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Analysis of experimental nucleation data for silver and SiO using scaled nucleation theory

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The experimental vapor phase nucleation data of Nuth *et al.*, for silver [J. A. Nuth, K. A. Donnelly, B. Donn, and L. U. Lilleleht, J. Chem. Phys. **77**, 2639 (1982)] and SiO [J. A. Nuth and B. Donn, J. Chem. Phys. **85**, 1116 (1986)] are reanalyzed using a scaled model for homogeneous nucleation [B. N. Hale, Phys. Rev. A **33**, 4156 (1986)]. The approximation is made that the vapor pressure at the nucleation site is not diminished significantly from that at the source (crucible). It is found that the data for $\ln S$ have a temperature dependence consistent with the scaled theory $\ln S \approx \Gamma \Omega^{3/2} [T_c/T - 1]^{3/2}$, and predict critical temperatures 3800 ± 200 K for silver and 3700 ± 200 K for SiO. One can also extract an effective excess surface entropy per atom $\Omega = 2.1 \pm 0.1$ and an *effective* surface tension $\sigma \approx 1500 - 0.45T$ ergs/cm^2 for the small silver clusters (assuming a range of nucleation rates from 10^5 to 10^{11} cm^{-3} s^{-1}). The corresponding values for SiO are $\Omega \approx 1.7 \pm 0.1$ and $\sigma \approx 820 - 0.22T$ ergs/cm^2 (assuming a range of nucleation rates from 10^9 to 10^{12} cm^{-3} s^{-1}).

I. INTRODUCTION

The motivation for this work has been to examine the application of a scaled nucleation model[1] to analysis of experimental nucleation data for refractory materials. Recent vapor phase homogeneous nucleation data taken by Nuth *et al.* for silver[2] and SiO[3] appeared to be inconsistent with classical nucleation theory. In this paper, we apply the scaled version of the classical nucleation model to the experimental data for silver and SiO.

In the scaled model for vapor to liquid nucleation, the scaled surface tension $\sigma_0[T_c - T]$, the excess surface entropy per molecule Ω, and critical point quantities (denoted by subscript c) are used to cast the homogeneous nucleation rate into an approximately material independent form.[1] This formalism predicts the following expression for the supersaturation ratio S required for a fixed nucleation rate J:

$$\ln S \approx \Gamma \Omega^{3/2} [T_c/T - 1]^{3/2}. \qquad (1)$$

The Γ is a weak function of T and S and approximately equal to 0.53 for a nucleation rate of 1 cm^{-3} s^{-1}. One can also apply Eq. (1) to data for $\ln S$ and extract information about Ω and T_c. In Ref. 1, it was shown that Eq. (1) agrees with experimental $\ln S$ homogeneous nucleation data for a wide variety of substances (water, toluene, nonane, ethanol, *n*-butylbenzene, sulfur hexafluoride, carbon tetrachloride, chloroform, octane, argon, and acetic acid).[1] In the present analysis, Eq. (1) is used to reanalyze homogeneous vapor phase nucleation data for silver[2] and SiO[3].

The experiments by Nuth *et al.*[2,3] use a crucible containing the vaporizing material (silver or SiO) enclosed within a mullite furnace. The site of nucleation (a distance d above the crucible) is determined by visual observation of scattered light for a xenon arc lamp beam which crosses the furnace above the crucible. In the original analysis of Refs. 2 and 3, the authors assumed a hemispherical cap of vapor at the top of the crucible acting as the vapor source with the vapor density falling off radially like $1/d^2$. Temperature "measurements" (via four thermocouples placed just outside the nucleation region) were made in the system during condensation. However, thermocouples could not be placed in the nucleation region during the runs since they would have provided heterogeneous nucleation sites. Temperature calibrations (to provide interpolation from the measured temperatures), therefore, were made after the runs with a total of nine thermocouples placed inside and outside the nucleation region. These calibrations could be (and were) made with and without small amounts of material in the heated crucible—and showed no effect due to evaporating source material. Comparison of d with the temperature measurements and calibrations allowed determination of the nucleation site temperature T_f.[3]

The analysis of Refs. 2 and 3 also assumed classical nucleation theory and a temperature-independent expression for the surface tension. The results suggested that the nucleation of silver vapor could not be described adequately by classical homogeneous nucleation theory[4,5]; furthermore it appeared that the nucleation of silver is pressure dependent and possibly affected by the silver dimerization reaction. [The data were taken at two filler gas hydrogen pressures (500 and 250 Torr) and using two different crucibles labeled "old" and "new."]

