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A Partition Function Model for Nucleation on Surfaces

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Using a procedure to minimize the total Helmholtz free energy of a system composed of an idealized substrate, a collection of surface clusters, and a vapor in contact with the surface, an expression is derived for the concentration of clusters of a given size on the substrate. The result is based on several assumptions about the system, the most important being that the surface clusters do not interact and that the substrate remains intact. The expression for the concentration of surface clusters together with the conventional form for the growth rate of clusters on a surface can be used to calculate surface nucleation rates.

KEY WORDS: Nonkinetic nucleation theory; heterogeneous nucleation; surface nucleation; atomistic model; molecular surface clusters; variational technique; Helmholtz free energy of formation; vapor–substrate–bulk system.

1. INTRODUCTION

The nonkinetic theory for nucleation on surfaces has been approached in general from two points of view: (1) that the critical cluster size is small and a two-dimensional atomistic model applies,(1,2) and (2) that the clusters are so large (or the molecular properties so unwieldy) that the clusters are treated macroscopically: as spherical caps,(3,4) monolayered disks, or as polyhedrals(5) attached to the surface. A good review of the general problem of surface nucleation has been given by Robertson and Pound.(6)

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The atomistic theory was initially developed by Walton in 1962 and 1963.(1,2) In this approach the system is two-dimensional and consists of the surface nucleation sites and the adsorbed cluster atoms. An approximated partition function is formulated including configurational entropy over the substrate sites. Refinements have included two-dimensional entropy of each cluster on any one of the identical sites(7) and translational and rotational energy of the cluster.(8) The change in Helmholtz free energy is approximated by the change in potential energy (essentially the binding energy) when an n-cluster is formed from n monomers on the surface. No attempt has been made to consider three-dimensional clusters, nor to include the effect of the overlying vapor or the bulk which has energy available in the form of surface tension.

The macroscopic approach is sometimes called the capillarity approximation because of the use of bulk surface tension in determining the energy of formation of the spherical caps, disks, and polyhedrals. Line tension along the perimeter of the cluster has also been considered.(9) One of the most widely used theories (especially for the nucleation of ice and water) has been the spherical cap model. It relies not only on bulk surface tension but also on the radius of curvature and the contact angle. Since surface clusters have the added stability of the surface-to-cluster bonds, the critical size for the prenucleation surface clusters is expected to be considerably smaller than that for homogeneous nucleation from the vapor. Based on this observation and on the very limited experimental data,(6) one expects the range of critical sizes for most prenucleation surface clusters to be less than about 50 molecules. In light of this the use of bulk properties in the calculation of cluster energies is questionable.

We feel that the atomistic theory for surface nucleation holds the most promise. However, the evaluation of the canonical partition function for the vapor–surface cluster–bulk system is not trivial. Even if the system is restricted to the adsorption sites and adsorbed clusters, the cluster partition function is difficult to evaluate—expecially for polyatomic molecules. Recently a model has been formulated for approximating the canonical partition function for specific molecular clusters in the vapor(10) and was extended to a simple case of surface nucleation: ice on ice. In order to apply the model to more general cases of surface nucleation, we have formulated an expression for the concentration of clusters with n' molecules in terms of canonical partition functions for the n'-clusters, the vapor, and the bulk. This is really an extension of the existing atomistic model. It has, however, the added advantages of including: (1) three-dimensional clusters; (2) some coupling between the vapor, n'-clusters, and bulk, and (3) energy available from the bulk in the form of "surface tension." It gives a general expression for the concentration of n'-clusters on the surface solely in terms of specific canonical partition functions. "Energies of formation" are not inserted or approximated, but in this approach are defined in terms of the partition functions.

2. THE MODEL

The goal is to construct a model that provides an expression for $N_{n'}$, the number of clusters with n' molecules on a specific surface, in terms of the canonical partition function of the n'-cluster. The model assumes the following:

(a) The system consists of three components at constant temperature: the vapor clusters, the surface clusters, and the bulk, whose surface is the substrate (see Fig. 1).

