A modified expression for the rate of homogeneous nucleation from an ideal supersaturated vapor was recently derived, in which the rate given by the classical expression was multiplied by a factor $e^\Theta / S$, where $S$ is supersaturation, $\Theta = (\alpha \sigma / kT)$, $\sigma$ is surface tension, and $s$, is monomer surface area. This factor represents a much larger and temperature-dependent correction to the classical expression. Values of $\Theta$ for various substances and realistic temperatures range from about 3 to 50.

This modified expression for the nucleation rate was derived in Ref. 1 as an extension of the “kinetic theory” of homogeneous nucleation proposed by Katz and Wiedersich. Several readers of Ref. 1, beginning with Katz himself, have pointed out to us privately that the modified expression could also have been derived within the context of the classical theory. That is because the factor $e^\Theta / S$ arises as a consequence of writing the Boltzmann expression for the equilibrium cluster distribution self-consistently, regardless of whether the classical or the kinetic theory approaches are followed. The primary purpose of this Comment is to clarify this point, and in so doing to correct the misleading interpretation Ref. 1 may have engendered regarding the source of the modified nucleation rate. A secondary purpose is to point out an interesting paradox concerning the effect of self-consistency on the expression for the evaporation coefficient.

The classical expression for the nucleation rate $J$ can be written in the form

$$ J = C n_e^m, $$

where $n_e$ represents the concentration of clusters containing $g$ monomers, $g^*$ is the critical cluster size, and the superscript $e$ denotes the constrained equilibrium of a vapor at temperature $T$ and supersaturation $S$. The factor $C$ combines a number of terms but is not affected by the proposed correction in the expression for the equilibrium cluster distribution. Clusters in the equilibrium state are assumed to follow a Boltzmann distribution,

$$ n_x^e = n_e \exp \left[ -\frac{\Delta G(g)}{kT} \right], $$

where $\Delta G(g)$ is the Gibbs free energy of cluster formation. Following the simplest model for $\Delta G$, the equilibrium cluster distribution takes the form

$$ n_x^e = n_e \exp \left( -\Theta g^{2/3} + g \ln S \right). $$

This expression is obviously not self-consistent, as it is not satisfied for $g = 1$. Several authors have remarked on this, but the problem has usually been dismissed by arguing that only the value of $n_x^e$ at $g = g^*$ is finally needed. Blander and Katz discussed the problem and formulated a self-consistent expression in general terms of chemical potentials. Equation (3) is made self-consistent by writing

$$ n_x^e = n_e \exp \left( -\Theta (g^{2/3} - 1) \right). $$

Aside from the advantage of self-consistency, the expression for $\Delta G$ implicit in Eq. (4) is justified on thermodynamic grounds following the arguments of Refs. 1 and 4.

The ratio of the cluster distributions given respectively by Eqs. (4) and (3) is

$$ \frac{(n_x^e)^{\text{self-consistent}}}{(n_x^e)^{\text{usual}}} = \frac{\Theta}{S}. $$

With reference to Eq. (1) we thus see that the classical nucleation rate should be multiplied by $\Theta / S$. In Ref. 1 the same result was derived within the context of the kinetic theory, which we believe to be conceptually preferable to the classical theory. It is evident, however, that self-consistency not the kinetic theory is the source of the modification. In view of the simplicity of the self-consistency correction, and of its obvious large effect on the nucleation rate, it is remarkable that the correction, so far as we are aware, had not previously been noticed.

The second part of this Comment concerns the effect of self-consistency on the evaporation coefficient. Classical theory takes as its starting point the expression

$$ J_g = \beta s_g n_g - E_g n_g, $$

where $J_g$ is the net rate of g-mer formation, $\beta$ represents the monomer flux to the surface, $s_g$ is the surface area of g-mer, and $E_g$ is the g-mer evaporation coefficient (s$^{-1}$). The whole point of introducing the equilibrium cluster distribution is as a means of replacing $E_g$. By referring to an equilibrium state at which $J_g = 0$, and substituting the usual kinetic theory expression for $\beta$, we obtain

$$ E_g = \frac{kT}{2 \pi m_1} s_g \left( n_{g-1}^e \right) \left( \frac{n_g^e}{n_{g-1}^e} \right), $$

where $m_1$ is the mass of a monomer.

Now consider three alternative expressions for the equilibrium cluster distribution: (1) the usual expression in classical theory, Eq. (3); (2) the self-consistent expression given by Eq. (4); (3) the self-consistent expression for the kinetic theory, given in Ref. 1 as

$$ n_x^e = n_e \exp \left( -\Theta (g^{2/3} - 1) \right), $$

where $n_e$ denotes the equilibrium monomer concentration for the saturated vapor ($S = 1$) at temperature $T$. 

Comment on: “Self-consistency correction to homogeneous nucleation theory”

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Noting that in the classical theory \( n_i^c = n_i \) whereas in the kinetic theory \( n_i^k = n_i = n_i/S \), we find upon inserting these three expressions into Eq. (7) that they all yield the same result for the evaporation coefficient:

\[
E_s = \left( \frac{kT}{2\pi m_1} \right)^{1/2} s_{z-1} n_z \exp\{\Theta (g^{2/3} - (g - 1)^{2/3})\}.
\]                      (9)

This result is due to the taking of the ratio of equilibrium cluster distributions in Eq. (7), so that the unity terms introduced by the self-consistency correction cancel. However the mathematical derivation of the nucleation rate results in the elimination of this ratio in favor of \( n_i^z \) itself, and therefore the self-consistency correction does have an effect. That is, the self-consistency correction does not affect either the forward or backward rates, yet it changes the nucleation rate. This paradox may lead one to question whether the self-consistency correction ought indeed to affect the nucleation rate, or whether instead the result is an artifact of the mathematical approximations in the classical theory. One way to answer this question is to compare the classical expression with a numerical solution to the time-dependent set of rate equations for the populations of monomers, dimers, trimers, etc., using Eq. (9) for the evaporation coefficient and the usual kinetic theory expression for condensation and coagulation coefficients. (Note that this is more exact than classical theory, which neglects cluster-cluster interactions.) I and my colleagues Chiu and McMurry have recently performed such a comparison. We find that the effective nucleation rate obtained by the numerical solution does not agree well at all with the classical expression, but that the agreement is excellent when the classical expression is multiplied by \( e^{\phi_i}/S \).

This result supports the validity of the modified nucleation rate. It also supports the validity of the set of mathematical approximations made in nucleation theory, including the outcome that self-consistency does matter in the final result even though it does not affect the evaporation coefficient.

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\[5\] The effect is obvious unless one is tempted to neglect unity in comparison to \( g^{2/3} \) in Eq. (4), which would lose the factor \( e^{\phi_i} \).