

Homogeneous nucleation with magic numbers: Aluminum

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Homogeneous nucleation of clusters that exhibit magic numbers is studied numerically, using as an example aluminum at 2000 K, based on recent calculations of free energies [Li *et al.*, *J. Phys. Chem. C* **111**, 16227 (2007)] and condensation rate constants [Li and Truhlar, *J. Phys. Chem. C* **112**, 11109 (2008)] that provide a database for Al_i up to $i=60$. The nucleation behavior for saturation ratios greater than about 4.5 is found to be dominated by a peak in the free energy change associated with the reaction $i\text{Al} \rightarrow \text{Al}_i$ at $i=55$, making it the critical size over a wide range of saturation ratios. Calculated steady-state nucleation rates are many orders of magnitude lower than predicted by classical nucleation theory (CNT). The onset of nucleation is predicted to occur at a saturation ratio of about 13.3, compared to about 5.1 in CNT, while for saturation ratios greater than about 25 the abundance of magic-numbered clusters becomes high enough to invalidate the assumption that cluster growth occurs solely by monomer addition. Transient nucleation is also predicted to be substantially different than predicted by CNT, with a much longer time required to reach steady state: about 10^{-4} s at a saturation ratio of 20, compared to about 10^{-7} s from CNT. Magic numbers are seen to play an important role in transient nucleation, as the nucleation currents for clusters of adjacent sizes become equal to each other in temporally successive groups, where the largest cluster in each group is the magic-numbered one. © 2009 American Institute of Physics.
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I. INTRODUCTION

In the theory of homogeneous nucleation of condensed-phase particles from a supersaturated vapor, a key role is played by the change in Gibbs free energy ΔG_i associated with the formation of a molecular cluster of size i (an “ i -mer”) from i molecules of the monomer vapor. In classical nucleation theory (CNT)^{1–4} ΔG_i is a smooth function of i , with a single maximum at a size known as the “critical size” which determines the thermodynamic bottleneck to nucleation. While CNT and its variants have provided a qualitatively powerful description of homogeneous nucleation, experimental tests of the theory have mostly involved liquids such as water and organic molecules.

On the other hand, it is less clear that CNT is relevant to the nucleation of various inorganic substances that exhibit magic numbers, meaning that clusters of specific sizes (the “magic numbers”) are more abundant, at equilibrium, than clusters of adjacent sizes. Magic numbers have been observed, for example, in substances such as silicon,⁵ carbon,⁶ metals,^{7–13} and noble gases.¹⁴ In particular, ΔG_i may have multiple local minima at the locations of the magic numbers, and local maxima at the locations of the “antimagic numbers.” This observation may have profound implications for nucleation theory, yet with few exceptions it has been ignored. A key objective of this paper is to explore these implications.

Magic numbers can be identified in various ways. In

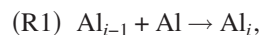
experiments, if a particular size cluster is found with especially high probability, relative to clusters with one more or one less monomer, experimentalists often label that size as a magic number,^{15,16} and cluster sizes with especially low abundance are sometimes called antimagic.¹⁷ Depending on the experiment, the concentrations observed for various cluster sizes may be controlled by either thermodynamics or kinetics; in the former case, these magic numbers correspond to minima in the free energy as a function of cluster size.¹⁸ Theoretical models are often used to “explain” magic numbers, and these are usually based on a special stability for the lowest-energy structure of a given cluster size. This special stability may in turn be explained by geometric or electronic arguments, such as perfect polyhedral symmetry or the filling of a closed shell of orbitals, and these arguments lead to predictions of the magic numbers.^{19–21} (Note though that not all studies of the size dependence of the electronic structure of metal clusters emphasize magic numbers.²²) However, the experiments are always at finite temperature and sometimes at a high temperature, and one needs to consider thermal energy and entropy as well as the energy of the lowest-energy structure.^{23–30} Thus the magic numbers determined from the energy of the lowest-energy structure need not agree with the magic numbers determined from free energies or from kinetically controlled experiments.¹⁸ In the present work we use the term “magic numbers” always to refer to local minima of the profile of free energy versus cluster size. The local maxima of the free energy profile will be called “antimagic numbers.”

Bahadur and McClurg¹³ considered homogeneous nucle-

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ation of monovalent metals (Li, Na, K, Rb, Cs, Cu, Ag, and Au), all of which have magic numbers. Using an approximate jellium model to account for the effects of electronic shell structure they obtained estimates of ΔG_i as a multi-peaked function of i , and used these estimates to calculate steady-state nucleation rates. Their model produced much better agreement than CNT with experimental data on nucleation of sodium³¹ and cesium.^{32,33}

In this paper we consider nucleation of aluminum, a trivalent metal. Our focus on aluminum is motivated by recent work of Li *et al.*,²³ who calculated the standard Gibbs free energy of stepwise addition $\Delta G_{i-1,i}^0$, i.e., the free energy change at standard pressure p^0 for the condensation reaction



up to size $i=60$, for temperatures in the range 1500–3000 K. Since our goal is to elucidate the qualitatively new features that arise when one uses such realistic data as input, rather than to make quantitative studies as a function of temperature, it is sufficient for our purposes to consider a single temperature, and we chose 2000 K, near the midpoint of the range where the calculations of Ref. 23 are most complete. The calculations of Ref. 23 involved Monte Carlo direct simulation of equilibrium constants, employing four validated potential energy functions. High-level terms were used to correct for known deficiencies in these functions with regard to the potential energy differences of the global minima and the contributions of electronic excitation and isomeric-rovibrational terms. These calculations are in general more accurate than the jellium model used by Bahadur and McClurg,¹³ as the latter considers only the electronic shell structure and ignores vibrational contributions and geometric configuration. At a temperature of 2000 K, all the clusters considered here are above their melting temperature³⁴ (at least for $i > 9$; for smaller clusters it becomes meaningless to discuss phase). Thus they are liquidlike particles not solid particles. A key element of the work of Li *et al.*²³ is that the results for given size of cluster do not correspond simply to small vibrations around the lowest-energy equilibrium structure, as if one had assumed the clusters to be nanosolids; the free energy computations include isomeric contributions from all structures low enough in energy or high enough in entropy to contribute to an equilibrium ensemble average.²³ In fact the magic numbers from the point of view of free energy are not the same as those ones would infer from the internal energies of the lowest-energy structures.^{18,19} One should keep in mind that the current state of practical theoretical methods does not allow one to produce fully reliable free energies. Nevertheless, to our knowledge, the Li *et al.*²³ results constitute both the most accurate and most extensive database of cluster Gibbs free energies that is currently available for any metal. Furthermore, they lead to qualitatively new features in the character of the nucleation process, and the existence and character of these features does not depend strongly on the precise values of the free energy data. They depend mainly on the free energy not being a smooth or monotonic function of cluster size.

By detailed balance, the ratio of the forward to the backward rate constant is the equilibrium constant, which can be

calculated from the free energy of reaction. The free energies obtained by Li *et al.*²³ include contributions from higher-energy isomers and higher electronic states as well as corrections for the difference between the highest-level affordable electronic structure calculations and the electronic energies implicit in the analytic potentials used for the molecular dynamics simulations. Recently Li and Truhlar³⁵ calculated values of rate constants of condensation reactions of Al clusters. While that work also included calculations of free energies, the emphasis was on rate constants, and no attempt was made to include all significant contributors to the free energies. The association rates are expected to be relatively insensitive to these higher-level corrections, but the dissociation rate constants would not be insensitive. Thus the most accurate results are obtained by combining the association rate constants of Li and Truhlar³⁵ with the equilibrium constants of Li *et al.*,²³ which can then be used to calculate the dissociation rate constants from the association ones.

