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A Monte Carlo Method for Approximating Critical Cluster Size in the Nucleation of Model Systems[1]

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A formalism is presented for estimating critical cluster size as defined in classical models for nucleation phenomena. The method combines Bennett's Monte Carlo technique for determining free-energy differences for clusters containing n and $n - 1$ atoms with the steady state nucleation rate formalism. A simple form for the free energy of formation of the n cluster [including a term $A(n)n^{2/3}$] is used to predict critical cluster size and critical supersaturation ratio, S^*. This approach is applied to Lennard-Jones vapor clusters at 60 K. Results for free-energy differences for the 13, 18, 24, and 43 clusters predict a critical cluster size of 70 ± 5 atoms at a critical supersaturation ratio given by $lnS^* = 2.45 \pm 0.15$. This method is intended to provide estimates of critical cluster size for more ambitious attempts to calculate cluster free energies or for initializing conditions in microscopic simulations of nucleating systems.

KEY WORDS: Homogeneous nucleation; critical cluster size; free energy of formation; Monte Carlo simulation; Lennard-Jones vapor clusters; critical supersaturation ratio; partition function.

1. INTRODUCTION

We present a method for estimating the number of atoms or molecules in the critical cluster as defined in classical models for nucleation phenomena. The critical cluster has equal probability of gaining or losing an atom (or molecule) and corresponds to a relative maximum in the work required to form the cluster from the parent phase. Hence, in most attempts to

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determine the critical cluster size for application to the steady state nucleation formalism, free energies are generated for a range of cluster sizes. In a recent paper, Garcia and Torroja(1) calculate energies of formation for 35 Lennard–Jones clusters for a range of temperatures using an integration technique similar to that of Lee, Barker, and Abraham(2). Results from Ref. 2 were combined with the data from the 35 clusters to predict the onset of nucleation at higher temperatures. While the determination of free energies is manageable when using bulk models for the clusters(3), the approach is nontrivial when the clusters are treated as atomic or molecular aggregates(1,2,4,5). The motivation for this work has been to obtain an estimate of the critical cluster size as input for subsequent work involving extensive calculations of free energy or for setting up initial conditions for Monte Carlo or molecular dynamics simulations. The method we propose avoids a direct calculation of free energy for the clusters and uses instead a free-energy difference for clusters containing n and $n-1$ atoms. The free-energy difference approximates the derivative of the free energy of formation of the n cluster with respect to n, and relates the critical cluster size, n^*, to the supersaturation, S, required at that temperature.

In this paper we outline the formalism for estimating critical cluster size in Section 2, describe the Metropolis Monte Carlo method using Bennett's technique(6) for calculating free-energy differences for the n and $n-1$ clusters in Section 3, and apply this method to Lennard–Jones vapor clusters at 60 K in Section 4. Additional comments and conclusions are given in Section 5.

The application of this method to Lennard–Jones vapor clusters (argon) predicts a critical cluster size of 70 ± 5 atoms at a critical supersaturation ratio given by $\ln S^* = 2.45 \pm 0.15$. The latter agrees reasonably well with experimental data. A more extensive study using this technique could provide additional temperature dependent data. However, it is our purpose here only to present the formalism and illustrate the method with a simple example. Presently, work is in progress on the application of this technique to water vapor clusters and to water clusters absorbed on surfaces of hexagonal silver iodide. In the latter case, the interest is in the use of n^* and $\ln S^*$ as probes for the nucleation efficiency of specific substrate features.