(b) The vapor clusters are a mixture of noninteracting ideal gases—each ideal gas being the collection of N_n clusters with n molecules.

(c) The surface clusters do not interact.

(d) The clusters interact with the surface only through $m(n')$ bonds between surface cluster molecules and surface molecules.

(e) The bulk and its surface remain unchanged in structure and their

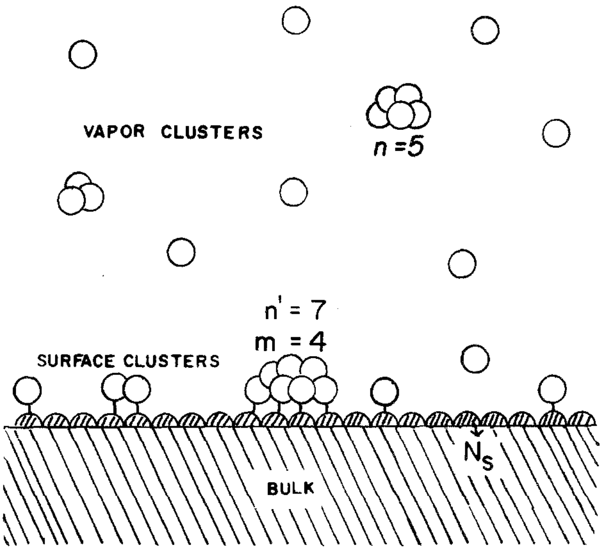

Fig. 1. A schematic representation of the three-component system: the vapor clusters, the surface clusters, and the bulk. N_s is a free surface bond, n is the number of molecules in a vapor cluster, and n' is the number of molecules in a surface cluster. m is the number of bonds between the surface cluster and the substrate.

energy states are changed only through external bonding to a surface cluster molecule.

(f) The total number of molecules in the vapor clusters and the surface clusters remains constant:

$$\sum_n nN_n + \sum_{n'} n'N_{n'} = \eta \tag{1}$$

(g) The total number of bonds available for bonding on the surface remains fixed:

$$\sum_{n'} m(n')N_{n'} + N_s = \eta_s \tag{2}$$

N_s is the number of free surface molecular bonds unattached to any surface cluster. In effect assumption (e) requires that N_s change only when a monomer is attached to or evaporates from the surface.

(h) Finally, we assume that the Hamiltonian for the system is

$$H = \sum_{n=1}^{\infty} N_n H(N_n) + \sum_{n'=1}^{\infty} N_{n'} H(N_{n'}, m(n')) + H_{\text{bulk}} \tag{3}$$

and that the canonical partition function for the system can be written

$$Z = Z_{\text{vapor clusters}} Z_{\text{surface clusters}} Z_{\text{bulk}} \tag{4}$$

$$= \prod_n Z_{N_n} \prod_{n'} Z_{N_{n'}} Z_{\text{bulk}} \tag{5}$$

The ideal gas assumption for the vapor clusters gives the simple form for its contribution to the factored partition function, as shown in Eq. (6). For the surface clusters we approximate the number of "sites" available to an n'-cluster by $M_1(n')$, the total number of bonds available to an n'-cluster divided by $m(n')$. Assumption (c) for the surface clusters is analogous to the ideal gas condition imposed on the vapor clusters and gives the similar form for $Z_{N_{n'}}$ in Eq. (6). We intend that the configurational entropy of the n' surface-cluster on a particular site be included in $Z(n')$. Z_{bulk}, at least symbolically, is left unchanged, so that Z becomes

$$Z = \prod_n \frac{Z(n)^{N_n}}{N_n!} \prod_{n'} \frac{[M_1(n')Z(n')]^{N_{n'}}}{N_{n'}!} Z_{\text{bulk}} \tag{6}$$

where

$$M_1(n') = \left[\eta_s - \sum_{l'} m(l')N_{l'} + m(n')N_{n'}\right] / m(n') \tag{7}$$

η_s is the total number of available bonds on the clean substrate. For the present we neglect the problems associated with $m(n')$ bonds that are not adjacent or in a favorable configuration. This is a reasonable approximation as long as the density of clusters on the surface is low.