In analyzing the data as reported in Refs. 2 and 3 using the scaled theory and Eq. (1), it was found that a plot of $(\ln S)^{2/3}$ vs $1/T$ predicted critical temperatures which were about 1500 K for both Ag and SiO. These T_c values are smaller than the boiling temperatures and are unphysical. The small value of T_c arises primarily because the reported

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values of S at the T_f in these experiments are about a factor of 10 smaller than one would expect for materials with critical temperatures of the order of 4000 K.[1] Since it was found in Ref. 1 that the temperature dependence in Eq. (1) agrees extremely well with homogeneous nucleation data for a broad range of materials, we decided to reassess the vapor pressure assumptions of Refs. 2 and 3. It was noted that the authors calculated the vapor pressure at the nucleation site from $(r_0^2/d^2)\ P_0(T_{\rm cru})$, where r_0 is the radius of the inner crucible and P_0 is the equilibrium vapor pressure at the crucible temperature. Since for most data in the experiment $r_0/d \approx 1/4$, the vapor pressure at the nucleation site is roughly reduced by a factor of 16 over the vapor pressure at the source.

This prompted us to examine the data with a much simpler approximation for the vapor pressure; that is, we assumed that the vapor pressure was given to first order by that of the source. When this approximation was used, we found that the predicted critical temperatures are about 3800 K—considerably more in line with what one expects. The question remains, what physical condition in the apparatus would give rise to vapor densities which at the nucleation site are nearly undiluted from those at the source?

One possibility is that the vapor (rather than diffusing radially) is confined to a column above the crucible by upward convection of the H_2 filler gas parallel to the outer cylindrical surface of the hot crucible. This convection of H_2 filler gas would exist independently of the condensing species and would be present during the temperature calibrations. Thus we see no reason to suspect that, given the presence of the confining convection, that the temperature calibration (and the temperature in the nucleation region) should be different from that reported in Refs. 2 and 3.

The original experimenters commented that there were no indications of thermally driven convective currents. However, the apparatus (with furnace walls which obscure all but a very small part of the condensation region) does not appear to permit a definitive statement about the presence or absence of convection. Since the crucible is at a higher temperature (1200–1500 K) than the furnace walls (400–600 K), one would expect a convective upward flow of the H_2 gas parallel to the hot cylindrical crucible. This flow should continue a small distance above the crucible and partially contain the vapor rising from the crucible. In fact, just such a constrained plume of condensing material has been observed in recent exploratory experiments of Mg and Zn nucleation using similar apparatus—but with a full view of the vapor region.[6]

We also note that the condensing species have molecular weights 22 and 54 times greater than the H_2 background gas (inhibiting diffusion of the condensing species relative to the H_2), that the vapor source is extended (1 in. in diameter in the Ag experiment) and can be 0.25–0.5 in. below the top of the crucible, and that the ambient H_2 pressures are moderatly large for the Ag data (250 and 500 Torr). In short, the probable "confinement" effect of the H_2 convection parallel to the hot crucible, the geometry, the molecular weights, and the ambient pressure all suggest a more nearly uniform vapor pressure just above the crucible. In this paper, we make the simple assumption that in the condensation region the vapor pressure of the nucleating species is given, to first order, by that at the source.

In this note, we shall discuss the scaled analysis and the results for the silver data in Sec. II and the corresponding results for the SiO data in Sec. III. Comments and conclusions are given in Sec. IV.

II. SILVER DATA

In this reanalysis, we assume that the silver vapor pressure at the nucleation site is given by the equilibrium vapor pressure at the crucible temperature $T_{\rm cru}$: $\log(P_0) = (-14\,464/T_{\rm cru}) + 8.925$, where P_0 is in Torr. (See the discussion in the paper describing the original apparatus.[3]) Using the latter approximation, the supersaturation ratio at the nucleation site is given by $\ln S = -33\,305(1/T_{\rm cru} - 1/T_f)$. It is noted that both the nucleation site temperature and the crucible temperature vary at each data point.

A plot of $(\ln S)^{2/3}$ vs $1/T_f$ is shown in Fig. 1. The scaling law given by Eq. (1) predicts a linear plot, with the ratio of slope to intercept giving the critical temperature T_c. For these data, we find $T_c = 3800 \pm 200$ K—surprisingly close to what one expects from the simple estimate $T_c \approx T_{\rm boiling}/0.6 \approx 4100$ K.[4] As far as we are aware there are no reported experimental values of a critical temperature for silver (and few attempts to measure T_c for metals in general).