2. FORMALISM FOR ESTIMATING CRITICAL CLUSTER SIZE

In the classical steady state nucleation rate formalism, the nucleation rate J, for homogeneous nucleation is given by(7)

$$J = \left[\sum_n 1/(C_n N_n / V) \right]^{-1} \simeq C_{n^*} N_{n^*} / V \tag{1}$$

where C_n is the rate at which monomers are condensing on the n cluster and N_n/V is the concentration of n clusters in the parent phase. The N_n is related to the canonical partition function for the n cluster by the following equation which assumes that the system is composed of a mixture of noninteracting ideal gases—each of cluster size n:

$$N_n = [N_1/Z(1)]^n Z(n) \tag{2}$$

The $Z(n)$ is the canonical partition function for the n cluster and is related to the configurational integral, $Q(n)$, as follows:

$$Z(n) = \Lambda^n V^n Q(n)/n! \tag{3}$$

where $\Lambda = (2\pi mkT/h^2)^{3/2}$ and m, k, and h are the mass, Boltzmann constant, and Planck's constant, respectively. The configurational integral is defined as follows:

$$Q(n) = V^{-n} \int\int \cdots \int \exp[-U(\bar{r}_1, \bar{r}_2, \ldots, \bar{r}_n)/kT]\, d\bar{r}_1\, d\bar{r}_2 \ldots d\bar{r}_n \tag{4}$$

where U is the interaction potential for the system, and the $\bar{r}_i$ are atomic position vectors. Combining Eqs. (2) and (3), one obtains

$$N_n = N_1 \exp\left\{ -\left[-\ln \frac{Q(n)}{n!\, N_1} - n \ln N_1 \right] \right\} \tag{5}$$

where the quantity $\{-\ln[Q(n)/(n!\, N_1)] - n \ln N_1\}$ is defined to be the free energy of formation for the n cluster, $\Delta w(n)/kT$.[3] The difference in free energies of formation for the n and the $n-1$ clusters approximates the derivative with respect to n and is given by

$$d[\Delta w(n)/kT]/dn \simeq -\ln \frac{Q(n)}{Q(n-1)} - \ln(N_1^0/n) - \ln S \tag{6}$$

Equation (6) has relevance in continuous variable steady state nucleation rate theory since the condition $d(\Delta w/kT)/dn = 0$ is satisfied at n equal to n^*. Thus the following condition can be used to estimate a value of $\ln S$ which corresponds to a critical cluster size of n^* at the temperature T:

$$0 \simeq -\ln \frac{Q(n^*)}{Q(n^*-1)} - \ln \frac{N_1^0/V}{n/V} - \ln S \tag{7}$$

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[3] In this form for the energy of formation we have omitted the -1 commonly found when comparing the statistical mechanical formalism with the classical (liquid drop) energy of formation. See, for example, Ref. 8. The -1 is associated with the translational free energy of the center of mass of the cluster.

In the above N_1^0/V is the equilibrium concentration of monomers at the temperature T. If one is able to calculate the first term in Eq. (7) for a few cluster sizes a range of S values can be predicted. In the method proposed $\ln S$ is plotted versus $n^{*-1/3}$ and a slope determined. If one further wishes to predict a critical supersaturation ratio it is necessary to make an additional assumption about the form for $\Delta w(n)/kT$. We assume[4]

$$\Delta w(n)/kT = A(n)n^{2/3} - n\ln S - \tfrac{3}{2}\ln(n) - \ln(\Lambda V/N_1^0) \tag{8}$$

where $A(n)$ is a temperature-dependent parameter representing the surface tension contribution to the energy of formation of the n cluster. Differentiation of Eq. (8) and use of $d[\Delta w(n^*)/kT]dn = 0$ relates $A(n^*)$, n^*, $\ln S$, and dA/dn:

