Mechanism of Metal Droplet Nucleation from Supersaturated Vapor[1]

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An analysis of the full nonlinear mechanism of condensation nucleation from a supersaturated vapor suggests that the classical Markovian growth mechanism may not apply to systems, such as metals, that exhibit pronounced magic-numbered clusters. Packing of atoms in concentric layers and/or quantum confinement of valence electrons lead to particular sized metal clusters that are anomalously stable. They are called magic-numbered clusters. Magic-numbered clusters are not explicitly addressed in the Markovian mechanism that assumes that clusters change size by accommodation or evaporation of one monomer at a time. This is a justifiable approximation only if the frequency of all cluster-cluster collisions is negligible compared with the frequency of the succession of monomer-cluster collisions required to produce an equivalent sized cluster to the cluster-cluster collision. Since the stability of magic-numbered clusters increases the likelihood of collisions between clusters, magic-numbered clusters can affect the nucleation mechanism and may have a significant influence on the nucleation rate from supersaturated metal vapors.

KEY WORDS: homogeneous nucleation; magic numbers; metal vapor.

1. INTRODUCTION

The kinetics of nucleation of metal droplets from a supersaturated vapor is important to a variety of fields. Nano-structured materials are often produced using particles synthesized from condensable vapors [1]. Since the condensation process is designed such that growth and coagulation are

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minimized, the nucleation step determines the size-distribution and structure of the particles. Therefore, nucleation kinetics determines the properties and ultimately the performance of the nano-scale particles. Controlling trace metal emissions during coal combustion requires an understanding of the processes that lead to fine particulates, including particle nucleation, growth, and aggregation [2]. Liquid metals are used as heat transfer media at elevated temperatures, particularly in the nuclear power industry. Accident scenarios for these systems often involve the release of a supersaturated vapor plume [3, 4]. Accurately modeling the fate of such a plume depends in part on the condensation kinetics of the vapor. Accurate nucleation rate predictions would benefit each of these applications. The rate predictions depend in turn on the condensation mechanism.

2. CLUSTER VERSUS MARKOVIAN GROWTH

Consider the reversible aggregation of clusters of size m and n,

$$C_m + C_n \leftrightarrows C_{m+n} \tag{1}$$
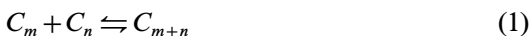
where subscripts refer to the number of monomers (atoms in this case) in the cluster. In the following discussion, the forward process is called aggregation and the reverse process is called fission. If m is restricted to equal one in Eq. (1), then the Markov process commonly used to model nucleation is recovered [5]. Equation (1) is more general than the Markov process since it allows clusters to grow by incorporating other clusters rather than by monomer addition alone. Although a few authors [6] have previously considered nucleation by cluster aggregation, I briefly review the governing equations in this Section to provide a description of my notation and to review the relevant approximations.

The species balance for clusters of size n, given the reactions in Eq. (1) is

$$\frac{dC_n}{dt} = \frac{1}{2}\left[\sum_{i=1}^{n-1}(k_{i,n-i}^{\text{agg}}C_iC_{n-i} - k_{i,n-i}^{\text{fiss}}C_n)\right] - \left[\sum_{i=1}^{\infty}(k_{i,n}^{\text{agg}}C_iC_n - k_{i,n}^{\text{fiss}}C_{n+i})\right] \tag{2}$$

where C_n is the number concentration of n-mers and the k's are aggregation and fission rate constants. The first summation in Eq. (2) represents aggregation and fission of clusters from (into) smaller clusters and the second summation represents aggregation and fission of clusters into (from) larger clusters. The factor of one half in the first term of Eq. (2) avoids double counting asymmetric reactions and accounts for indistinguishability in symmetric reactions. No factor is necessary in the second

term since the symmetric reaction removes (produces) two n-mers. Detailed balancing relates the fission rate constant to the aggregation rate constant and the equilibrium cluster concentrations at saturation [7],

$$k_{m,n}^{\text{fiss}} = k_{m,n}^{\text{agg}} \frac{C_m^{\text{eq}} C_n^{\text{eq}}}{C_{m+n}^{\text{eq}}} \tag{3}$$

Defining an ideal gas cluster activity relative to the cluster concentration at saturation,

$$a_n = C_n / C_n^{\text{eq}} \tag{4}$$

and a scaled rate constant,

$$\hat{k}_{m,n} = k_{m,n}^{\text{agg}} C_m^{\text{eq}} C_n^{\text{eq}} \tag{5}$$

allows a re-casting of Eq. (2) in terms of activities,

$$C_n^{\text{eq}} \frac{da_n}{dt} = \frac{1}{2} \left[\sum_{i=1}^{n-1} \hat{k}_{i,n-i} (a_i a_{n-i} - a_n) \right] - \left[\sum_{i=1}^{\infty} \hat{k}_{i,n} (a_i a_n - a_{n+i}) \right] \tag{6}$$

Equation (6) is a useful form because activities defined in this way are smooth functions of cluster size and the scaled rate constants contain all of the information regarding relative aggregation rates and cluster energetics.

It is often (wrongly) assumed that the Markovian growth mechanism is appropriate if the scaled rate constant for monomer aggregation is much greater than for cluster aggregation for each cluster size (n),

$$\hat{k}_{1,n} \gg \hat{k}_{m,n} \tag{7}$$

for $m > 1$. Since the aggregation rate constant (k^{agg}) is a slowly increasing function of cluster size [8] and the equilibrium cluster concentrations are often modeled as stretched-exponential decreasing functions [9], this condition is generally met. Unfortunately, Eq. (7) is not a sufficient condition for Markovian growth. Markovian growth is a justifiable approximation only if the frequency of all cluster-cluster collisions is negligible compared with the frequency of the succession of monomer-cluster collisions required to produce an equivalent sized cluster to the cluster-cluster collision. Although this is often the case, metals that exhibit strong magic numbered clusters are a potential exception.

Magic numbered clusters are more stable than clusters of one more or one fewer atom [10]. Therefore, they are preferentially observed in molecular beam experiments. At low temperatures, the observed magic numbers are rationalized in terms of packing of atoms in concentric layers.

Completion of a face or a complete layer determines the size of each magic numbered cluster. Above the cluster melting temperature, a different set of magic numbers corresponding to filled electronic shells is observed. Here, the shell structure is a result of quantum confinement of the valence electrons in the cluster. In either case, the equilibrium cluster concentration for magic numbered clusters is larger than for other clusters of similar size. Therefore, the scaled rate constant in Eq. (5) is anomalously large when n and/or m correspond to magic-numbered clusters.

3. DISCUSSION

The nucleation rate is the rate of formation of clusters larger than a given size. For the Markovian growth mechanism, the nucleation rate can be expressed as an analytic function of the monomer activity [5]. For cluster growth, Eq. (6) must be solved numerically [6]. The added computational difficulty associated with the more complex mechanism is justified only if it results in substantially different nucleation rate predictions. Metal vapor condensation may present such a case due to the stability of magic numbered clusters. Nucleation rate calculations, to be published elsewhere, suggest that the nucleation rate for cluster growth (J) is larger than for the Markovian growth mechanism (J_{Markov}),

$$J \approx J_{\text{Markov}} \, \text{Exp}[\varDelta G/kT] \tag{8}$$

where $\varDelta G$ is the magnitude of the oscillatory contribution of the free energy that results in the magic numbers. For pronounced magic numbers and/or low temperatures, this can be a large factor.

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