In this work we use these data to predict steady-state nucleation rates as well as the transient homogeneous nucleation behavior of aluminum at 2000 K. We compare these results to the predictions of classical theory, and we draw general conclusions regarding the homogeneous nucleation behavior of magic-numbered substances.

Homogeneous nucleation of aluminum is of practical interest, because aluminum nanoparticles are used for applications such as electronics,^{36,37} detection of biomolecules,³⁸ plasmonics,³⁹ as a solid fuel,^{40–44} and to enhance the properties of various nanocomposites.^{45–47} A number of high-temperature gas-phase processes are used to synthesize aluminum nanoparticles, including electric arcs,⁴⁸ thermal plasmas,⁴⁹ inert gas condensation⁵⁰ and aerosol flow reactors,⁵¹ and aluminum nanoparticles can be inadvertently produced as metal fumes in processes such as welding⁵² and high-speed milling.⁵³

Several investigators have modeled the homogeneous nucleation of aluminum from its vapor.^{51,54–56} These models have used either CNT^{51,54} or a size-dependent surface tension that is a monotonically increasing function of particle size,⁵⁵ or only considered low-temperature conditions where evaporation from clusters is negligible.⁵⁶ These previous models ignore the fact that aluminum clusters exhibit magic numbers. To our knowledge, no experimental studies of homogeneous nucleation rates of aluminum have been reported.

II. HOMOGENEOUS NUCLEATION IN THE CONDENSATION-EVAPORATION REGIME

Most homogeneous nucleation theory is concerned with the “condensation-evaporation regime,” in which cluster growth can be assumed to occur only by addition of single monomers, and cluster growth reactions up to some critical size are reversible. The boundaries of this regime are determined by the vapor saturation ratio

$$S \equiv \frac{p_1}{p_s(T)}, \quad (1)$$

where p_1 is the partial pressure of the monomer vapor and $p_s(T)$ is its equilibrium vapor pressure at temperature T . The condensation-evaporation regime exists for values of S greater than unity but not so high as to cause all condensation reactions down to dimerization to become effectively irreversible.⁵⁷ High supersaturations can also cause the assumption that cluster growth occurs only by monomer addition to break down, as the abundance of clusters larger than the monomer can become comparable to or larger than that of the monomer. The upper bound on S for the condensation-evaporation regime to apply depends on the substance and on temperature.

Assuming that one is in the condensation-evaporation regime, then cluster growth proceeds through a series of reactions of the form given by (R1). Let A_i represent an i -mer of a condensable substance A. The forward rate $R_{f,i}$ of reaction (R1), applied to substance A, can be written as

$$R_{f,i} = k_{f,i} n_{i-1} n_1, \quad i \geq 2, \quad (2)$$

where $k_{f,i}$ is the rate constant for the reaction in the forward direction and n_i represents the number density of A_i . The reverse or backward rate $R_{b,i}$ of (R1) can likewise be written as

$$R_{b,i} = k_{b,i} n_i, \quad i \geq 2, \quad (3)$$

where $k_{b,i}$ is the reverse rate constant for reaction (R1). Here (and throughout) we assume that the system total pressure is sufficiently high that (R1) is in the high-pressure limit where $k_{b,i}$, the rate constant for unimolecular decomposition, is not affected by pressure falloff effects. Similarly isothermal nucleation is assumed. That is, it is assumed that the total pressure is sufficiently high, and the condensable vapor sufficiently dilute with respect to an inert background gas, that the heat of condensation is rapidly accommodated by collisions with molecules of the background gas.

The nucleation current J_i for each size i , defined by

$$J_i \equiv k_{f,i} n_{i-1} n_1 - k_{b,i} n_i, \quad i \geq 2, \quad (4)$$

represents the net transfer rate from out of size $(i-1)$ and into size i , due solely to condensation/evaporation reactions of the form (R1). Then the net rate of change of the i -mer number density attributable to all such condensation/evaporation reactions is given by

$$\frac{dn_i}{dt} = J_i - J_{i+1}, \quad i \geq 2. \quad (5)$$

For values of i up to some arbitrarily large size M , Eqs. (4) and (5) constitute $(M-1)$ coupled differential equations for the variables n_i and J_i that, with appropriate initial and boundary conditions, can be integrated in time to predict the transient nucleation behavior, that is, the evolution of the cluster number densities and nucleation currents at each size. If M is sufficiently large, then for the case of fixed monomer concentration one has the condition that n_M becomes vanishingly small in comparison to n_1 , and the choice of the value of M makes negligible difference in the results.

If the monomer number density and temperature are held constant then the system eventually reaches a steady state, such that

$$\frac{dn_i}{dt} = 0, \quad i \geq 1. \quad (6)$$

From Eqs. (5) and (6) it follows that the steady-state nucleation currents for all sizes i are equal to each other

$$J_2 = J_3 = J_4 = \dots = J_i = \dots = J_M = J_{ss}, \quad (7)$$

where J_{ss} is the steady-state nucleation rate.

One can define an equilibrium constant for (R1) in dimensionless form by

$$K_{i-1,i} \equiv \frac{n_i/n^0}{(n_{i-1}/n^0)(n_1/n^0)}, \quad (8)$$

where n^0 is defined as

$$n^0(T) \equiv \frac{p}{kT}. \quad (9)$$

From thermodynamics,

$$K_{i-1,i} = \exp\left(-\frac{\Delta G_{i-1,i}^0}{kT}\right), \quad (10)$$

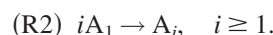
where k is the Boltzmann constant. From the law of mass action the forward and reverse rate constants of (R1) are related to each other by

$$\frac{k_{f,i}}{k_{b,i}} = \frac{K_{i-1,i}}{n^0}. \quad (11)$$

Using these relations to substitute for the reverse rate constants in (R1) in favor of the equilibrium constants, and, with the aid of a recursion relation, summing all such equations for values of i up to M , one obtains an expression for the steady-state nucleation rate in the form of a summation that can be written as⁵⁸

$$J_{ss} = n_1^2 \left\{ \sum_{i=1}^M \left[k_{f,i+1} \exp\left(-\frac{\Delta G_i(p_1)}{kT}\right) \right]^{-1} \right\}^{-1}, \quad (12)$$

where ΔG_i is the free energy change associated with the overall reaction



We refer to ΔG_i as the “free energy of multary association,” as “multary” is the generalization of binary, ternary, quaternary, etc.

In CNT, Eq. (12) is an intermediate result for the steady-state nucleation rate. This theory assumes the capillarity model as a means to estimate ΔG_i . In the “self-consistent” version of the theory⁵⁹ assumed herein, which sets ΔG_i for the monomer to 0, the result for ΔG_i is given by

$$\frac{\Delta G_i(S,T)}{kT} = (i^{2/3} - 1)\Theta - (i-1)\ln S. \quad (13)$$

Here Θ is a dimensionless surface tension defined by

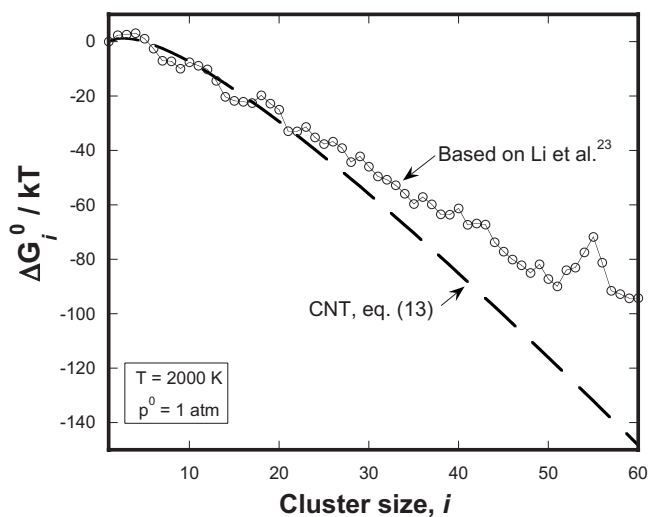


FIG. 1. Standard Gibbs free energy of multistep association ΔG_i^0 of Al clusters at 2000 K. Symbols show results based on calculations in Li *et al.* (Ref. 23). Solid line shows self-consistent classical model, Eq. (13), at $p_1 = p^0 = 1$ atm, corresponding to $S = 156.4$.

$$\Theta \equiv \frac{\sigma s_1}{kT}, \quad (14)$$

where σ represents surface tension, assumed in CNT to be the same as for the bulk liquid in equilibrium with its vapor, and s_1 is the surface area of a monomer.