The total Helmholtz free energy of the system F characterized by the partition function in Eq. (6) is

$$\begin{aligned} F &= -kT \ln Z \\ &= -kT \sum_{n} \left[N_n \ln Z(n) - N_n \ln N_n + N_n \right] - kT \ln Z_{\text{bulk}} \\ &\quad -kT \sum_{n'} \left[N_{n'} \ln Z(n') - N_{n'} \ln N_{n'} + N_{n'} + N_{n'} \ln M_1(n') \right] \end{aligned} \tag{8}$$

where we have used Stirling's approximation for the factorials of N_n and $N_{n'}$.

3. DERIVATION OF $N_{n'}$

The system of interest is at constant temperature T and we search for the vapor and surface cluster size distributions N_n and $N_{n'}$ that minimize the total Helmholtz free energy F subject to the conservation of the total number of cluster molecules η. Thus the following condition is imposed:

$$\delta(F - \lambda\eta) = 0 \tag{9}$$

Using Eq. (8) for F and Eq. (1) for η, Eq. (9) becomes

$$\begin{aligned} &\sum_{n} [\ln Z(n) - \ln N_n - n(\lambda/kT)]\, \delta N_n \\ &\quad + \sum_{n'} \{\ln Z(n') - \ln N_{n'} + \ln M_1(n') + n'(\lambda/kT) \\ &\quad + \partial(\ln Z_{\text{bulk}})/\partial N_{n'} - m(n') \sum_{k \neq n'} N_{k'}/[M_1(k')m(k')]\}\, \delta N_{n'} = 0 \end{aligned} \tag{10}$$

The Lagrange multiplier λ is obtained from

$$\ln Z(1) - \ln N_1 - (\lambda/kT) = 0 \tag{11}$$

and N_n is the same as in the case for homogeneous nucleation from the vapor to the liquid:

$$N_n = Z(n) \exp(\lambda n/kT) = Z(n)[N_1/Z(1)]^n \tag{12}$$

Similarly, $N_{n'}$ is given by

$$\begin{aligned} N_{n'} &\underset{n' \neq 1}{=} Z(n') \left[\frac{N_1}{Z(1)} \right]^{n'} M_1(n') \\ &\quad \times \exp\left[\frac{\partial \ln Z_{\text{bulk}}}{\partial N_{n'}} - m(n') \sum_{k' \neq n'} \frac{N_{k'}}{N_s + m(k')N_{k'}} \right] \end{aligned} \tag{13}$$

This is the concentration of clusters of size n' on the surface of the bulk.

4. DISCUSSION OF THE RESULTS

In order to compare the expression for $N_{n'}$ with the conventional form, Eq. (13) is rewritten as

$$N_{n'} = N_{1'} \exp(-\Delta\phi/kT) \tag{14}$$

where $\Delta\phi$ is defined to be the "energy of formation." In making this comparison we also approximate the sum in the exponent of Eq. (13) as follows:

$$-m(n') \sum_{k' \neq n'} \frac{N_{k'}}{N_s + m(k')N_{k'}} \simeq -m(n') \frac{N_{1'}}{\eta_s} \tag{15}$$

This assumes (as have the previous atomistic theories) that the concentration of surface monomers $N_{1'}$ dominates all other surface cluster concentrations and that

$$N_{1'} \simeq \sum_{n'} N_{n'} \tag{16}$$

We also assume that the surface coverage is low, i.e., that $\eta_s \gg N_{1'}$. Using Eq. (15) and dividing $N_{n'}$ by $N_{1'}$, we obtain the following expression for $\Delta\phi/kT$:

$$\begin{aligned}\frac{\Delta\phi}{kT} \simeq & -\ln Z(n') + n' \ln\left[\frac{Z(1)}{N_1{}^0}\right] - n' \ln S \\ & + m(n') \frac{\partial \ln Z_{\text{bulk}}}{\partial N_s} - \ln\left(\frac{M_1}{N_{1'}}\right) + \frac{m(n')N_{1'}}{\eta_s}\end{aligned} \tag{17}$$

$N_1{}^0$ is the equilibrium number of monomers in the vapor at temperature T, and $S = N_1/N_1{}^0$ is the supersaturation ratio.