$$\ln S = \tfrac{2}{3}A(n^*)n^{*-1/3} - 3/(2n^*) + (dA/dn)n^{*2/3} \tag{9}$$

If dA/dn is small, it can be neglected in the first approximation and the slope of $\ln S + 3/(2n^*)$ provides an estimate for $A(n^*)$. A determination of $A(n^*)$ for a range of n^* values allows a check on the assumption that the last term in Eq. (3) is negligible. Substitution of n^*, $A(n^*)$, and the corresponding $\ln S$ into Eq. (8) gives $\Delta w(n^*)/kT$. Using the latter quantity and Eqs. (1) and (5), $J(n^*, T)$ can be determined in this simple model. The value $J(n^*, T) = 1\ \text{cm}^{-3}\,\text{sec}^{-1}$ locates the value of n^* corresponding to the critical supersaturation ratio, S^*. For this calculation, C_{n^*} can be approximated by $4\pi a_0^2 n^{*2/3}\ [kT/(2\pi m)]^{1/2} N_1^2 \gamma$, where $\gamma = [\ln S/(6\pi n^*)]^{1/2}$ and $(4\pi a_0^3/3)^{-1}$ is the bulk liquid number density.[(3)] When evaluated in the cgs system, $\ln C_{n^*} = 60 + 2\ln S \pm 5$ for a range of systems and temperatures.

3. THE MONTE CARLO TECHNIQUE

This technique is adapted from that developed by Bennett[(6)] for determining free-energy differences between systems with slightly differing interaction potentials. The two systems which we consider are clusters of n and $n-1$ atoms, each of which is constrained to be within a volume, V. In order to equalize the degrees of freedom in both systems, we retain all n atoms in the "$n-1$ cluster" and gradually turn off the interaction between the nth atom and all other atoms in the cluster.[5] Thus, in ensemble A the n atoms have a total interaction potential given by

$$U_A = (U + \Delta U)/(kT) \tag{10}$$

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[4] The general form for Eq. (8) is suggested by the work of King *et al.* and Binder and Stauffer (Ref. 9).

[5] We are indebted to F. F. Abraham for pointing out this method to us.

and in ensemble B the n atoms have a total interaction potential given by

$$U_B = (U + \lambda \Delta U)/(kT) \tag{11}$$

where

$$U = \sum_{i,j>i}^{n-1} u(r_{ij}) \tag{12}$$

and

$$\Delta U = \sum_{i=1}^{n-1} u(r_{in}) \tag{13}$$

The $u(r_{ij})$ is the effective pair potential between the ith and jth atoms. In ensemble B, as values for λ are reduced to zero the interaction between atom n and the rest of the cluster is turned off and

$$\operatorname*{limit}_{\lambda \to 0} Q_A(n)/Q_B(n) = Q(n)/Q(n-1) \tag{14}$$

Thus we use Bennett's technique to calculate $Q_A(n)/Q_B(n)^{(6)}$:

$$Q_A(n)/Q_B(n) = \langle f(U_A - U_B + C_\lambda)\rangle_B / \langle f(U_B - U_A - C_\lambda)\rangle_A e^{C_\lambda} \tag{15}$$

where $f(x) = (1 + e^x)^{-1}$, $\langle f \rangle_A$ denotes a Metropolis Monte Carlo average of f in the A ensemble, and C_λ is a constant for fixed λ. In the Bennett technique one calculates the Fermi function averages for a range of C_λ values and searches for the value of C_λ which makes $\langle f(x)\rangle_B / \langle f(-x)\rangle_A = 1.0$. This value of C_λ then satisfies

$$C_\lambda = \ln[Q_A(n)/Q_B(n)] \tag{16}$$

One can further show that for C_λ satisfying Eq. (16),

$$\frac{d}{d\lambda} C_\lambda = \langle \Delta U \rangle_B / kT \tag{17}$$

and

$$\frac{d^2}{d\lambda^2} C_\lambda = [\langle \Delta U \rangle_B^2 - \langle \Delta U^2 \rangle_B]/(kT)^2 \tag{18}$$

Thus an efficient procedure is to calculate C_λ for λ close to zero and use

$$C \equiv \ln[Q(n)/Q(n-1)] \simeq C_\lambda - \lambda \langle \Delta U \rangle_B / kT \tag{19}$$

A direct calculation of C, i.e., setting $\lambda = 0$, results in unmanageable fluctuations in the Fermi function averages.