For the condensation rate constants $k_{f,i}$, CNT assumes that the monomer flux to an i -mer is given by hard sphere gas kinetic theory for the flux of molecules to a stationary surface, and assumes unity sticking coefficients. It then converts the summation over discrete variables in Eq. (12) to an integral over an assumed continuous function. The final result can be written

$$J_{ss} = A \frac{n_1^2}{S} \exp \left[\Theta - \frac{4}{27} \frac{\Theta^3}{(\ln S)^2} \right], \quad (15)$$

where A is a constant (for a given substance at given temperature) given by

$$A = \frac{d_1^2}{6} \sqrt{\frac{2\sigma s_1}{m_1}}, \quad (16)$$

where d_1 and m_1 are respectively the monomer diameter and mass.

If more accurate data than given by CNT are available for ΔG_i and $k_{f,i}$, these can be used directly in Eq. (12) to calculate the steady-state nucleation rate.

III. PROPERTIES OF ALUMINUM CLUSTERS

As (R2) is equivalent to a sequence of monomer addition reactions, the free energy of multistep association, ΔG_i of (R2), can be related to the free energies of stepwise addition, $\Delta G_{i-1,i}$ of (R1), by the relationship

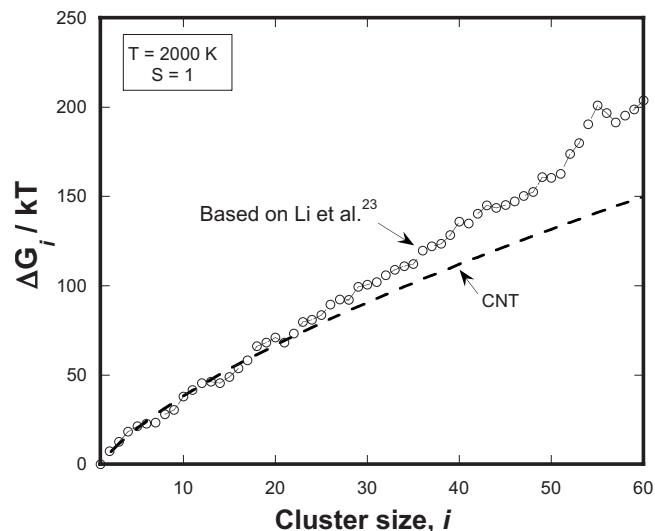


FIG. 2. Gibbs free energy of multistep association ΔG_i of Al clusters relative to vapor at 2000 K and a saturation ratio of 1, based on either Li *et al.* (Ref. 23) or CNT.

$$\Delta G_i = \sum_{j=2}^i \Delta G_{j-1,j}, \quad i \geq 2. \quad (17)$$

The standard free energies of stepwise addition calculated by Li *et al.*²³ can thus be used in this equation to calculate ΔG_i^0 . Figure 1 shows the results for aluminum at 2000 K, and compares these results to CNT, Eq. (13). For the CNT calculation, values from the literature⁶¹ were used for the surface tension⁶⁰ and mass density⁶¹ of aluminum at 2000 K.

The reason that ΔG_i^0 is negative except at the smallest cluster sizes is that p^0 corresponds to a high saturation ratio. Considering the effect of pressure on the Gibbs free energy of an ideal gas, and using Eq. (1), ΔG_i at any saturation ratio can be related to ΔG_i^0 by

$$\Delta G_i(S) = \Delta G_i^0 - (i-1)kT \ln \left(S \frac{p_s}{p^0} \right). \quad (18)$$

Alternatively one can relate ΔG_i at any saturation ratio to its value for the saturated vapor, using

$$\Delta G_i(S) = \Delta G_i(p_s) - (i-1)kT \ln S. \quad (19)$$

The equilibrium vapor pressure of aluminum at 2000 K equals about 648 Pa, based on an extrapolation of the analytical relationship for $p_s(T)$ recommended by Alcock *et al.*⁶² up to 1800 K. Thus $p_1 = 1$ atm (the value of p^0 assumed by Li *et al.*²³) corresponds to a saturation ratio of approximately 156. At such high saturation ratios ΔG_i is dominated by the second term on the right-hand side of Eq. (19). A more revealing comparison of ΔG_i calculated from the Li *et al.*²³ data to CNT is obtained by setting $S = 1$. In this case ΔG_i in CNT is given simply by the surface tension term in Eq. (13), which represents the essence of the capillarity model. This comparison is shown in Fig. 2. It can be seen that the values of $\Delta G_i(p_s)$ obtained from the Li *et al.*²³ data lie close to the CNT values up to $i \approx 25$, but for larger sizes they increase more rapidly than $i^{2/3}$, which is the power law corresponding to the capillarity model.

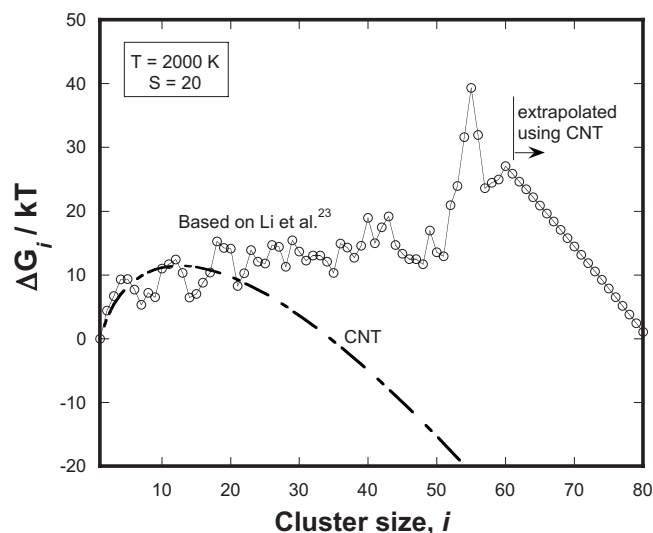


FIG. 3. Gibbs free energy of multistep association ΔG_i of Al clusters relative to vapor at 2000 K and a saturation ratio of 20, based on Li *et al.* (Ref. 23) up to cluster size 60, and extrapolated beyond $i=60$ using the CNT expression for the free energy of stepwise addition, Eq. (20).

At intermediate saturation ratios the comparison becomes more interesting. For example, Fig. 3 shows ΔG_i at 2000 K for $S=20$. Whereas CNT gives a smooth curve with a single maximum at $i \approx 12.6$ (neglecting the fact that i is an integer), the values of ΔG_i based on Li *et al.*²³ are highly nonmonotonic, exhibiting numerous local maxima and minima, with a strong global maximum at $i=55$.