The fourth term on the right in Eq. (17) is very similar to the term $-\sigma_{sv}A_{n's}$ in the spherical cap model for nucleation on surfaces.(3) (Here σ_{sv} is the surface tension of the flat substrate–vapor interface and $A_{n's}$ is the area of substrate covered by the n'-cluster.) This analogy is more evident from the following:

$$\begin{aligned} kTm(n')\left(\frac{\partial \ln Z_{\text{bulk}}}{\partial N_s}\right)_T &= -m(n')\left(\frac{\partial A}{\partial N_s}\frac{\partial F_{\text{bulk}}}{\partial A}\right)_T \\ &\simeq -A_{n's}\sigma_{sv}\end{aligned} \tag{18}$$

In this interpretation $\partial A/\partial N_s$ is the area per available substrate bond and $m(n')$ times the latter quantity is the "area" of the n'-cluster–substrate interface $A_{n's}$. Here $(\partial F_{\text{bulk}}/\partial A)$, the variation in the Helmholtz free energy of the bulk with substrate surface area at constant temperature, is the surface tension σ_{sv}.(12) The latter assumes surface tension is a function of temperature only. Thus, the fourth term in Eq. (17) accounts for the energy available from the bulk when a "free" surface bond is lost. There appear to be no atomistic theories that include such a term in the expression for the concentration of n'-clusters on a substrate.

For further comparison we rewrite $N_{n'}$ as follows:

$$N_{n'} = N_{1'} \frac{M_1(n')}{N_{1'}} \exp\left[-\frac{\Delta F}{kT} - m(n') \left(\frac{\partial \ln Z_{\text{bulk}}}{\partial N_s} \right)_T - m(n') \frac{N_{1'}}{\eta_s} \right] \tag{19}$$

where

$$\Delta F/kT \equiv -\ln Z(n') + n' \ln [Z(1)/N_1{}^0] - n' \ln S \tag{20}$$

We note that $N_{n'}$ is not proportional to $(M_1/N_{1'})^{n'}$ as in previous theories and that the change in Helmholtz free energy ΔF is the difference in Helmholtz free energy between the n'-cluster on the surface and n' monomers in the vapor (instead of n' monomers on the surface).

The canonical partition function for the surface cluster $Z(n')$ includes: (1) possible translation and rotation of the center of mass of the cluster; (2) binding energy internal to the cluster; (3) intermolecular, intramolecular, and librational motions for all the cluster molecules; (4) binding energy of the cluster to the substrate; (5) configurational entropy of $m(n')$ bonds on the "average" site; and (6) configurational entropy of the constituent n' molecules in the surface cluster. These contributions to $Z(n')$ depend on the substrate and the vapor and can only be appropriately treated when the model is applied to a specific case.

5. CONCLUDING REMARKS

Using an extension of the atomistic theory for surface nucleation,⁽¹⁾ we have formulated an expression for the concentration of molecular clusters adsorbed on an idealized surface. The treatment includes limited interaction among the vapor, the bulk, and the surface clusters and does not restrict the clusters to be two-dimensional. In applying the model to specific surface nucleation problems, the major effort will be in evaluating the canonical partition functions. This has, however, been outlined in some previous work⁽¹⁰⁾ and appears feasible for several systems.

The surface considered in this paper is assumed to have a homogeneous distribution of surface bonds. The formulation and application of a similar model to surfaces whose absorption sites vary in binding potential is presently under investigation.

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