Since Γ in Eq. (1) depends on the logarithm of the nucleation rate (which was only estimated for the data points in this experiment), only an approximate value for Ω can be calculated. Assuming that the nucleation rates range

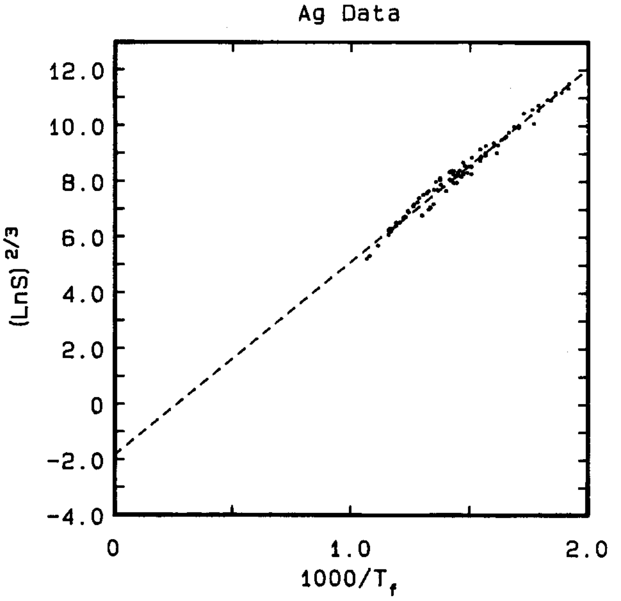

FIG. 1. Natural logarithm of the supersaturation ratio to the 2/3 power as a function of $1000/T$ (where T is in K) for the silver vapor from the data of Nuth and Donn (Ref. 2) (dots). The vapor pressure at the nucleation site is assumed to be given by the crucible temperature. The (least-square fit) dashed line has an intercept (-1.82) and slope (6.93) which predict a critical temperature ≈ 3800 K for silver. Assuming that the average nucleation rate nucleation rate is approximately 10^8, a value of $\Omega \approx 2.1$ is predicted.

from 10^5 to 10^{11} cm^{-3} s^{-1}, and using $T_c = 3800$ K, $\Omega = 2.1 \pm 0.1$ is obtained. This value is consistent with the excess surface entropy per molecule for a nonassociated liquid[1] and predicts an "effective" surface tension for the small liquid silver clusters $\sigma \approx 1500 - 0.40T$ ergs/cm^2. The latter expression for σ assumes bulk liquid density (9.07 g/cm^3)[5] for the clusters. For all the data points, an average value of the nucleation rate $\approx 10^8$ cm^{-3} s^{-1} is predicted and the predicted average Γ for use in Eq. (1) is 0.81.

One can estimate the number of silver atoms in the critical cluster n^* from the expression[1]

$$n^* = [2A/3B]^3, \tag{2}$$

where $A = [36\pi]^{1/3}\Omega[T_c/T - 1]$ and $B \equiv \ln S$. Using $T_c = 3800$ K and $\Omega = 2.1$ Eq. (2) gives a value of n^* ranging from 2 to 6 for the experimental silver data. Since we have approximated the partial pressure of silver at the point of nucleation by that above crucible (clearly giving an upper limit to S), the "true" value of n^* could be expected to be somewhat larger.

III. SiO DATA

The SiO data are similarly analyzed assuming the SiO vapor pressure at the nucleation site is approximated by the SiO equilibrium vapor pressure at the crucible temperature [see Eq. (1) of Ref. 3]. Figure 2 shows $(\ln S)^{2/3}$ vs $1000/T$ for combined data taken at three ambient H_2 pressures 20, 35, and 50 Torr.

For the data of Fig. 2, the scaled analysis predicts a T_c for SiO $= 3700 \pm 200$ K. Assuming nucleation rates ranging from 10^9 to 10^{12} cm^{-3} s^{-1} for the SiO experimental data, an approximate value of $\Omega = 1.7 \pm 0.1$ is predicted. The corresponding effective surface tension for the small SiO clusters (assuming a bulk liquid density ≈ 2 g/cm^3) is $\sigma = 820 - 0.22T$ ergs/cm^2 or ≈ 670 ergs/cm^2 at $T = 700$ K. Critical cluster sizes predicted from Eq. (2) range from three to four over the experimental SiO data points. As in the case of the Ag data, the $\ln S$ values are overestimated and n^* values could be larger.