Here one confronts a limitation in using atomistic data in Eq. (12). The summation in Eq. (12) is dominated by terms close to the critical size. Indeed, if ΔG_i has a sharp maximum, as is shown in Fig. 3, then to close approximation the summation will be given by the single term associated with that maximum. Yet, as the calculations of Li *et al.*²³ extend only to $i=60$ it is unknown whether a higher maximum exists for $i > 60$. If such a higher maximum in ΔG_i does exist, then the steady-state nucleation rate will be lower. For example, magic numbers have been observed for sodium up to size 2500,¹² although it should be noted that the second term on the right-hand side of Eq. (19) makes it unlikely that ΔG_i would have a global maximum at such large sizes for saturation ratios that are large enough to result in observable homogeneous nucleation. In any case it therefore follows that J_{ss} calculated using the Li *et al.*²³ data in Eq. (15) can only be said to represent an upper bound, to within the accuracy of the Li *et al.*²³ data. Inevitably such atomistic calculations must be truncated at some finite cluster size. As a cluster grows it must eventually approach bulk behavior, as represented by the capillarity model of CNT (assuming that the cluster is liquidlike). In this limit the free energy of stepwise addition is given by

$$\frac{\Delta G_{i-1,i}}{kT} = [i^{2/3} - (i-1)^{2/3}] \Theta - \ln S. \quad (20)$$

This expression is used in Fig. 3 to extrapolate ΔG_i based on Li *et al.*²³ to sizes larger than $i=60$. The specific form of this extrapolation will have negligible effect on J_{ss} as long as $i=55$ does in fact represent the global maximum of ΔG_i .

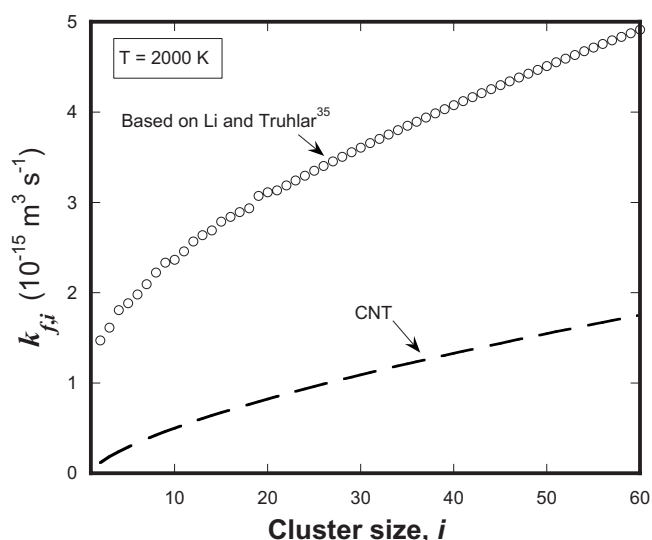


FIG. 4. Forward rate constants of (R1) at 2000 K, calculated either by classical molecular dynamics trajectory simulations of Li and Truhlar (Ref. 35) or by CNT.

However some such extrapolation is needed for the transient nucleation calculations in the next section.

The reason for the peak in ΔG_i at $i=55$ in Figs. 1–3 is closely related to the fact that the lowest-energy structure of Al_{55} is particularly stable for symmetry reasons. Thus it has a low thermodynamic energy, but this does not translate into a low thermodynamic free energy. The free energy also contains important contributions from isomeric and vibrational entropy.^{23,24} For example, Al_{56} has 53 isomers within 0.2 eV of the global minimum energy structure.²⁴ Three of these correspond to one Al atom adsorbed on the surface of the particularly stable Al_{55} structure, and the other 50 correspond to insertion of one Al into the surface of this Al_{55} structure.²⁴ A similar entropically favorable multitude of low-energy structures can explain that Al_{57} is also particularly stable, as shown in Figs. 2 and 3. The existence of a peak at $i=55$ is also sensitive to the accuracy of the electronic structure calculations in that a change in cohesive energy on the order of 5% can cause this kind of structure; ordinarily one would hope that any errors in the electronic structure calculations would be smooth functions of i , but in the vicinity of magic numbers, the dominant structures can be markedly different from one value of i to the next, so it is difficult to estimate the uncertainties even in relative energies.

In addition to the free energies ΔG_i , Eqs. (4) and (11) require the forward rate constants of (R1). Li and Truhlar³⁵ calculated these using classical molecular dynamics trajectory simulations, for temperatures in the range 1100–3300 K. The results of these simulations for $k_{f,i}$ at 2000 K are shown in Fig. 4, together with the CNT values. Differences in $k_{f,i}$ are less important for steady-state nucleation than are differences in ΔG_i , as the latter are exponentiated in Eq. (11). Nevertheless, it is noteworthy that the values of $k_{f,i}$ calculated by Li and Truhlar³⁵ are seen in Fig. 4 to be several times higher than the corresponding CNT values. This difference can be attributed mainly to the neglect of attractive forces in the hard sphere model. Such forces are especially important for open-shell atoms such as Al.

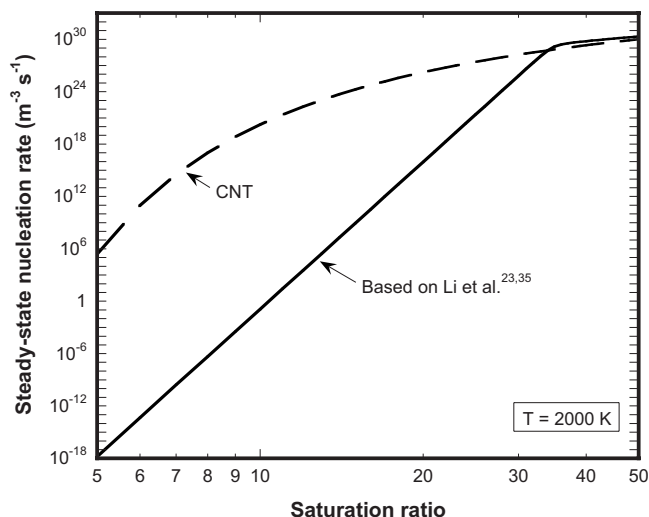


FIG. 5. Steady-state nucleation rate versus saturation ratio at 2000 K, using either self-consistent CNT, Eq. (15), or Eq. (12) using thermodynamic data of Li *et al.* (Ref. 23) and kinetic data of Li and Truhlar (Ref. 35).

IV. RESULTS: STEADY-STATE NUCLEATION

The free energy data of Li *et al.*²³ together with the data on condensation rate constants of Li and Truhlar³⁵ were used in Eq. (15) to calculate steady-state nucleation rates at 2000 K over a range of saturation ratios. The results are shown in Fig. 5, where they are compared to the self-consistent CNT values given by Eq. (15). It is evident that there is not only a large quantitative difference but also an important qualitative difference between the two curves.