4. APPLICATION TO LENNARD-JONES CLUSTERS

The Monte Carlo technique discussed in the last section is applied to clusters of Lennard-Jones atoms where $u(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, $\epsilon =$

Table 1. **Values for n, the number of atoms in the cluster, N, the number of Monte Carlo steps ($K = 1000$), C_λ, $-\langle \Delta U \rangle_B \lambda$, and C. For all the Calculations $\lambda = 0.1$**

n	N	C_λ	$-\langle \Delta U \rangle_B \lambda$	C
13	$1100K$	3.50	0.019	3.66
18	$1300K$	4.03	0.021	4.21
24	$1300K$	4.36	0.022	4.55
43	$1100K$	4.95	0.021	5.13

119.4 K, and $\sigma = 3.4$ A. In these calculations we adopt the following definition of a cluster: n atoms confined to a spherical volume centered on the center of mass and with number density 4.87×10^{-3} atoms/A^3. This density is approximately one fifth that of bulk liquid and gives constraining volumes which have been suggested by Lee *et al.*(2) to produce minimal effects on the free energy of the clusters.

The results of the calculations for C as determined from Eq. (19) are given in Table I, together with the number of Monte Carlo steps, N, for each run. In Eq. (7) a value of 8.0 is used for $-\ln[(N_1^0/V)/(n/V)]$. This corresponds to a value of 16.4 for $\ln(\Lambda V/N_1^0)$.[6] The n/V in this formalism is the number density used in the Monte Carlo calculations. In order to maintain consistency with the potential formalism, we use the predicted intercept as determined by plotting C v. $n^{-1/3}$ and fitting a straight line to the data. The value of C at infinite n should be equal to $-\ln[(N_1^0/V)/(n/V)]$. As a further check on this procedure the results reported by Torrie and Valleau(11) were extrapolated to 60 K with a prediction of about 16.1 for $\ln(\Lambda V/N_1^0)$.

In Fig. 1 are presented the values of $\ln S + (3/2)n^{-1}$ [using Eq. (7)] for $n = 13$, 18, 24, and 43 plotted as a function of $n^{-1/3}$. A straight line fit to these points passes through $\ln S$ equal to zero at infinite critical cluster size —as it should. Also shown in Fig. 1 are the corresponding values for $A(n^*)$ as determined from Eq. (9) with $dA/dn = 0$. The average value of $A(n^*)$ for the four calculations, $\bar{A}$, is 15.1 and corresponds to an effective surface tension for the clusters of about 22 ergs/cm^2. [To make this approximation the surface tension is assumed to be $(4\pi a_0^2)^{-1}\bar{A}kT$.]

The energy of formation as a function of critical cluster size, n^*, can be approximated by substituting $\ln S$, n^*, and $A(n^*)$ into Eq. (8) for the four cluster sizes examined. Intermediate values of n^* can be treated by interpolating between the data points in Fig. 1. For larger clusters, energies

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[6] The value 16.4 for $\ln(\Lambda V/N_1^0)$ can also be obtained by substitution of the N_1^0/V from the extrapolation procedure of Ref. 10.

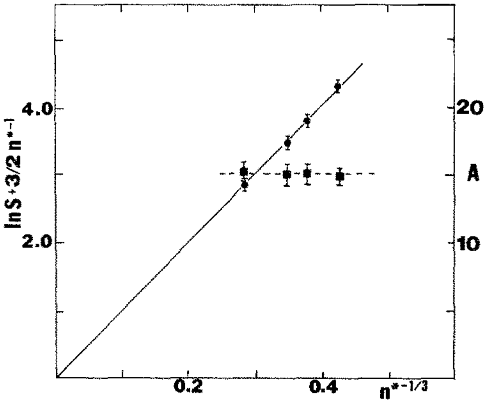

Fig. 1. The quantity $\ln S + (3/2)n^{*-1}$ plotted as a function of $n^{*-1/3}$ (●) and the corresponding values of $A(n^*)$ (■), at $T = 60$ K for Lennard–Jones vapor clusters.

of formation can be estimated from Eq. (8) using extrapolations of the results in Fig. 1. We find a value of $\Delta w(n^*)/kT$ equal to $\ln C_{n^*}$ at $n^* = 70$, which predicts a critical supersaturation given by $\ln S^* = 2.45$. This value corresponds to an experimental value of $\log_{10}p(\text{atm}) = -0.9 \pm 0.2$.[7] Figure 2 shows the predicted value superimposed on experimental results obtained by Wu *et al.*,(12) and by Stein(13) for the onset of nucleation in argon vapor.