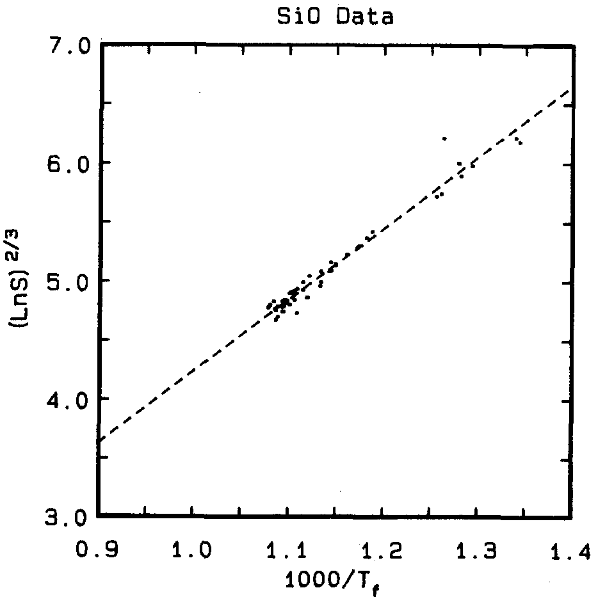

FIG. 2. Natural logarithm of the supersaturation ratio to the 2/3 power as a function $1000/T$ (where T is in K) for the SiO vapor from the data of Nuth and Donn (Ref. 3) (dots). The vapor pressure at the nucleation site is assumed to be given by the crucible temperature. The (least-square fit) dashed line has an intercept (-1.58) and slope (5.84) which predict a critical temperature ≈ 3700 K for SiO. Assuming that the average nucleation rate is approximately 10^{11}, a value of $\Omega \approx 1.7$ is predicted.

IV. COMMENTS

The reanalysis of the silver and SiO nucleation data[2,3,6] suggests that the vapor pressure in these experiments is more nearly given by the equilibrium vapor pressure at the source. The reanalysis with the above simple approximation appears to bring the data into good agreement with the scaled classical nucleation theory. In addition, the present analysis predicts critical temperatures for both silver and SiO near 3800 K and critical clusters sizes in these experiments of the order of two to six atoms/molecules. The previous analysis[2,3] predicts a negative surface tension for the 500 Torr Ag data, suggests the failure of classical nucleation theory for refractory materials, and [using Eq. (1)] implies nonphysical critical temperatures near 1500 K for both materials.

We note the scaled formalism does not use bulk surface tension, or bulk liquid number density $\tilde{n}$. The latter quantities appear in the scaled model as a ratio $\sigma/[k\cdot\tilde{n}^{2/3}] = \Omega[T_c - T]$ (where k is the Boltzmann constant) and are replaced by Ω. Furthermore, the free energy of formation is expressed in terms of n, the number of atoms/molecules in the cluster. This use of n, together with an effective Ω for small clusters, extends the physically meaningful range of the model to smaller clusters than would be appropriate in the usual classical nucleation theory. Even so, the calculated values for n^* (2 to 6) are small and should be viewed as an order of magnitude prediction. One consequence of using Ω derived from small cluster data is that the resulting expression for effective surface tension will not necessarily agree with bulk surface tension values. However, the effective surface tension predicted for Ag using $\sigma = 1500 - 0.40T$ gives 1000 ergs/cm^2 at 1273 K. This is to be compared with 916 ergs/cm^2 reported for liquid silver.[5]

Finally, it is noted that the smaller value of $\Omega \approx 1.7$ for SiO is consistent with bulk liquid Ω values for polar materials (the bulk water Ω value ≈ 1.5). The value $\Omega \approx 2.1$ for Ag reflects the larger excess surface entropy per atom characteristic of normal (nonassociated) liquids. For example, bulk liquid Ω values range from 2.12 (for argon and toluene) to 2.35 (for nonane).[1] In this sense, the Ω values derived via the scaled model from the data of Nuth *et al.*[2,3] are surprisingly reasonable. We note that in the case of the SiO experiment, solidlike smoke particles are observed in the nucleation region. However, the results of this scaled nucleation model analysis imply that the nucleation process is vapor to liquid. The Ω values for vapor to solid nucleation are expected to be about 20%–30% higher than those predicted in this work for the SiO and silver nucleation embryos.[1] After nucleation of the small liquidlike clusters, the final solidlike smoke particles would emerge via growth and solidification. Small clusters (of the order of 5 to 20 atoms/

molecules) are in any case more easily supercooled, and a liquidlike state at temperatures below the bulk melting point is not unexpected.[7]

In summary, the present study of the Ag and SiO data suggests that the scaled classical nucleation model can be useful in analyzing the nucleation of refractory materials. However, it is clear that data on the nucleation of a wide variety of refractory systems are needed before theoretical treatment of this problem can be evaluated conclusively.

ACKNOWLEDGMENT

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