The quantitative difference is caused mainly by the strong peak in ΔG_i at size 55 based on the Li *et al.*²³ data, which causes J_{ss} to be many orders of magnitude lower than predicted by CNT for values of saturation ratio below about 30. Indeed the discrepancy may be even greater, because, as discussed in the previous section, the values of J_{ss} calculated from the Li *et al.*^{23,35} data represent an upper bound. The saturation ratio required for the onset of observable nucleation, conventionally defined as the saturation ratio at which J_{ss} equals $1 \text{ cm}^{-3} \text{ s}^{-1}$, is much higher based on the Li *et al.*^{23,35} data than from CNT: it equals about 5.1 based on CNT but about 13.3 based on Li *et al.*^{23,35}

The qualitative difference, which concerns the slopes of the curves, can be attributed to the existence of magic numbers for Al clusters. With $J_{ss}(S)$ plotted on a log-log plot, as in Fig. 5, the linearity of the curve for the calculations based on the Li *et al.*^{23,35} data is an illustration of the Nucleation Theorem,⁶³ together with the fact that the global maximum in ΔG_i at $i=55$ exists over a wide range of saturation ratios. The Nucleation Theorem can be written in the form

$$\left(\frac{\partial \ln J_{ss}}{\partial \ln S} \right)_T = i^* + 1, \quad (21)$$

where i^* is the critical cluster size. The derivation of this expression is independent of the model assumed for ΔG_i , whether classical or atomistic.⁶⁴

The value of i^* is plotted over a range of saturation ratios in Fig. 6. In CNT i^* is a continuous function of S , given by

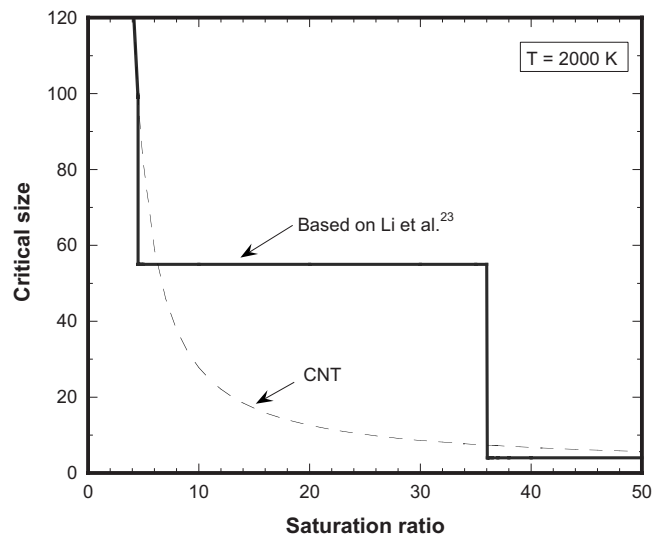


FIG. 6. Critical cluster size, i.e., size at which ΔG_i is a maximum, at 2000 K, based either on Li *et al.* (Ref. 23) or on CNT.

$$i^* = \left(\frac{2}{3} \frac{\Theta}{\ln S} \right)^3. \quad (22)$$

In contrast, because of the strong peak in ΔG_i at size 55, the Li *et al.*²³ data predict $i^*=55$ for saturation ratios ranging from about 4.5 to 36. Thus, over this entire range, integrating Eq. (21), $J_{ss} \propto S^{56}$, and this is indeed consistent with the result shown in Fig. 5.

We emphasize that $i^*=55$ over only a finite range of S . Above $S \approx 36$ the value of i^* drops suddenly from 55 to 4 which produces the knee in the curve at $S \approx 36$ seen in Fig. 5. To understand this behavior, consider Fig. 7, which shows ΔG_i based on Li *et al.*²³ for saturation ratios of 10, 20, and 30. At all of these saturation ratios the global maximum of ΔG_i occurs at $i=55$. As S increases the second term on the right-hand of Eq. (13) increases, until finally at $S \approx 36$ the value of ΔG_{55} drops below the value of ΔG_4 , which at that point represents the global maximum in ΔG_i .

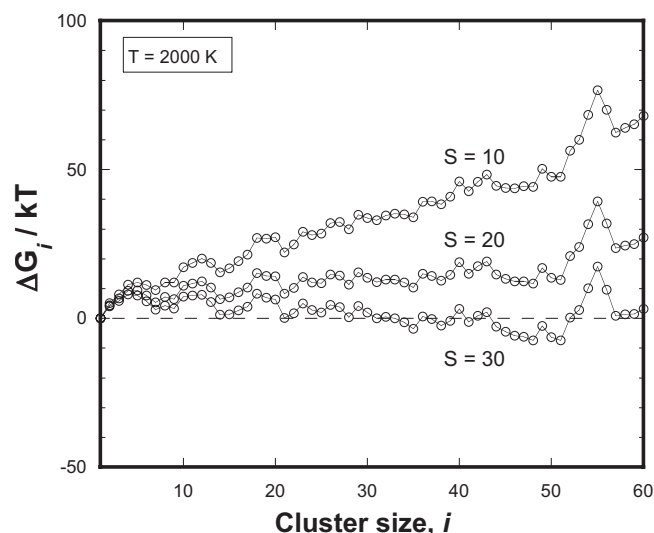
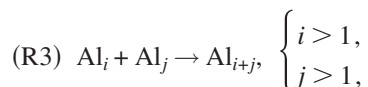


FIG. 7. Free energy of multimer association ΔG_i of Al clusters relative to vapor, based on Li *et al.* (Ref. 23), at 2000 K and at saturation ratios of 10, 20, and 30.

For low saturation ratios, when S drops below about 4.5, i^* jumps suddenly from 55 to 99 and increases thereafter, i.e., it becomes equal to the values obtained from CNT. The latter effect is simply an artifact of the CNT-based extrapolation of the Li *et al.*²³ data for cluster sizes greater than 60. In the limit as $S \rightarrow 1$, $i^* \rightarrow \infty$, consistent with the equilibrium between the vapor and the bulk liquid at $S=1$.

The above calculations assume that cluster growth is dominated by monomer condensation. However this assumption becomes invalid at sufficiently high values of saturation ratio. The reason for this is evident from Fig. 7. For saturation ratios of 10 and 20 the values of ΔG_i are positive for all values of $i > 1$, meaning that the equilibrium cluster number densities are all smaller than the monomer, and the steady-state cluster number densities during nucleation are yet smaller (as required to have a positive nucleation current). However for $S=30$ it is seen that clusters of a number of different sizes smaller than the critical size have negative values of ΔG_i , meaning that they are more abundant than the monomer at equilibrium. In this case cluster-cluster interactions are important, the monomer growth model is no longer valid, and Eq. (12) does not apply. In this regime the critical size i^* is no longer a relevant bottleneck to nucleation, as reactions of the form



can dominate cluster growth, and for the case $i+j > i^*$, cluster growth can leapfrog over the critical size. Since magic-numbered clusters will be the most abundant, nucleation will be dominated by reactions of the form (R3), where either i or j , or both, are magic numbers. Bahadur and McClurg¹³ concluded, based on the conditions they considered for monovalent metals, that the existence of magic numbers must produce such a “cluster growth” (as opposed to “monomer growth”) mechanism. Here we reach a similar conclusion, except that we also find a window of conditions for which the monomer growth mechanism is valid in spite of the existence of strong magic numbers. For the case of aluminum at 2000 K, the monomer growth mechanism appears to be reasonable for saturation ratios below about 25.

V. RESULTS: TRANSIENT NUCLEATION

The transient nucleation behavior in the condensation-evaporation regime can be calculated by integrating Eqs. (4) and (5) numerically, subject to the auxiliary conditions

$$n_1 = S n_s, \quad t \geq 0, \quad (23)$$

$$n_i = 0, \quad i \geq 2, \quad t = 0, \quad (24)$$

and

$$n_M = 0, \quad t > 0, \quad (25)$$

where $n_s(T)$ is the saturation number density of the monomer vapor. Here the largest cluster size M should be larger than the critical size and sufficiently larger that the choice of its value makes effectively no difference in the results.