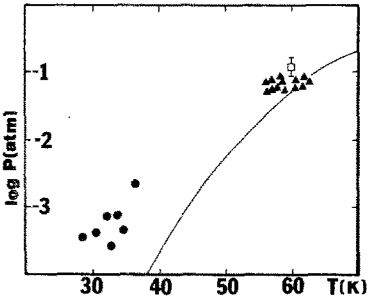

Fig. 2. Onset of argon condensation by homogeneous nucleation. Solid circles are experimental results from Ref. 12; solid triangles are experimental results from Ref. 13. The solid line is the classical model prediction. The predicted value from this work is □, corresponding to a critical supersaturation ratio of 2.45 at $T = 60$ K for Lennard–Jones vapor clusters.

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[7] Uncertainties reflect differences in extrapolation formulas for $\log_{10}p_\infty$ for argon. Ref. 10 gives -0.80 and Eq. (12) of Ref. 1 gives -1.01 for $\log_{10}p(\text{atm})$ at 60 K for $\ln S = 2.45$.

During the course of this work, some calculations were done on the $n = 80$ cluster. Preliminary results indicate a lower value of $A(n^*)$ (14.8) than that obtained for the other four clusters. However, more extended runs on the 80 cluster are necessary because of the additional degrees of freedom. Comparisons of the free-energy differences for the n and the $n - 1$ clusters in this calculation with the results of Refs. 1 and 2 can be only approximate since Ref. 1 reports free energies of formation at a specific pressure, and Ref. 2 gives the free energies for clusters which differ in size by 10–30 atoms. However, for $n = 13$, 18, 24, and 43 we obtain $f(n) - f(n-1) = -11.9$, -12.5, -12.9, and -13.5, respectively, where $f(n) \equiv -\ln Z(n) + \ln(\Lambda V/N_1^0) + (3/2)\ln(n)$. These values can be compared to $[f(43) - f(13)]/30 \simeq -13$ from Ref. 2, and $f(13) - f(12) \simeq -12$ from Ref. 1. For the latter number we use equilibrium vapor pressure at 60 K for argon as calculated in Ref. 10. In the present procedure for estimating critical cluster size eight Monte Carlo runs of about 10^6 steps each are required. In the procedures of Refs. 1 and 2, from five to ten times as many Monte Carlo runs (of about 10^6 steps) are required to examine the n dependence of the free energies of the clusters.

5. CONCLUSIONS AND COMMENTS

We have proposed a method for estimating critical cluster size which utilizes Monte Carlo calculations of the free-energy difference between clusters of size n and $n - 1$. This free-energy difference can be used to estimate the supersaturation ratio required to produce a critical cluster size, $n = n^*$, at the prescribed temperature. With the aid of an assumed analytic form for the free energy of formation for the n^* cluster, an effective surface tension for that cluster size can be approximated. Using this formalism applied to Lennard–Jones vapor clusters (argon) we estimate a critical cluster size of about 70 ± 5 atoms at a critical supersaturation ratio of 2.45 ± 0.15 at 60 K. This result agrees with experimental data for the onset of nucleation in argon vapor.

We view this method as a tool for approximating critical cluster size when considering more extensive calculations of free energies and for initializing conditions for the simulation of nucleation phenomena via molecular dynamics. Our particular interest in this method will be in probing the ice nucleation efficiency of substrate features by estimating critical cluster sizes on specific surface environments. Work is in progress on the application of this method to water vapor clusters using effective pair potentials(14), and to monolayer water clusters absorbed on surfaces of hexagonal AgI(15).

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