621$, the first term in the summation is the largest. In such a case the replacement of the sum by a Gaussian integral is obviously invalid. It is indeed surprising that even in these extreme situations the mathematical approximation is as good as it turns out to be. In practical situations none of these anomalies are important as indicated by the scales in the figures which indicate the range appropriate to realistic rates of nucleation for typical liquids. For $p \equiv \bar{x}\ln S > 50$ (I roughly larger than 10^{10}) the error introduced by using the asymptotic expression is less than 1 % and decreases with increasing p. For any practical supersaturation the error, for fixed p, is independent of S. Although these conclusions are based on calculations with the classical model, Figs. 2a and 2b should also apply with reasonable validity to any of the nucleation models which are considered by Katz,(1) when expressed in terms of the value of $\bar{x}$, the size of the critical nucleus, calculated for that particular theory.

REFERENCE

1. J. L. Katz, *J. Stat. Phys.* 2(2):137 (1970).