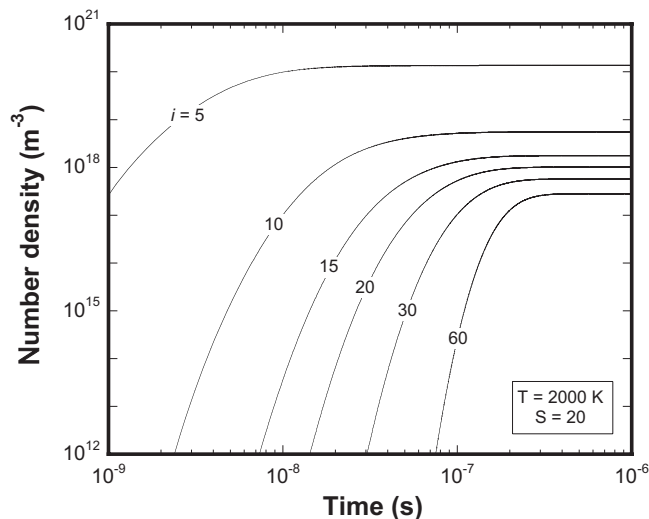


FIG. 8. Temporal evolution of cluster number densities at 2000 K and a saturation ratio of 20 based on CNT.

Abraham⁶⁵ carried out such a numerical integration for the case of nucleation of water droplets, with the exception that instead of using Eq. (23) he set the number density of clusters of size $i=10$ to a constant value (in equilibrium with the monomer number density) in order to avoid taking the extremely small time steps required to resolve the transient behavior of the smallest clusters. Abraham assumed CNT to model the forward and backward rate constants in Eq. (4), and set $M=110$.

To our knowledge no previous studies have considered the effect of magic numbers on transient nucleation. Here solutions are obtained to Eqs. (4), (5), and (23)–(25) for aluminum at 2000 K and a saturation ratio of 20, based either on CNT or on the data of Li *et al.*^{23,35} The value of M was set to 100. The Li *et al.*²³ values of ΔG_i were extrapolated beyond $i=60$ using CNT, as shown in Fig. 3, while the Li and Truhlar³⁵ values of $k_{f,i}$ were extrapolated beyond size 60 by setting them proportional to $i^{2/3}$, again consistent with CNT.

Abraham⁶⁵ noted that the solution to this simple set of equations presents surprising numerical difficulty. This is partly because of the large range of time scales required for clusters of different sizes to reach steady state. More importantly, however, it is because as steady state is approached the forward and backward rates of (R1) become quite close to each other. In this case the nucleation current in Eq. (4) equals the relatively small difference between two large numbers, which causes potential problems with roundoff error. Abraham, who assumed CNT, noted that double precision was required for the conditions he considered. For our calculations using the Li *et al.*²³ free energy data we found this problem to be more severe. For example, at 2000 K and $S=20$, as steady state is approached the value of J_2 equals approximately one part in 10^{16} of either the forward or backward rates. We thus found that quadruple precision was necessary to obtain values of J_i that converge as they should to a common steady-state value.

Figures 8 and 9 show results for number densities and nucleation currents, respectively, for selected cluster sizes, based on CNT. The behavior is qualitatively similar to that

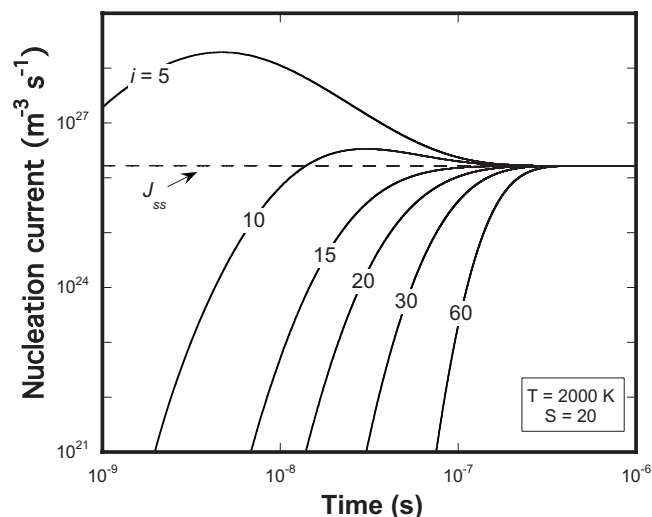


FIG. 9. Temporal evolution of nucleation currents at 2000 K and a saturation ratio of 20 based on CNT. Line labeled “ J_{ss} ” is the steady-state nucleation rate given by Eqs. (15) and (16).

observed by Abraham⁶⁵ in his calculations for water. As indicated in Fig. 8, both the value of the steady-state number density and the time required for clusters of each size to reach their steady-state vary monotonically with cluster size. For clarity only selected cluster sizes are shown. However this is confirmed by examination of all cluster sizes.

In addition to the nucleation currents for selected cluster sizes, Fig. 9 also shows the value of the steady-state nucleation rate calculated independently by Eq. (15). As noted above, the critical size as given by CNT for this case equals about 12.6 (where CNT neglects the integer nature of i). In Fig. 9 it is seen that the nucleation currents for clusters smaller than the critical size initially overshoot J_{ss} , while clusters larger than i^* do not. Within a short time—a few tenths of a microsecond—the nucleation currents for clusters of all sizes asymptotically approach the common steady-state value given by J_{ss} .

As an aside, it is interesting to note that J_{ss} in this figure represents the value given by the self-consistent version of CNT,⁵⁹ and that it agrees excellently with the steady-state nucleation rate obtained by the transient calculation. The standard (nonself-consistent) version of CNT gives a value of J_{ss} here that is lower by a factor $e^{\Theta/S}$,⁵⁹ which for this case equals about 2000.

Now we repeat these calculations using values for free energies and condensation rate constants based on Li *et al.*^{23,35} Results for the number densities of selected cluster sizes are shown in Fig. 10. As can be seen by inspection of the free energy data in Fig. 3, several of the cluster sizes shown represent either magic numbers (local minima in ΔG_i at $i=7, 14, 21$, and 51) or anti-magic numbers (local maxima at $i=5, 12, 18, 49$, and 55). The qualitative behavior here is markedly different than that obtained by CNT in Fig. 8. Because of the initial conditions, given by Eqs. (23) and (24), at the very earliest times the cluster number densities must order themselves monotonically with increasing cluster sizes. In CNT that ordering remains, whereas in Fig. 10 it is seen that the number densities reach a steady state that is not at all

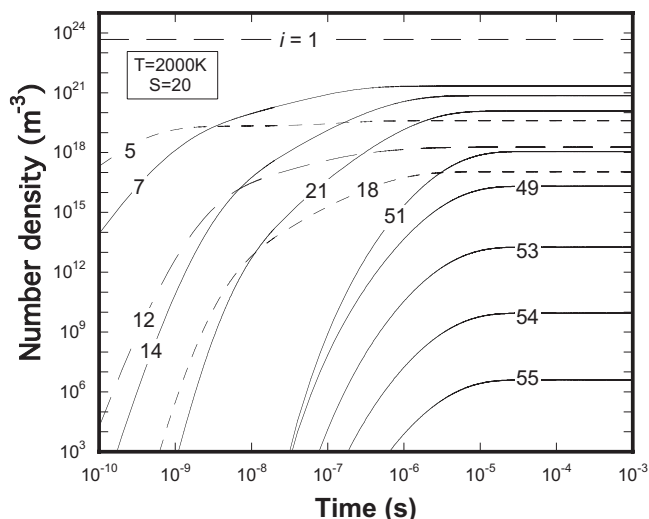


FIG. 10. Temporal evolution of cluster number densities at 2000 K and a saturation ratio of 20, based on thermodynamic data of Li *et al.* (Ref. 23) and kinetic data of Li and Truhlar (Ref. 35).

ordered by cluster size. Instead the magic-numbered clusters become much more abundant than the antimagic-numbered clusters to which they are nearest in size. This is most striking for the comparison between cluster sizes 51 and 55, which comprise the sharpest change in ΔG_i in Fig. 3: at steady state n_{51} is greater than n_{55} by a factor of about 10^{12} .

Figure 11 shows the nucleation currents for the same case and selected cluster sizes. Also shown is the steady-state nucleation rate calculated from Eq. (12). As in the CNT calculation, nucleation currents for clusters smaller than the critical size $i^*=55$, overshoot J_{ss} and then converge to the value given by J_{ss} , while nucleation currents for size 55 as well as larger clusters (not shown) approach J_{ss} from below. However the time required to reach steady state is dramatically longer than in CNT: about 10^{-4} s, based on convergence of the nucleation currents to a common value, compared to a few tenths of microseconds for CNT.

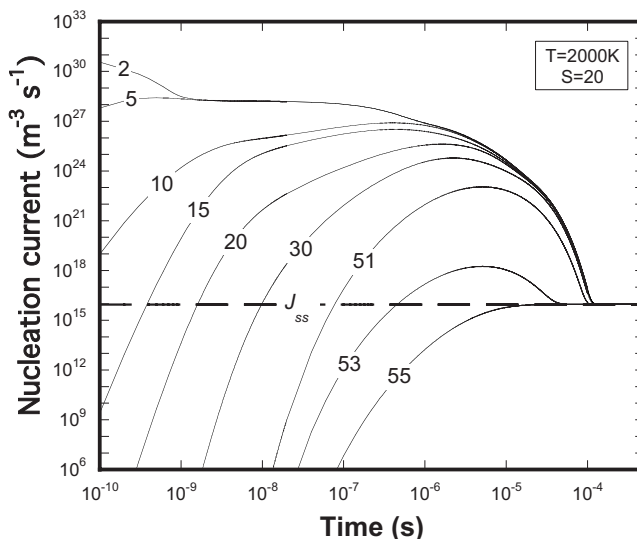


FIG. 11. Temporal evolution of nucleation currents at 2000 K and a saturation ratio of 20, based on thermodynamic data of Li *et al.* (Ref. 23) and kinetic data of Li and Truhlar (Ref. 35). Line labeled “ J_{ss} ” is the steady-state nucleation rate given by Eq. (12).

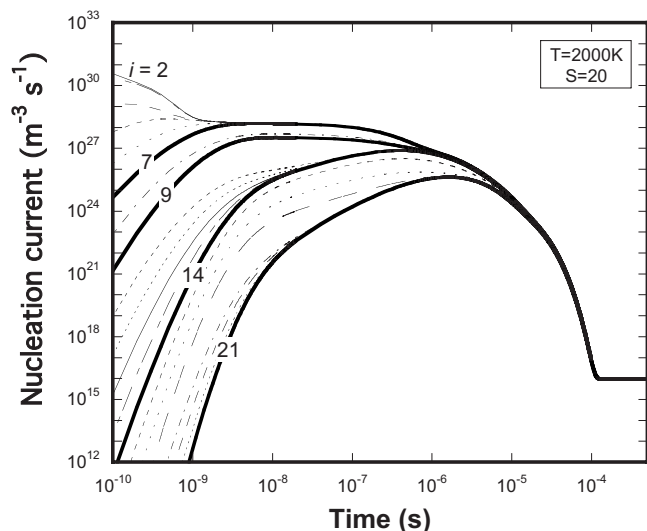


FIG. 12. Temporal evolution of nucleation currents for all cluster sizes 2 through 21, at 2000 K and a saturation ratio of 20. Solid bold lines are curves for magic numbers.

The much slower approach to steady state compared to CNT for the calculations using the Li *et al.*^{23,35} data is due to a combination of factors, including the larger critical cluster size and, most interestingly, the presence of multiple local maxima and minima in the curve of $\Delta G_i(i)$.

Figures 12 and 13 illustrate the last point. Figure 12 shows the nucleation currents J_i for all values of i from 2 to 21, while Fig. 13 shows J_i for all values of i from 36 to 55. Bold solid lines in both figures show the nucleation currents for magic numbers, while the bold dashed line in Fig. 13 shows the nucleation current for the most important anti-magic number, the critical size at $i=55$. Close inspection of these figures reveals that the nucleation currents for clusters of adjacent sizes become equal to each other in successive groups, where the largest cluster in each group is the magic-numbered one. For example, the nucleation currents for sizes 2–7 (a magic number) become equal to each other after a few

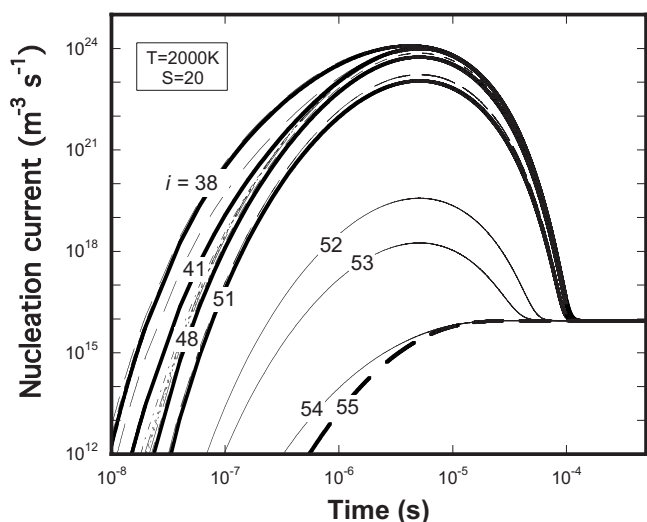


FIG. 13. Temporal evolution of nucleation currents for all cluster sizes 36–55, at 2000 K and a saturation ratio of 20. Solid bold lines are curves for magic numbers. Size 55, the critical size, is an antimagic number.

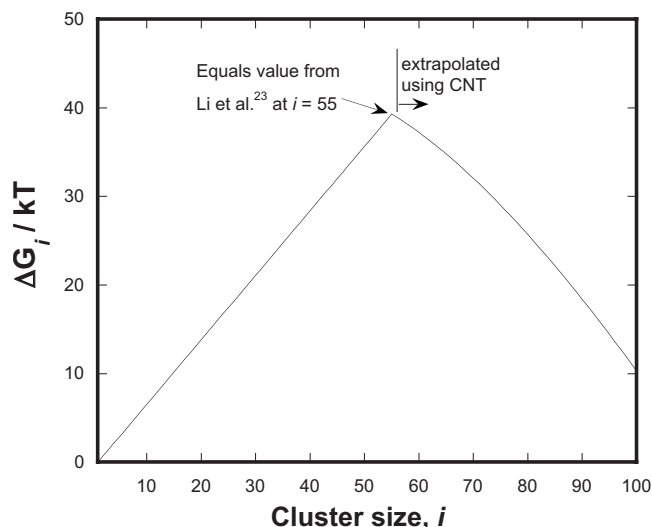


FIG. 14. Hypothetical linear curve of $\Delta G_i(i)$ that has the same critical size, 55, and the same value of ΔG_{55} as obtained from the Li *et al.* (Ref. 23) data at 2000 K and $S=20$. Curve is extrapolated beyond size 55 using the CNT expression for the free energy of stepwise addition, Eq. (20).

nanoseconds; clusters of sizes 8 and 9 (a magic number) join this equality after a few hundred nanoseconds; clusters of sizes 10–14 (a magic number) join this equality at about 1 μ s; and clusters of sizes 15–21 (a magic number) join at about 10 μ s. The same behavior is found for the entire size spectrum up to the critical size.

To understand this behavior, it is instructive to consider the analogy with the flow of water that at time 0 is released from a reservoir and then flows over a riverbed of undulating elevation. Magic numbers correspond to basins in the riverbed and antimagic numbers to relative hills. At steady state the depth of the river (analogous to number density) is greatest at the locations of the basins. As each basin fills the currents upstream adjust until a common current is reached, at which time the current downstream of the basin increases, pushing water over the next hill, which may properly be termed a “prominence,” and then on to the next basin, until that basin fills, and so forth. The highest prominence (critical size) represents the final rate-limiting kinetic bottleneck. In a somewhat different context, the concept of free energy minima representing basins into which clusters are funnelled has previously been discussed by Wales.⁶⁶

The transient behavior of the nucleation currents is thus affected by the detailed structure of $\Delta G_i(i)$. To demonstrate this, we conduct an exercise in which the transient nucleation behavior calculated with the Li *et al.*²³ data is compared to that obtained from a hypothetical linear curve of $\Delta G_i(i)$, shown in Fig. 14. The hypothetical $\Delta G_i(i)$ curve has the same critical size, 55, and the same value of ΔG_{55} as obtained from the Li *et al.*²³ data at 2000 K and $S=20$, but has no magic numbers, i.e., it has no local minima for $i>1$. Figure 15 shows the corresponding nucleation currents calculated using the hypothetical ΔG_i values, together with the condensation rate constants of Li and Truhlar.²⁹ The steady-state nucleation rate calculated from Eq. (12) using these hypothetical values is only about 4 times lower than that obtained using the Li *et al.*²³ free energy data, because the

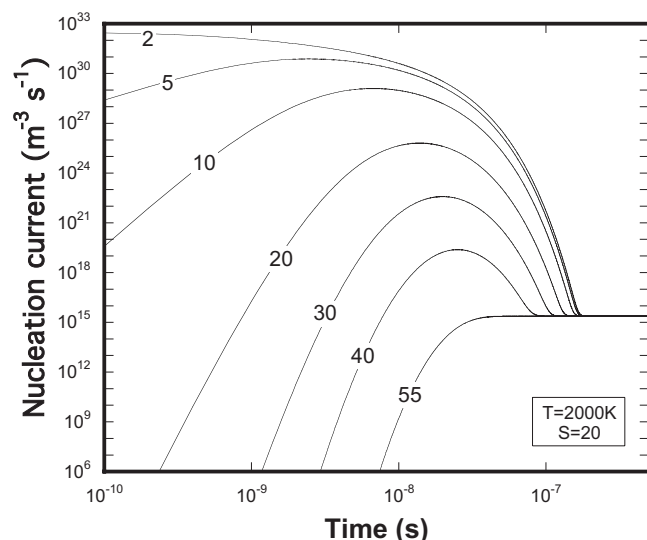


FIG. 15. Temporal evolution of nucleation currents based on the hypothetical linear curve of $\Delta G_i(i)$ in Fig. 14, together with the condensation rate constants of Li and Truhlar (Ref. 29).

term for $i=55$ is by far the largest term in the summation. However the time required to reach steady state is drastically different, about 10^{-7} s based on the hypothetical linear ΔG_i , compared to about 10^{-4} s based on the Li *et al.*²³ data.

Moreover the magnitude of the time required to reach steady-state nucleation, about 10^{-4} s based on the Li *et al.*²³ data, has important implications. Steady-state nucleation has received vastly more attention in the literature than has transient nucleation. The justification for this is the belief that in most realistic scenarios the time required to reach steady-state nucleation is much shorter than the time scales for change in forcing parameters (temperature and saturation ratio). However this assumption derives mainly from the modest literature on transient homogeneous nucleation, which generally is based on CNT. The CNT analysis above indicates that steady-state nucleation is reached in this particular case within a few tenths of a microsecond. If this analysis were correct, then steady-state nucleation would be a reasonable assumption even for situations such as rapid nozzle expansions where the rate of temperature change can equal 10^6 – 10^7 K/s, with a correspondingly rapid change in saturation ratio.

On the other hand, if the time required to reach steady-state nucleation is on the order of 10^{-4} s, as in the analysis based on the data of Li *et al.*,^{23,35} then steady-state nucleation is much less likely to be a valid assumption, and in many cases a transient analysis would be required to correctly model nucleation.

Another interesting difference with CNT concerns the effect of saturation ratio on the time required to reach steady state. In CNT, all else being equal, the time required to reach steady state decreases as the saturation ratio increases, the main reason being that a higher saturation ratio corresponds to a smaller critical size.⁶⁵ However, in our calculations based on the Li *et al.*^{23,35} data, we find the opposite result, at least over the range of conditions where the critical size is unaffected by the saturation ratio. For example, at 2000 K and a saturation ratio of 15, we find that the time to reach

state equals about 20 μ s, compared to about 100 μ s in the $S=20$ case. The reason for this contrary behavior is that, unlike in CNT, the change in saturation ratio here does not cause the critical size $i^*=55$ to change. The steady-state number densities and the nucleation current are much higher in the $S=20$ case than in the $S=15$ case (J_{ss} being about 10^8 times higher), and, with no reduction in i^* for the higher saturation ratio, it takes longer for these number densities and currents to build up to their steady-state values.

VI. SUMMARY AND CONCLUSIONS

Homogeneous nucleation of aluminum, a substance that exhibits magic numbers, has been examined by conducting both steady-state and transient nucleation calculations based on thermodynamic data for aluminum clusters up to size 60 of Li *et al.*²³ and the corresponding kinetic data of Li and Truhlar,³⁵ for a temperature of 2000 K. Aside from the strong quantitative differences with CNT, the existence of magic numbers creates important qualitative effects that are not found in CNT.

A strong peak in ΔG_i at size 55 causes that size to constitute the critical size over a wide range of saturation ratios, from about 4.5–36. Consequently, and consistent with the Nucleation Theorem, $d(\ln J_{ss})/d(\ln S)=56$ over that entire range. However this calculation is only meaningful for saturation ratios below about 25, as above that value magic-numbered clusters become more abundant than the monomer, invalidating the assumption that clusters grow only by monomer addition. In this regime (of higher saturation ratios) cluster growth may be dominated by cluster-cluster interactions, particular those involving magic-numbered clusters, and can leapfrog over the critical size.

Transient nucleation calculations using the Li *et al.*^{23,35} data also show strong differences from CNT. Magic-numbered clusters, at early times less abundant than smaller clusters of adjacent sizes, become over time more abundant. The time required to reach steady state is much longer than in CNT, requiring for $S=20$ about 10^{-4} s, compared to only a few tenths of a microsecond in CNT. This implies that under many realistic conditions steady-state nucleation may not be a valid assumption, contrary to the prediction of CNT.

Magic numbers are seen to play an important role in transient nucleation, as the nucleation currents for clusters of adjacent sizes become equal to each other in temporally successive groups, where the largest cluster in each group is the magic-numbered one. Another qualitative difference is that in CNT the time required to reach steady-state decreases with increasing saturation ratio, whereas the calculations based on Li *et al.*^{23,35} show the opposite behavior over the range of values of S for which the critical cluster size is unchanged.

As the Li *et al.*²³ calculations are limited to clusters up to size 60, it is possible that magic numbers at larger sizes could cause the critical size to be greater than 55 over some range of saturation ratio. In that case the differences with CNT would be even stronger than those reported here.

It should finally be noted that the work presented here refers specifically to homogeneous nucleation, i.e., self-nucleation, of pure aluminum. As noted above, to our knowledge no experiments on homogeneous nucleation of aluminum have been reported. Such experiments would be difficult to conduct, particularly under high-temperature conditions, because of the role that may be played by relatively small concentrations of ions, or of reactive impurities such as oxygen. On the other hand, many of the qualitative trends found here are more general than Al, and they may be important for nucleation of other metals as well as other substances that exhibit magic numbers.

ACKNOWLEDGMENTS

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